ORGANOMETALLIC COMPLEXES

OF PLATINUM, PALLADIUM AND MERCURY.

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DOCTOR OF PHILOSOPHY

by

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ABSTRACT.

A synthetic route to a series of 2-(arylazo)arylmercury compounds has been developed in the hope of providing a good transfer reagent for the high-yield synthesis of other 2-(arylazo)aryl metal complexes.

Reaction of a series of sodium 2-(arylazo)arylsulphinates (which are prepared in two stages from bis(2-nitroaryl)disulphides) with mercuric chloride resulted in formation of 2-(arylazo)arylmercuric chloride complexes. The range of known substituted 2-(arylazo)arylsulphinates has been extended by this work and their reaction with mercuric chloride is a new development of the Peter's Reaction. Derivatives with a variety of ring substituents on both rings have been prepared by this method. A combination of IR and NMR spectroscopic investigations established the substitution patterns involved and demonstrated a retention of specific substitution patterns throughout the synthetic route.

Those compounds were found to be useful reagents in the synthesis of other 2-(arylazo)aryl metal complexes. Reaction with $PdCl_2$ gave quantitative yields of the ring-substituted dimers, $((azb)PdCl)_2$, although with $PtCl_2$ decomposition occurred. The formation of $(PhN{:}NC_6H_4)M(PEt_3)_2Cl$ (M=Pt or Pd) was achieved using $(PhN{:}NC_6H_4)_2Hg$ and was also more successful with palladium than platinum. Transfer of the 2-(phenylazo)phenyl group from mercury to nickel and manganese has also been established by reactions with $(\underline{h}^5\text{-}C_5H_5)_2Ni$ and $Mn(CO)_5Cl$. These reagents produced high yields of $(azb)Ni(\underline{h}^5\text{-}C_5H_5)$ and $(azb)Mn(CO)_4$, respectively, when treated with the 2-(phenylazo)phenyl mercurial.

Cleavage of the metal-carbon bond of the 2-(arylazo)arylmercuric chloride complexes occurred in several reactions. The organic products were in many cases new and in some cases are known to be difficult to prepare by other means. Ready Hg-C bond cleavage by halogens produced

the corresponding 2-(arylazo)arylhalides in high yield while reaction of $(PhN{:}NC_6H_4)HgCl$ with nitrosyl chloride produced a nitrogen-containing heterocycle; 2-phenylbenzotriazole-1-oxide. Another organic heterocycle, 1H-2phenyl-3indazolone, was formed under mild conditions by carbonylation of $((azb)PdCl)_2$.

All the syntheses using these mercurials have the potential for specific and predictable ring substitution of the products. This is not afforded by many other routes to these compounds and indicates the value of 2-(arylazo)arylmercurials as synthetic reagents.

The ^1H NMR of trans$(PhN{:}NC_6H_4)Pt(PMePh_2)Cl$, prepared as part of the study of 2-(arylazo)aryl metal complexes, was found to show line broadening. This has been investigated by variable temperature studies and arises from rapid phosphine exchange. The system $(Ph_2MeP)_2PtX_2/Ph_2MeP$ (X=Cl, Br or I) also shows phosphine exchange broadening and it too has been examined. The conclusions from these observations have been combined with reported examples of phosphine exchange and an assessment made of the importance of the various factors governing this process.

The complex (azb)Pt(CO)Cl, prepared by carbon monoxide bridge-cleavage of $((azb)PtCl)_2$, was found to undergo CO displacement with a variety of Lewis Bases. In an attempt to gain further insight into carbonyl insertion reactions, several other mononuclear platinum carbonyl complexes have been prepared and investigated. The interaction of $(PhMe_2P)Pt(CO)X_2$ (X=Cl, Br, or I) and $(R_3P)Pt(CO)Br(Ph)$ (R_3P=Et_3P or $PhMe_2P$) with a wide variety of reagents showed that the extent of carbon monoxide displacement compared to insertion is great, although Ph_4Sn and $(o\text{-tolyl})_2Hg$ did produce insertion with $(PhMe_2P)Pt(CO)Cl_2$. The displacement reaction, however, predominated and in the reaction of bromine with $(Et_3P)Pt(CO)Br(Ph)$ a new platinum(IV) bridged complex, $((Et_3P)PtBr_3Ph)_2$, was formed. A rationalisation of carbonyl insertion and displacement reactions has been proposed.

TABLE OF CONTENTS.

INTRODUCTION

Historical Background

The last twenty years has seen a dramatic upsurge of interest in organometallic systems, particularly compounds of the transition elements. Early investigators were mostly concerned with compounds of the main group elements. Frankland, in 1849, was the first to isolate an organometallic compound and then establish its constitution[1]. Although his aim was the preparation of the free ethyl radical, he correctly identified his reaction product as diethyl zinc,

$$2C_2H_5I + 2Zn \longrightarrow (C_2H_5)_2Zn + ZnI_2$$

By extension to complexes of mercury, tin, antimony and arsenic he laid the foundation for our present understanding of organometallic chemistry. Furthermore, from these fundamental researches emerged the first clear statement of what was to become the theory of valence for, from these studies, Frankland "became impressed with the fixity in the maximum combining power or capacity of saturation in metallic elements which had not before been suspected"[2].

Organometallic complexes of mercury, platinum, and palladium, elements which feature prominently in this thesis, have held key positions in the advances of the last century. Mercury has long held a fascination for chemists and organomercurials are amongst the earliest organometallic compounds synthesised. Frankland's pioneering synthesis of ethylmercuric iodide[3] was followed by Dimroth's studies of aromatic mercuration reactions in 1898[4]. Such advances paved the way for the shift of emphasis from main group organometallic chemistry to transition metal organometallic chemistry which probably now predominates. This shift of emphasis has come by way of such discoveries as Grignard's preparation of organomagnesium halides in 1900[5], Schlenk's researches in organoalkali metal compounds in 1914[6] and Ziegler's direct preparation of lithium

alkyls in 1930[7]. All these systems are still of vital importance in organic chemistry.

Zeise's salt, $K(PtCl_3C_2H_4)$, the first organometallic compound synthesised and originally formulated as an ethylene "solvate", was prepared in 1827[8]. Pope and Peachy synthesised the first platinum (IV) alkyls in 1907[9]. Platinum and palladium organometallic chemistry, however, along with all transition metal chemistry took longer to gain momentum than the earlier studies with main group elements. This may well be due to the failure to prepare simple alkyls of these metals. Indeed, before 1950, the belief in the inherent weakness of transition metal carbon bonds was widespread. Those few compounds which were known, such as Pope and Peachy's Pt(IV) alkyls, were generally thought to be exceptions and were not understood.

Fresh impetus came with the discovery of ferrocene in 1951[10] and the subsequent elucidation of its novel sandwich structure by Wilkinson and Woodward[11]. Theory had not predicted the existence of such cyclopentadienyl complexes before their discovery and, as with Frankland's simple alkyl complexes, the synthetic discovery led to new ideas on bonding and structure and renewed interest in organo-transition metal chemistry.

Organometallic chemistry has a central position in the discipline as a whole, involving as it does both the way the metal influences the organic ligand and the way in which the organic ligand modifies the characteristics of the metal. The prominence of organo-transition metal chemistry may be ascribed trivially to the vast number of feasible compounds. More significally, the ease of metal-carbon bond-making and bond-breaking results in the use of organo-transition metal complexes in stoicheiometric or catalytic organic synthesis. The established position of Grignard and organolithium

reagents in the organic chemist's synthetic weaponry has already been mentioned.

Many industrial processes now involve organo transition metal species as intermediates in catalytic processes. The polymerisation of olefins by the Ziegler-Natta process, for example, is thought to involve coordination of olefin to titanium followed by a rearrangement and subsequent transfer of the organic chain to aluminium. The essential features of organo-transition metal complexes which make them effective catalysts are the availability of easily accessible oxidation states and the potential for variable coordination number. This is well illustrated by the chemistry of platinum which has three oxidation states (Pt(0) d^{10}, Pt(II)d^8, and Pt(IV) d^6) with well documented examples.

Palladium catalyses a large number of organic reactions[12] including olefin oxidation, olefin oligomerisation, carbonylation and arene coupling reactions. The Wacker Process for the synthesis of acetaldehyde from ethylene exhibits the main features of such catalytic processes.

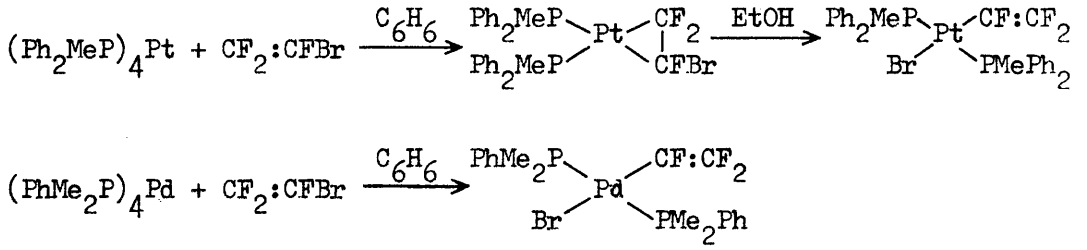
$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd(0) + 2HCl$$

$$Pd(0) \xrightarrow[CuCl_2/O_2]{} PdCl_2$$

This system has received much attention[13] but is still not fully understood. The main features are the formation of an olefin-palladium (II) π -complex, insertion of ethylene into a Pd-OH bond, decomposition (perhaps by β-elimination) and reoxidation of palladium(0) by copper(II).

The study of palladium and platinum complexes has the advantage that there already exists a fund of background literature and considerable insight into the understanding of the mechanisms and processes involved. Study of the more stable (and hence catalytically

less useful) platinum systems can give a helpful indication of the mechanisms involved in the palladium reactions. Thus it is often possible to isolate stable platinum species where the palladium analogues exist only as reactive intermediates. The reaction of zerovalent phosphine complexes of platinum and palladium with bromotrifluoroethylene illustrates this point. In the platinum[14a] case a stable fluoro-olefin complex was isolated and is the presumed intermediate in the palladium reaction[14b].



Salient Properties of Organometallics of Mercury, Platinum and Palladium

Organomercury compounds can be subdivided into two classes; the diorganomercurials R_2Hg, and the organomercuric halides RHgX. Interconversion of these types can be easily achieved and the symmetrisation reaction will be discussed in some detail below (Chapter I). Organic derivatives of mercury are stable towards air and moisture. This contrasts with the behaviour of organic compounds of alkali metals, organo-aluminium derivatives or Grignard Reagents. Consequently the range of organic groups which form easily handled complexes of mercury is great. Derivatives containing saturated, unsaturated, alicyclic, aromatic, or heterocyclic organic groups are known[15]. One outcome of this stability of organomercurials is the variety of preparative methods which have been developed and these will be outlined below (Chapter I).

An increase in reactivity of organic complexes of the Group II elements is found with decreasing electronegativity of the metal. In

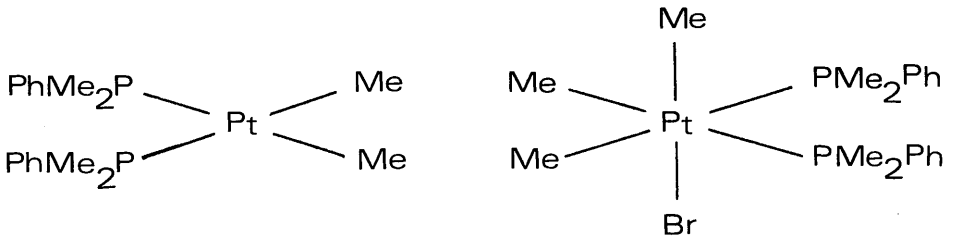
the presence of oxygen, dimethylzinc spontaneously inflames and dimethylcadmium is oxidised. In contrast, dimethylmercury is stable to oxygen and water. The use of Group II organometallics in organic synthesis depends on the balance between adequate reactivity and ease of handling. In many cases Grignard Reagents or organomercurials provide the most suitable combination of these requirements. Nevertheless, the toxicity of organomercurials is now well appreciated and necessitates careful handling, especially of the more volatile compounds.

The metal in its two-covalent compounds is thought to use its 6s and 6p atomic orbitals in the formation of two collinear bonds[16]. Methylmercuric chloride and methylmercuric bromide have been shown by microwave studies to have a linear structure[17]. The Infra Red[18] and Raman[19] spectra of dimethylmercury show that the mercury-carbon bonds are collinear. The results of dipole moment investigations remain a matter of dispute. The non-zero dipole moments of diphenylmercury[20] and several substituted aryl mercuric halides[21] have been interpreted in terms of a bent C-Hg-Y bond. The electron diffraction of bis (p-bromophenyl) mercury also indicates a bent structure[22]. The crystal structures of diphenylmercury[23] and of di-p-tolylmercury[24] have shown these molecules to be linear in the solid state.

In contrast to organomercurials, organoplatinum and palladium complexes, as is typical of organotransition metal complexes, display a greater potential for variable oxidation state and coordination number. Divalent 16-electron d^8 organic complexes of platinum and palladium are, for reasons mentioned below, favoured over zerovalent 18-electron d^{10} and tetravalent d^6 complexes. The divalent complexes are square planar while the tetravalent complexes are octahedral and the zerovalent olefin or acetylene complexes have slightly distorted

square planar structures.

Platinum forms crystalline complexes containing M-C σ- bonds in both the +2 and +4 oxidation states[25] e.g.



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Although the first Pt(IV)-C σ- bonds were reported over 60 years ago, it was not until 1957 that the first complexes containing Pt(II) and Pd(II)-carbon σ- bonds were prepared. These are now well known and outnumber those of the +4 oxidation state. With the exception of the pentafluorophenyl complex $((Ph_3P)_2Pd(C_6F_5)_2Cl_2)$[27] palladium forms complexes with M-C σ- bonds only in the +2 oxidation state.

Platinum forms halogen bridged species $R'(R_3P)Pt(\mu\text{-}X)_2Pt(PR_3)R'$ (X=Br,I). Analogues with other bridging groups (R_2P,R_2As or RS)[28] are known but not with chlorine as the bridging atom. Methyl[29] and benzyl[30] palladium complexes with, respectively, sulphide bridges and chloride bridges have been prepared.

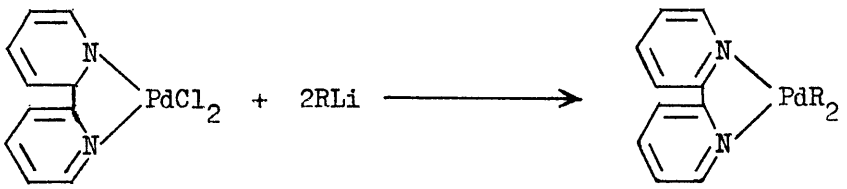
Pt(II) complexes are thermally, oxidatively and hydrolytically stable enough to allow easy handling in air. Pd(II) complexes are slightly less stable in this respect. The thermal stability of these platinum and palladium complexes has been found to depend on the organic group and follow the order[31],

ortho - subs$^{td.}$ phenyl > C_6H_5-C≡C- > phenyl > alkyl > H-C≡C-

Amongst the alkyls themselves Chatt and Shaw[31,32] established the order

$$Me > Et > nPr > nBu > PhCH_2.$$

Both cis and trans platinum dialkyls and diaryls are known whereas for palladium only trans diaryls and predominantly trans dialkyls are found. Cis dimethyl compounds of palladium can be prepared when stabilised by a bidentate phosphine or bipyridyl ligand. Interestingly, the reaction



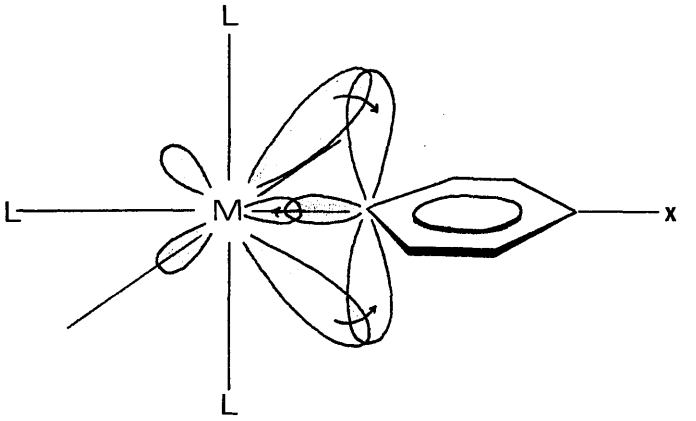
succeeds when R= Me[29], C_6F_5[33] or C_6Cl_5[33] but when R=Ph no diphenyl palladium complex was isolated and biphenyl was produced[33], perhaps indicating lower thermal stability of the cis diphenyl complex over the cis dimethyl complex.

Bonding and Stability

The development of theories of bonding and concepts of stability of organometallic complexes has generally, and not surprisingly, lagged behind synthetic advances in the field. From the early statements on valence that arose from Frankland's discovery of zinc alkyls to the more refined bonding theories that resulted from the determination of the structure of ferrocene, perparative and theoretical advances have gone hand in hand.

The simplest description of the metal-carbon σ-bond commonly formed with alkyl, aryl or alkynyl groups is a localised 2 electron covalent bond. These groups are formally thought of as 1-electron

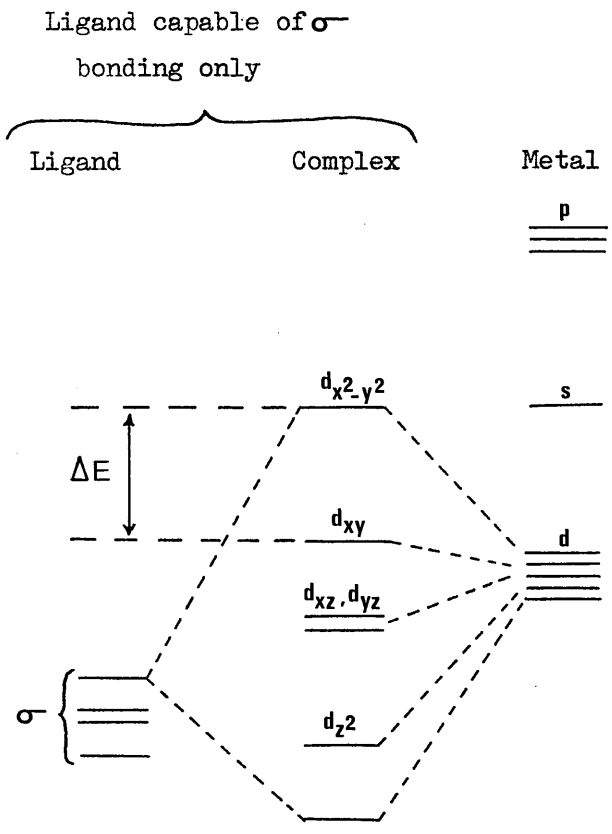
donors and the bonds involve overlap of a filled sp^3, sp^2 or sp hybrid on carbon with an empty spd hybrid orbital on the metal (the M-C bond being taken as the x-axis). There exists too the possibility of π-back bonds from filled metal hybrid orbitals to empty π^*- orbitals of the aryl.

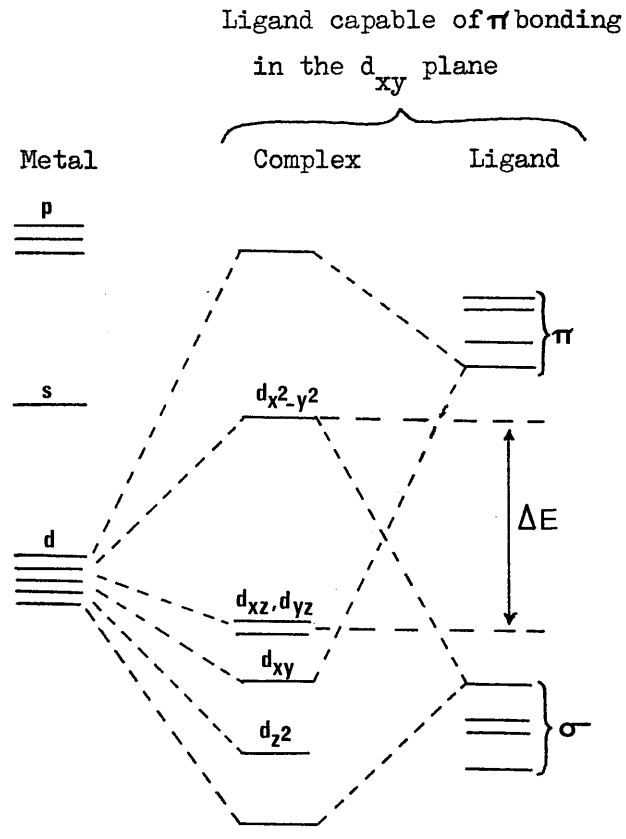


Even in methyl complexes of Pt(II), n.m.r. evidence suggests that there is some π-back donation[34].

The ideas of metal-carbon σ- bonding in transition metal complexes have shifted from the view that metal-carbon bonds are inherently unstable. Stabilisation by π-accepting ligands which increase the energy separation between filled and empty d-orbitals on the metal was formerly thought to be necessary[35] (see Diagram). On this model, M-C bond cleavage (leading to radicals, carbonium ions or carbanions) resulted from thermal promotion of one of the high energy d-electrons to an antibonding orbital - a route not possible for main group complexes which have no readily available d-electrons. As is seen from the diagram, the effect of π-accepting ligands is to lower the energy of the d-orbitals and consequently increase the activation energy ΔE for decomposition.

Energy level diagram for square-planar complexes.

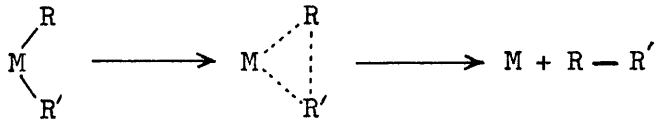


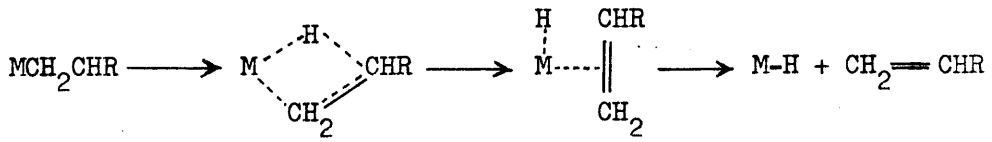


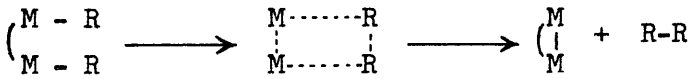
This rationalisation can account for many of the observed stability trends. Thus, the order of thermal stability of the organic derivatives of the nickel triad, Ni < Pd < Pt, is explained by the increased interaction of the metal $d_{x^2-y^2}$ orbital with the ligand orbitals (and hence greater ΔE) for the elements with higher atomic number. Nevertheless, the isolation of compounds such as WMe_6[36] which have no strong π-acceptor supporting ligands has cast doubt on the general validity of the above theory.

The viewpoint which the bulk of evidence now appears to support[37] is that there exists no fundamental difference between transition metal carbon bonds and carbon bonds to other elements. This is not to deny that many complexes are indeed very labile and that most (including, significantly, those first prepared) contain other π-acceptor ligands. The instability of some simple alkyl complexes is exemplified by dimethylmanganese, a spontaneously flammable solid which explodes on impact. The lability of many organo-transition metal complexes may, therefore, be ascribed, not to any inherent weakness of the M-C bond, but to the potential for variable oxidation state and coordination number which makes available many decomposition routes. Trans $(Et_3P)_2PtPh_2$, for example, has a Pt-C bond energy of about 272 kJ mol^{-1} [38] which is similar to that of a C-C single bond (~348 kJ mol^{-1} [39]) or a C-H bond (~395 kJ mol^{-1} [40]). Accordingly, the role of the so-called "supporting" ligands is in the prevention of decomposition pathways by blocking coordination sites which are used in decomposition reactions. The marked stability of organo-nickel complexes containing secondary alkyl phosphines over their primary alkyl analogues may be such an example. Thus, the compound trans $(Pr^i_3P)_2NiHCl$ was found to be thermally stable[41] while the Pr^n_3P analogue could not be isolated.

When thermal decomposition occurs it is likely to be by paired electron processes and generally by a concerted mechanism.[37a] These fall into 3 main classes; reductive elimination, β- elimination, and dinuclear elimination. They are illustrated below by three general equations

1) 

2) 

3) 

The electronic requirements for stability find their expression in the long recognised[42] empirical rule - the 18-Electron Rule. According to this rule stability is favoured if the electronic configuration of the inert gas of that period is achieved. It has a clearly defined origin in the ligand field - molecular orbital description of transition metal compounds, according to which only nine stable orbitals can be derived from the nine valence orbitals (e.g. 3d, 4s, and 4p) of a transition metal atom. Compounds in which this orbital occupation is higher than usual will undergo elimination. Towards the end of the periodic table and in particular for elements of the nickel triad, reduction of d-orbital energies and increasing nd $\longrightarrow$ (n+1)p promotion energies makes full orbital occupation leading to 18-electron molecules less favourable[37a]. 16-electron molecules of nickel, palladium and platinum are therefore common. Furthermore, because

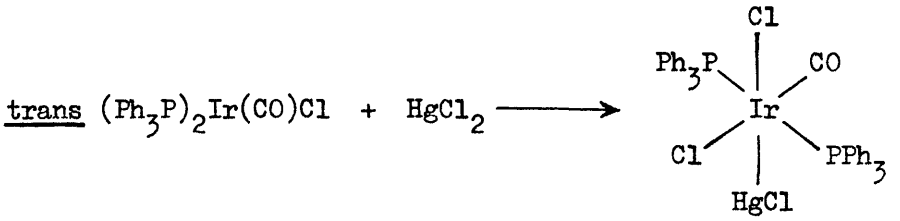
of the Lanthanide Contraction, the nd $\longrightarrow$ (n+1)p promotion energies are not regular as a group is descended. This means that the trend for preference of the 18e-configuration is 1st row > 3rd row > 2nd row. In particular nickel is the most likely and palladium the least likely element of that triad to favour 18-electron molecules. In the same way, 5-coordinate 16-electron molecules of Rh(III) are favoured while 6-coordinate complexes of Ir(III) are the more common.

The significance of 16- and 18-electron molecules in transition metal organometallic chemistry has been reviewed by Tolman[43]. The essence of his review is that 16- and 18-electron configurations are readily accessible to diamagnetic organotransition metal complexes and easy interconversion is possible at least at the end of the transition series. Species with other configurations or reactions by other paths will generally be energetically so unfavourable by comparison that, in this area of the periodic table, they are negligible. On this basis many catalytic reactions can be understood and many different types of organometallic reactions can be unified. Such reactions include; Lewis Base Dissociation (Association), Insertion (Deinsertion) and Reductive Elimination (Oxidative Addition).

Oxidative Addition/Reductive Elimination

These reactions are of prime importance for platinum and palladium complexes[44]. Oxidative addition may be defined as a reaction where an increase in the formal oxidation state (the charge left on the central metal after all the ligands have been removed in their "normal" closed shell configurations) is accompanied by an increase in coordination number. Oxidative addition occurs especially with those transition elements on the R.H.S. of the transition series which have low coordination numbers and low total number of valence electrons.

Oxidative addition reactions of four-coordinate d^8 species are among those which have received considerable attention in recent years. This can be illustrated by the reactions



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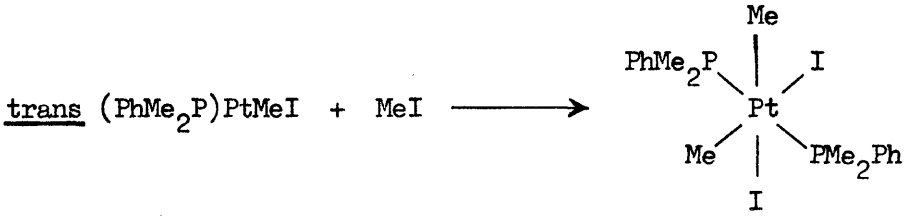
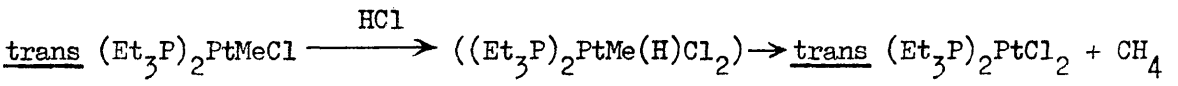
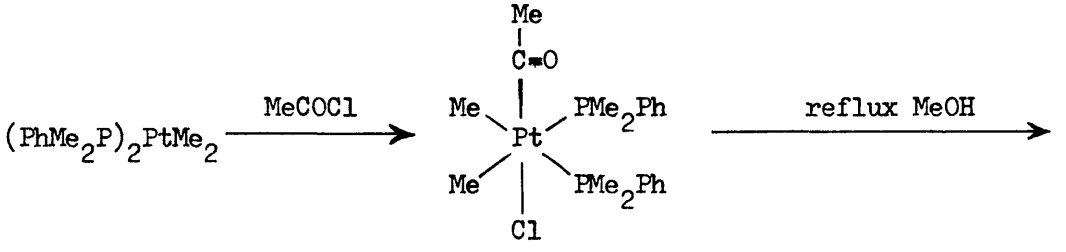


Ref. 26

In the last example a stable 6-coordinate Pt(IV) complex is isolated. In many cases a Pt(IV) complex is formed only as an unstable intermediate which undergoes reductive elimination producing a Pt(II) complex. Such a reaction is that of trans chloro-methylbis(triethyl-phosphine) platinum (II) with hydrogen chloride[46].



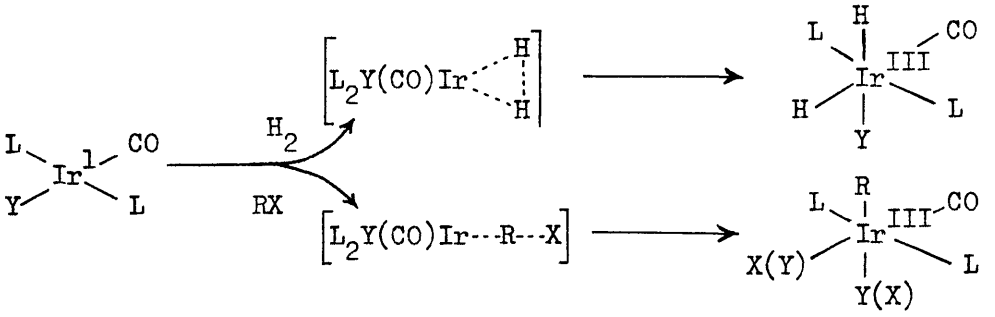
Even when an isolable Pt(IV) species is produced, it may with more forcing conditions undergo reductive elimination.



Ref. 47

trans $(PhMe_2P)_2PtMeCl$ + $(Me)_2CO$

There seems to be no unique mechanism of oxidative addition at d^8 centres. Different mechanisms are likely to operate for four or five - coordinate substrates[44b]. Even for the four coordinate species two different mechanisms seem to operate as established for addition of H_2 or RX to $Ir(CO)L_2Y$. These two limiting mechanisms can be represented as follows[44a]



Clark and his coworkers have studied several oxidative addition, reductive elimination and isomerisation reactions at platinum[47]. On the basis of the information to hand at the present time, they have drawn several conclusions.

1) Oxidative addition reactions to square planar Pt(II) complexes proceed initially to give the <u>trans</u> - adduct. (This may not necessarily be the thermodynamically most stable isomer).

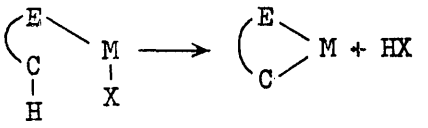
2) The stereochemistry of the isomerisation product seems to be that where a ligand at one end of the series $CH_3^- > C_6H_5^- > CF_3^- > PR_3 > AsR_3 > I^- > CH_3C(O)CH_3$, CH_3OH is trans to a ligand at the other.

3) The reductive elimination reaction products may be predicted from the 'leaving group order' Me-C(O)- > Me > C_6H_5 > CF_3.

One process which very likely occurs in many cases by a mechanism involving oxidative addition followed by reductive elimination is that of internal metallation.

Internal Metallation

The internal metallation process involves formation of a metal carbon bond by reaction of a C-H bond in the organic group of a donor ligand with the central transition metal atom.



E = N,P etc.

M = Fe,Mn,Ru,Co,Rh,Ir,Ni,Pd,Pt,Au etc.

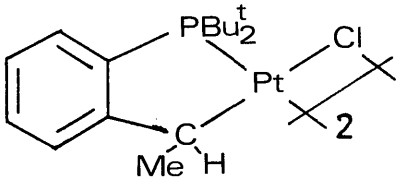
X = Halide, NO_3,H,Me etc.

In 1969 Parshall reviewed the more specific case where the organic group is an aryl[49]. Since that time numerous examples of ortho-metallation of N[50-56] and P[50,57-64] donor ligands by transition metals have appeared. In addition recent examples involving carbon[65], sulphur[66-70] and oxygen[71] donor ligands demonstrate the generality of this process.

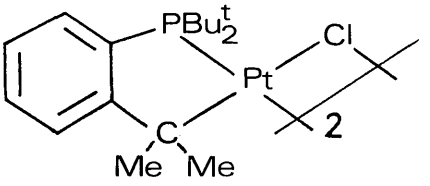
Although this section will consider mainly the ortho-metallation of aromatic rings, examples of internal metallation where the organic group is not aromatic are well documented. Complexes containing internally metallated secondary carbon atoms have been prepared from olefinic tertiary phosphines by nucleophilic attack[72,73a](analogous to the case of simple coordinated olefins), electrophilic attack[74-77] and insertion into a metal hydrogen bond.[73,78,79] Similarly metallation of allylic sulphide ligands has been shown to be promoted by nucleophilic attack[80].

Shaw[56, 81-84] and others[85] have shown that metallation is possible with alkyl substituents on phosphine ligands. Bulky substituents on tertiary phosphines were found to promote metallation of secondary and

tertiary carbon atoms. Thus, the ortho-ethylphenyl or ortho-isopropylphenyl groups can be metallated in refluxing n-propanol to give I and II respectively[81].

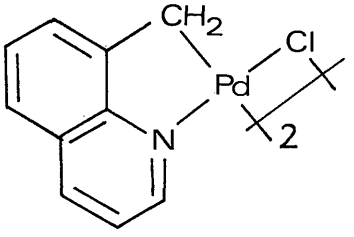


I

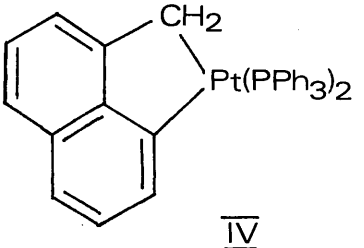


II

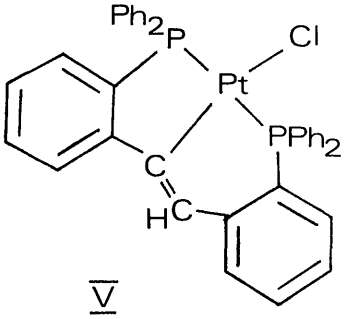
Other examples of such metallations of aliphatic carbon atoms are found with 8-alkylquinolines[86,87] (e.g. III), with 8-methylnaphthalene[65] (IV) and with olefinic tertiary phosphines[88] (e.g. V).



III



IV



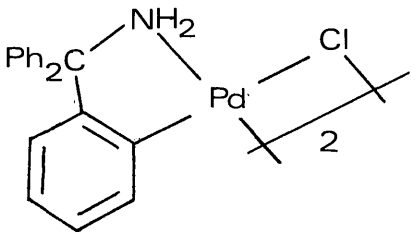
V

The X-Ray Crystal Structure[88] of this latter complex confirms the structure assignment shown.

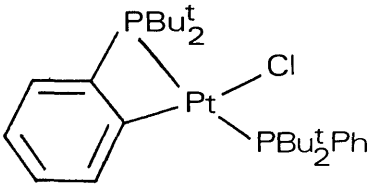
Although the ortho-metallation reaction represents the best studied of these internal metallation processes, very little positive information concerning the mechanism/s of the reaction exists. In systems which have the potential of forming 4- or 6- membered rings as an alternative to a 5-membered ring it is found that the latter usually forms. This is true for N-donor ligands[89], or P-donor ligands be they

ortho-tolyl phosphites[90] (which give a 5-membered chelate structure by ortho-metallation of the ring) or ortho-tolylphosphines[82,83,91,92] (which give a 5-membered chelate structure by metallation of the methyl group). Examples do exist, however, where 4-[91,48] or even 3-[94] membered rings are reported.

It appears that another factor of some generality is the effect of bulky substituents on promoting the ortho metallation process. This factor also seems to apply both to N-[89,95] and P-[91] donor ligands. Thus, it is found that benzylamine and monoalkylbenzylamines do not metallate with Pd or Pt salts, but instead give simple coordination complexes such as $(PhCH_2NH_2)_2PdCl_2$.[89] Substitution of the α-benzyl position with bulky groups, however, favours the formation of the metallated complex[95]. The ortho metallation of the primary and secondary amines triphenylmethylamine, VI, and N-methyltriphenylmethylamine are the first examples with other than a tertiary amine. (The failure of the metallation reaction with primary benzylamines in contrast to tertiary benzylamines has been taken as a reflection of the stronger coordination, which results from steric considerations, decreasing the electrophilic character of the metal. On purely electronic grounds, however, one would expect the presence of N-methyl groups to decrease the electrophilicity of palladium and reduce the tendency to metallate).



VI

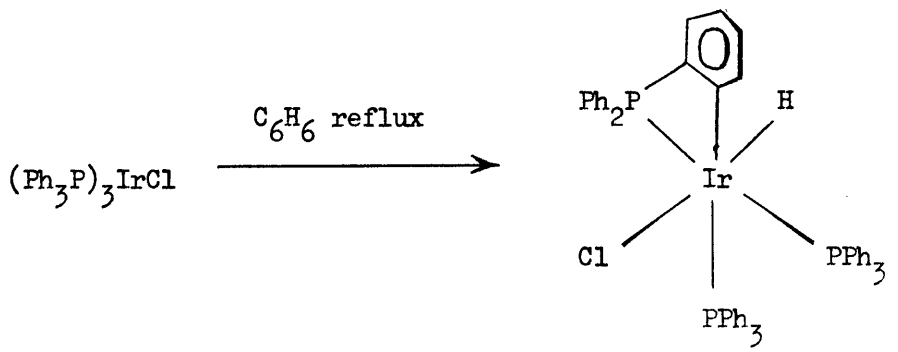


VII

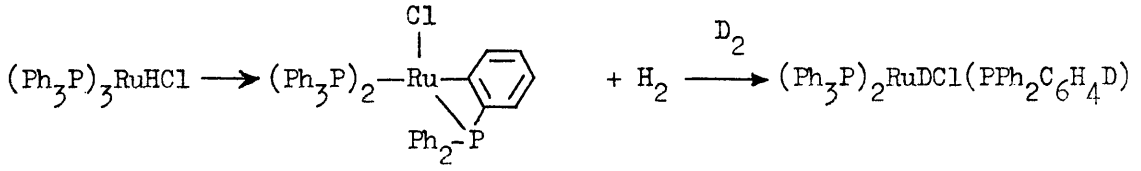
In accordance with the foregoing, a refluxing solution of *cis* $(PhMe_2P)_2PtCl_2$ produces no *ortho* metallated products, whereas the analogous, more sterically-crowded complex, *trans* $(PhBu^t_2P)_2PtCl_2$ gives good yields of VII.[91] It is not known whether the effect of bulky ligands in favouring *ortho* metallation is thermodynamic or kinetic in origin. If thermodynamic, the explanation may lie in the stronger bonding between metal and phosphorus brought about by metallation. If kinetic, the reason may be the smaller free energy of activation for bulky phosphines which results from the smaller loss of entropy for those ligands.

To these two factors can be added further, perhaps less general, information. Acetate ion promotes metallation[56,96] probably acting as a hydrogen acceptor. The tendency towards metallation of aryl phosphines L_2MX_2 (L = phosphine, M = Pt,Pd X = halogen) increases in the order $Cl < Br < I$[91] but for aryl phosphites of Pd and Pt the opposite order holds[90]. This may reflect a different mechanism. For both substituted azobenzenes[97] and triarylphosphines[98], the ring substituent effects suggest that electrophilic attack by the central metal atom is the rate-determining step in these cases. The opposite order which obtains for the phosphite case may imply a mechanism involving oxidative addition leading to a Pt(IV) hydride intermediate which then undergoes reductive elimination of hydrogen halide. The electronegativities and 'leaving group' ability of the halogens would indeed fit such a mechanism. Alternatively, since steric factors are thought to be very important in these systems, the order may simply be a reflection of the relative steric requirements of the halogens. A different mechanism may again be indicated by the relative tendency of the metal atom to promote metallation; Pt > Pd for phosphites[90], but Pd > Pt for azobenzene[99] or tertiary amines[89]. With phosphines, however, metallation has been observed to occur both more[91] and less[83]

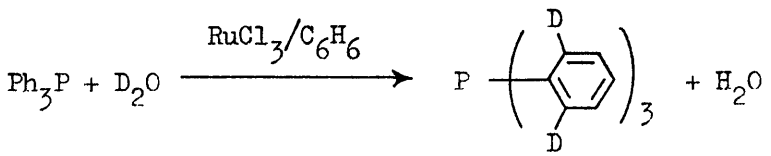
readily with platinum than palladium. Evidence for the intermediacy of a hydride complex is obtained by the isolation of an Ir(III) hydride from the reaction [98]



One of the most useful practical consequences of facile ortho metallation is in the preparation of phosphines, fully deuterated in the ortho positions. $(Ph_3P)_3RuHCl$, for example, is an effective catalyst for the selective ortho-deuteration of triphenylphosphine in the presence of deuterium[100]. The key steps will be those shown in the equation, combined with a phosphine exchange process.



A more convenient method for the complete ortho-deuteration of triphenylphosphine is again thought to involve ortho-metallation by ruthenium[101],



Removal of water as it is produced, and replacement by heavy water leads to 99% exchange of ortho protons for deuterons after 5 days.

Trans Effect and Trans Influence

A distinction has been made by Pidcock et al.[102] between the kinetic and thermodynamic consequences which result from the presence of one group trans to another in metal complexes. The term trans influence was coined to cover the thermodynamic aspects, while the term trans effect refers to kinetic aspects. Consequently the trans effect of a group may or may not be related to its trans influence. The trans effect, therefore, can be defined as the effect of a coordinated group, A, upon the rate of substitution of the group opposite A. The trans influence, however, is defined as the extent to which a ligand weakens the bond trans to itself in the equilibrium state of that complex. Hartley[103] has recently reviewed the cis and trans effects of ligands. The measurement and significance of trans influence has been comprehensively appraised by Clark et al[104].

The recent theories have moved away from the view that the high trans effect of say carbon monoxide and tertiary phosphines arises from their π- bonding capacity and that the relative instability of trans $(R_3P)_2PtX_2$ compared to the cis isomer is due to competition for d-electrons. The present ideas are based on strong σ- inductive effects weakening the trans ligands. This better explains the high trans effects of H^- or CH_3^- and the fact that phosphines weaken the bonds to trans atoms even if they do not have strong π -bonding characteristics[105].

Langford and Gray[106] have emphasised metal-ligand overlap and the directional nature of the p_σ orbitals in Pt(II) (which has $5d_{x^2-y^2}$ 6s and 6p hybrid orbitals). They conclude that the large trans effects of PR_3, CH_3^- and H^- are due to large overlap with the Pt $6p_\sigma$ orbital. However theoretical studies, though they agree that metal rehybridisation is induced by formation of strong covalent bonds to L, do not agree on

the type of metal orbital that tends to concentrate in the M-L bond at the expense of the trans bond.

Trans influence has been measured by X-Ray crystallography, vibrational spectroscopy, n.m.r., n.q.r. and photoelectron spectroscopy. These techniques have various limitations and varying sensitivities to trans influence.[104] It seems that the results can best be understood on the basis of trans influence having both hybridisation and electrostatic components i.e. trans influence depends on

a) the effect of L on the hybrid orbital used by the metal in its bond to trans ligand A.

b) the net charge transfer ($\sigma_{cov.} - \pi$) from ligand to metal

The different experimental techniques mentioned above have different sensitivities to these two factors. N.m.r. coupling constants depend mainly on the first while vibrational frequencies and bond lengths depend on both. Furthermore, the sensitivity of ν (M-A) depends on A. This is exemplified by the fact that ν (Pt-H) differentiates between ligands of moderate or weak trans influence (e.g. RNC, CO, C_2H_4, Py, or Cl) while ν (Pt-Cl) is almost constant for these ligands. ν (Pt-Cl) can, however, distinguish between fine differences in those ligands with strong trans influence (e.g. different aryl substituted silyl groups). These findings also hold for bond length variations.

Because of the different sensitivities to different aspects of trans influence it is difficult to construct trans influence series. Allen and Sze[107] combined several sets of results from ^1J(Pt-P) measurements to obtain the series, in order of increasing coupling constants

$SiMePh_2^- > Ph^- > Me^- \gg PEt_3$, $PBu^n_3 > PMe_2Ph > Ph_3P > P(OPh)_3$, $CN^- > AsEt_3$
$NO_2^- > p\text{-}MeC_6H_4NH_2 > EtNH_2 > Et_2NH > py$, N_3^-, NCO^-, $NCS^- > Cl^-$, Br^-, $I^- > ONO_2^-$.

This order represents a decreasing tendency for the ligands to concentrate

Pt(6s) character into their bonds with Pt(II) (i.e. decreasing trans influence). From X-Ray data an order of structural trans influence has been obtained[108],

$R_3Si^- \triangleq \sigma\text{-}C \triangleq H^- \geqslant$ carbenes $\triangleq PR_3 \geqslant AsR_3 >$ CO $\triangleq$ RNC $\triangleq$ -C=C- $\triangleq Cl^- \triangleq NH_3 >$ O (acac).

CHAPTER I.

2-(ARYLAZO)ARYL METAL COMPLEXES.

CHAPTER I.

INTRODUCTION.

This chapter is concerned with the synthesis of specifically substituted azobenzene complexes of mercury, their use as transfer reagents in the synthesis of azobenzene complexes of other metals, and their potential as reagents for organic synthesis.

Preparation of organic compounds of mercury.

Organomercurials form an extensive class of organometallic compounds whose uses in the field of organic synthesis and in the formation of other organometallic derivatives are widespread. The methods of preparation of organomercurials are numerous[15] but three main categories, within which many variations have been made, are relevant here. These categories involve reaction with other organometallics, direct mercuration, and replacement of another functional group.

Pfeiffer first demonstrated[105] the synthesis of an organomercury compound by reaction with a Grignard Reagent. This now represents one of the most common preparative methods.

$$HgX_2 + RMgX \longrightarrow RHgX + MgX_2$$
$$RHgX + RMgX \longrightarrow R_2Hg + MgX_2$$
$$R_2Hg + HgX_2 \longrightarrow 2RHgX$$

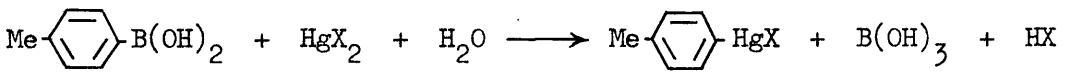
Syntheses using organolithium reagents are also of significance. Of lesser importance is the use of other light-metal organometallics, although sodium, silver, zinc and aluminium have all been used in this respect[15].

Direct mercuration involves replacement of a hydrogen atom of the organic substrate by electrophilic attack of $(HgX)^+$

$$RH + HgX_2 \longrightarrow RHgX + HX$$

The burden of experimental reactions of this type are with aromatic substrates. The electrophilic nature of the substitution has been confirmed by the observation that attack occurs at the most electronegative carbon atom. The reaction is not limited to aryl groups and has been extended to aromatic heterocycles (e.g. thiophene) and metallocenes (e.g. ferrocene). The potential for aliphatic derivatives is not large, however, and the method carries the general disadvantage of the possibility of uncontrolled, non-specific polymercuration.

Replacement of a variety of other functional groups has been demonstrated. $-B(OH)_2$, $-SO_2H$, $-SO_2Na$, and $-CO_2H$ groups have all been displaced by mercury.[15] e.g.

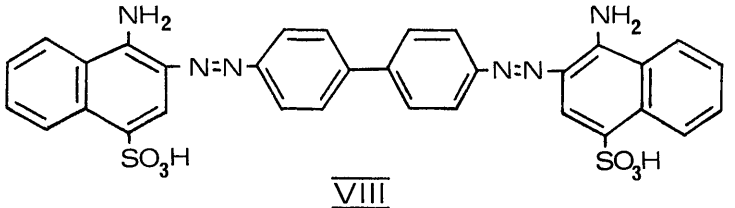


These reactions, however, have not received any systematic treatment nor does it seem likely that they will rival the general applicability of other methods. The drawbacks are the difficulty in obtaining suitably substituted organic derivatives and an uncertainty as to the universal success of each type (especially with $-CO_2H$). The distinct advantage lies in the specific substitution point afforded. This has been utilised in the present work for the preparation of specifically substituted (2-(arylazo)aryl) mercury complexes.

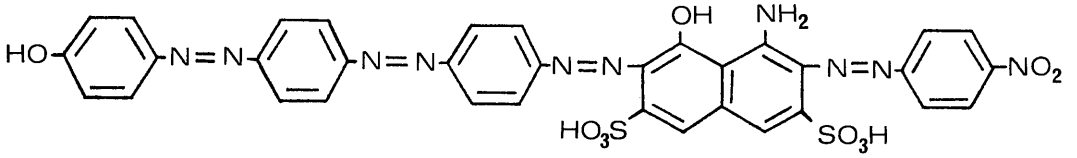
The significance of azo-compounds.

Substituted azobenzenes are common intermediates in the preparation of dyestuffs, insecticides, and pesticides[109,110]. In particular monochloroazobenzenes are useful pigments for oils, lacquers and plastics[109]. Azo compounds are not only the largest chemical class of colouring matters by number, but also by value and weight manufactured. Aromatic azo compounds have been prominent dyestuffs for some 90 years. Those compounds

containing one or two azo linkages are the most important while for those containing four or more azo links the significance applies only to specific compounds. Direct dyes such as Congo Red, VIII, and Diamine Green B, IX, can be applied directly to cellulose fibres whereas in other cases an insoluble azo compound is formed by carrying out the coupling reaction on the fibre[110].

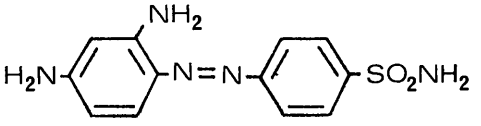


VIII



IX

Derivatives containing the -N=N- link, namely the sulphonamides, are used against bacterial infection[111]. The first of these synthesised, Prontosil, X, which contains the -N=N-bond typical of the azo-dye, was made in 1935 and shown to be strongly bacteriocidal.

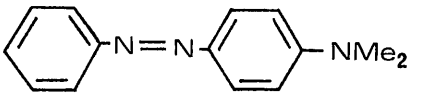


X

In the biochemical field two azomercurials have been synthesised[112] which have potential usefulness for the determination of thiol groups in proteins. The method involves the attachment of the coloured azo moiety to the thiol group by a mercury-sulphur bond and takes advantage of the intense colour and water solubility.

Although azo compounds are the most common synthetic colourings used in foods, pharmaceuticals, and cosmetics, comparatively little work

on their toxicity was published before the last decade. The carcinogenic properties of many of these compounds is now realised. The former food-colouring matter, "Butter Yellow", XI, (p-dimethylaminoazobenzene) is now a known carcinogen[113].

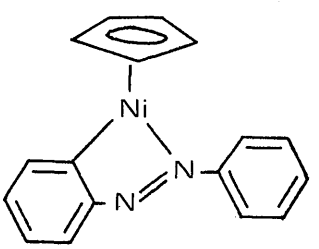


XI

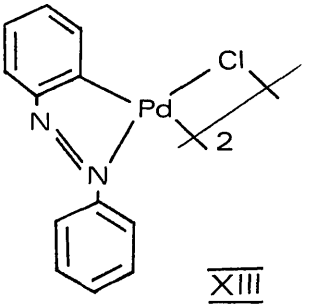
It has been suggested that some of the occupational cancers which were found among workers in the dyestuffs industry may be the result of azo-compounds. Although most of the known carcinogenic azo-compounds are derivatives of 4-aminoazobenzene the 4-amino group is not essential for carcinogenic activity[114]. Furthermore, studies have so far failed to provide a basis for the prediction of physiological activity from chemical structure.

Nomenclature.

A diversity of nomenclature exists in the literature for metal derivatives of azobenzene which contain a bond from the metal to the carbon atom adjacent to that bonded to the nitrogen atom. Thus, XII has been called $\underline{h}_5$-cyclopentadienyl(2-(phenylazo)phenyl)nickel(II)[115] or $\underline{h}_5$-cyclopentadienyl(phenylazophenyl-C^2,N')nickel(II)[116]. Likewise, XIII has been referred to as both the (2-(phenylazo)phenyl)[117] and the (phenylazophenyl-C^2,N')[93] derivative.

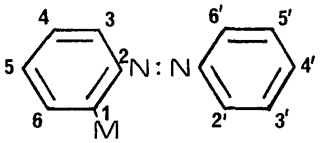


XII

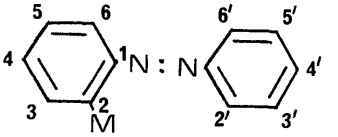


XIII

It can be seen that the conflict lies in whether the numbering of the ring is made with respect to the metal (as in A) or with respect to the phenylazo substituent (as in B).



A

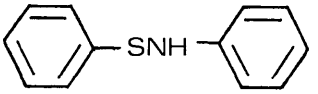


B

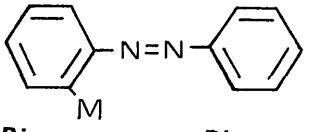
For uniformity the (2-(arylazo)aryl) nomenclature using the numbering system of A is followed predominantly. This has the slight disadvantage that immediate recognition of the presence of a chelate, afforded by the C^2,N' nomenclature, is not possible. Nevertheless, no ambiguity of structure arises if only chemically reasonable compounds are allowed (e.g. 3-coordinate platinum complexes are ruled out). The uniformity is maintained by extending this nomenclature to the sulphinate and halide derivatives of azobenzene, even though the halide compounds are usually described in the literature as haloazobenzenes. In some cases where this nomenclature would be too cumbersome and less clear the compounds are described as derivatives of azobenzene.

For conciseness and according to established practice, the chelating (2-(phenylazo)phenyl) group will often be abbreviated to "azb" in chemical formulae. Thus, for example, di-μ-chloro-di(2-(phenylazo)-phenyl)diplatinum(II) becomes $(azbPtCl)_2$.

For ease of description the aromatic ring which is at some stage bonded to the metal atoms is referred to as <u>ring one</u> and the other non-coordinated ring as <u>ring two</u> throughout.



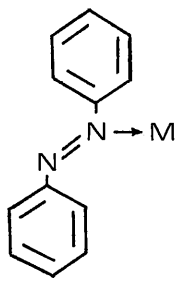
Ring 1 **Ring 2**



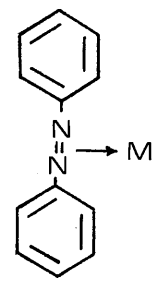
Ring 1 **Ring 2**

Survey of azobenzene metal complexes.

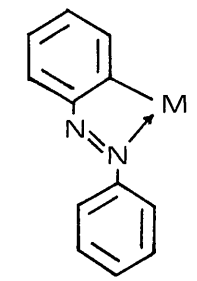
Kleiman and Dubeck reported[118] the first ortho-metallated transition metal complex of azobenzene, XII, in 1963. This was followed by Cope and Siekman's isolation of the dimeric complexes of platinum and palladium, XIII, in 1965[99]. A growing interest in metal complexes of azobenzene has since developed, some of which has probably been generated by the bonding of dinitrogen metal complexes and the relevance of the coordinated azo compound diimide, HN=NH, to the nitrogen fixation process. Azobenzene complexes have now been shown to exhibit four general types of bonding.



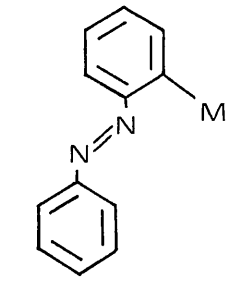
(i)



(ii)



(iii)



(iv)

X-Ray Crystal Structures have established the bonding mode of three of these classes: $[Ni(C_6H_5N{=}NC_6H_5)(Me_3C{-}N{=}C)_2]$[119] and $[Ni(C_6H_5N{=}NC_6H_5)(P(C_6H_4\text{-}\underline{p}Me)_3)_2]$[120] (class ii); $[(C_6H_5N{=}NC_6H_4)_2Rh(O_2CMe)]$[121], $[(C_6H_5N{=}NC_6H_4)_2RhCl_2\cdot Rh(CO)_2]$[122] and $[(C_6F_5N{=}NC_6F_4)Ru(Ph_2PC_6H_4\text{-}\underline{h}^5\text{-}C_5H_4)]$[123] (class iii); $[(C_6H_5N{=}NC_6H_4)Pd(PEt_3)_2Cl]$[124] (class iv).

In addition to establishing the overall bonding mode these structures allow comparisons with the structure of azobenzene itself. As with the bonding of olefins and acetylenes to transition metals, coordination of the -N=N- double bond to the central metal atom is expected to increase the -N=N- bond length over that found in free azobenzene. Accordingly, values of 1.371(6)Å[120] and 1.385(5)Å[119] compared to 1.24(3)Å for azobenzene[125] were found.

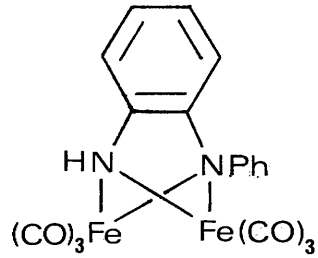
Structure determinations on the ortho-metallated derivatives confirm the presence of a five-membered chelate ring system with the azobenzene molecule bonded to the metal through the ortho-carbon atom and the non-adjacent nitrogen atom. The bond lengths and bond angles in the complexes $(azb)_2RhO_2CMe$ and $(azb)_2RhCl_2 \cdot Rh(CO)_2$ are very similar to azobenzene itself. A significant shortening of the Rh-N and Rh-C bond distances from those in comparable structures may be interpreted in terms of a $d_{\pi}-p_{\pi}$ interaction between filled metal orbitals and the π-bonding system of the chelate skeleton. In both complexes the free phenyl group is twisted out of the plane of the rest of the azobenzene ligand by rotation about the C-N bond. Similar twisting of the free pentafluorophenyl ring has been observed in the fully fluorinated derivative $C_6F_5N{=}NC_6F_4Ru(Ph_2PC_6H_4\text{-}\underline{h}^5\text{-}C_5H_4)$. This structure also reveals the unusual σ-, π chelating arrangement of the $(Ph_2PC_6H_4\text{-}\underline{h}^5\text{-}C_5H_4)$ unit.

Ortho-metallated complexes of azobenzene.

($\underline{h}^5$-cyclopentadienyl)(2-(phenylazo)phenyl) nickel (II), XII, is a typical member of this class of compounds but was originally formulated[118] as containing, in addition to the M-C bond, a coordinate bond from the π-electrons of the -N=N- double bond. The bonding is now known, through IR data and the X-Ray structures mentioned above, to occur through the more distant nitrogen lone pair. Ortho metallation was originally established by lithium aluminium deuteride cleavage of the complexes. The mass spectrum and n.m.r. spectrum of the organic cleavage product from $((azb)PtCl)_2$, for example, were identical with those of azobenzene-$2d_1$.[99] In these examples the formation of the ortho metallated complex occurs on reaction of azobenzene itself with the appropriate metal substrate.

The range of such derivatives thus prepared is now extensive and

is summarised in Figure I. The yields in many cases are low (<10%) and other complexes where the azobenzene function has undergone rearrangement to the ortho semidine ligand[116,126-8] e.g. XIV, or reduction to aniline[129] are sometimes formed.



Ref. 128

XIV

The product from the interaction of platinum tetrachloride and excess azobenzene in glacial acetic acid was originally thought to contain a -N=N- π bond between azobenzene and platinum[130]. Re-examination of this reaction revealed that azobenzene had undergone reduction to a cationic species. The exact formulation of this species is in doubt and both $(PhNH{\cdot}NH_2Ph)^+$[131] and $(PhN{:}NHPh)^+$[132] have been proposed. The mechanism of these transformations is not generally understood.

Some deductions on the mechanism of formation of the ortho metallated complexes have been made from the carbonylation reaction of a series of the chlorine bridged palladium dimers, II, containing a variety of ring substituents[97]. This reaction proceeds to give 2 aryl-3-indazolinones.

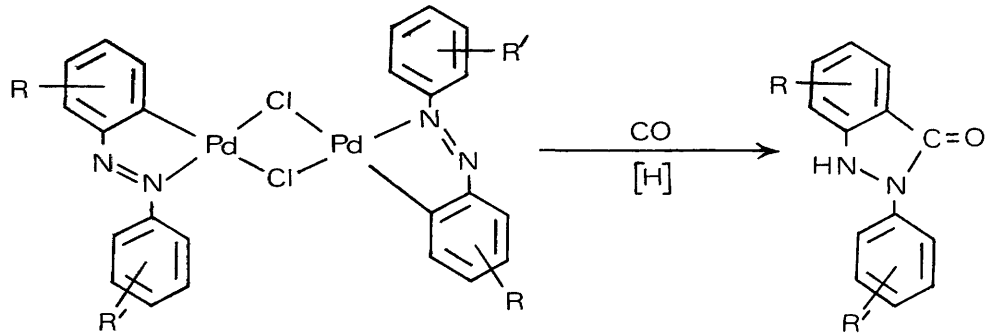
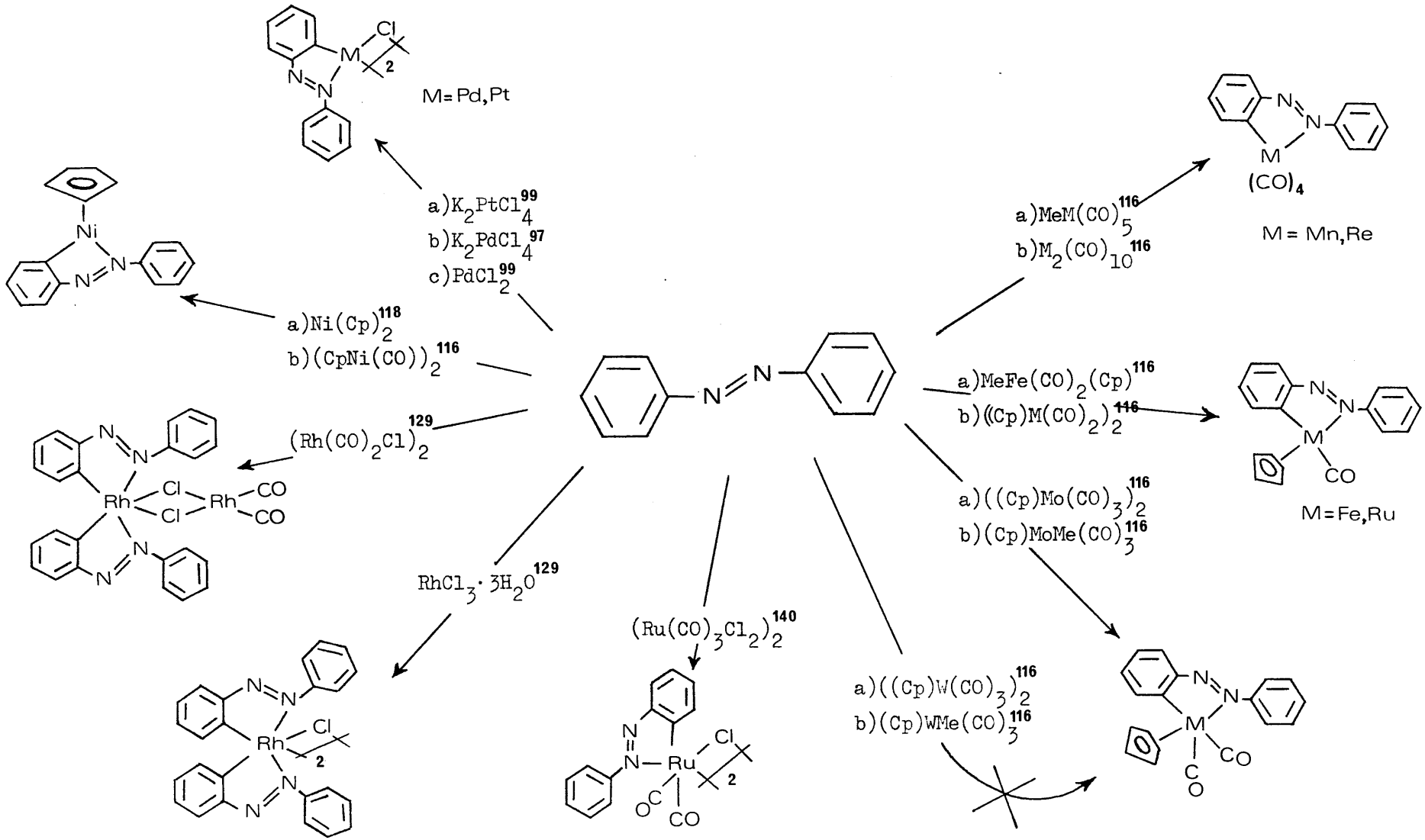
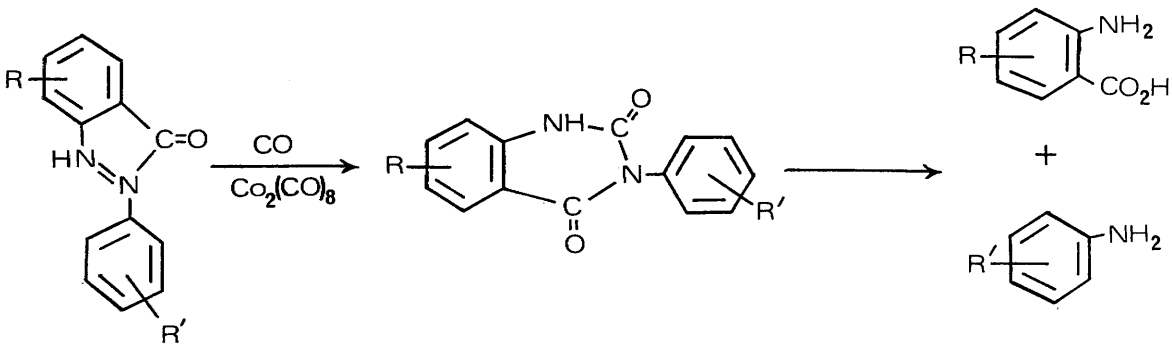


Figure I. Syntheses of C,N' bonded 2-(phenylazo)phenyl metal complexes by ortho metallation of azobenzene.



Subsequent conversion of the arylindazolinones to the corresponding anthranilic acid and aniline derivatives established the orientation of the initial σ— bond formation.



Takahashi and Tsuji concluded that ortho metallation occurs preferentially at the ring carrying the greater electron density (i.e. $4MeO\text{-}C_6H_4 > 4Me\text{-}C_6H_4 > C_6H_5 > 4Cl\text{-}C_6H_5$). This indicates that σ— bond formation proceeds by electrophilic attack by palladium. Similar conclusions were reached by Fahey[117] from the proportions of ortho chlorinated derivatives produced by the $PdCl_2$ catalysed chlorination of azobenzene. The majority (80%) of metallation took place at the non-chlorinated ring, again indicating electrophilic attack by palladium.

This mechanism seems unlikely, however, for reactions involving low-valent, electron-rich complexes such as $MeMn(CO)_5$. With these complexes Bruce et.al[133] have shown, again using substituent effects, that the main mechanism operating involves nucleophilic attack by the metal on the ring. In addition, their results for (h^5-cyclopentadienyl)-(2-(phenylazo)phenyl) palladium derivatives support the conclusion that the predominant mode of attack is electrophilic in the palladium cases. Thus, even when a fluorinated ring becomes metallated it occurs at the most electron rich position. In all cases the ratios of isomers produced were readily established by ^1H and ^{19}F NMR.

The effect of ring substitution on the σ— -donor ability of the

azo nitrogen atoms has not received much consideration. Bruce remarked that meta substitution would have little effect on their donor power[133]. In contrast, the oxidation of substituted azobenzenes to the corresponding azoxybenzene derivatives indicated that meta halogen substituents produced a much greater decrease in electron density at the azo link than para halogen substituents[134]. Meta methyl groups too were found to act as electron donors to the azo-nitrogen atoms and steric hinderance was observed in the reaction of 2,2'dimethylazobenzene[134].

The complex trans $(PhN{:}NPh)_2PdCl_2$[131,135], containing N-Pd bonds only, has been suggested as a precursor of the ortho metallated dimers[135]. It seems unlikely, however, that it is the prior coordination of nitrogen which directs the metallation to one ring or the other. Stronger coordination would be expected from the nitrogen atom adjacent to the more electron rich ring. This would direct the metallation process to the less electron rich ring, the opposite to what is found. Nevertheless, if an electrophilic process is important, it would also be favoured by prior coordination of the poorer donor nitrogen atom since this would make palladium more electrophilic.

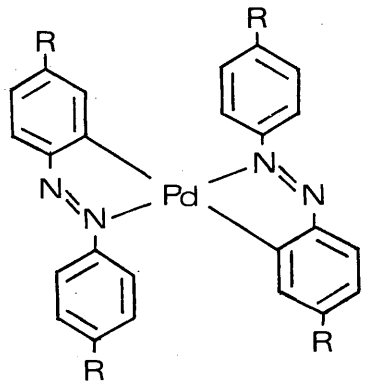
Electron donor substituents on the aromatic ring have been found to accelerate the reaction if nickelocene with azobenzene [49]. In the absence of any further information, it is possible this does reflect the greater σ^- donor character of nitrogen since $\pi \rightarrow \sigma^-$ conversion of a cyclopentadienyl group, produced by nucleophilic attack by nitrogen, is a likely first step [136]. Fahey observed a decrease in reactivity of ortho chlorinated azobenzenes with $PdCl_2$[117].

Reactions of ortho metallated azobenzene complexes.

Although many reactions of azobenzene transition metal complexes have been studied, their reactions fall into three main categories:

transfer of the phenylazophenyl group to other metals, bridge cleavage and replacement of other ligands, and syntheses of organic products by cleavage of the phenylazophenyl group from the metal.

The transfer of the phenylazophenyl group to other metals can be thought of as an extension to the method of preparing azobenzene metal complexes. The yields, however, are generally poor and the reactions of limited synthetic value. Heck demonstrated[137] that the reaction of $((azb)PdCl)_2$ with the ionic metal carbonyls, $NaCo(CO)_4$, $NaMn(CO)_5$ and $NaRe(CO)_5$, results in transfer of the phenylazophenyl group and formation of $(azb)M(CO)_n$ ($M = Co$, $n = 3$; $M = Mn, Re$ $n = 4$). He extended the reaction to several <u>meta</u> or <u>para</u> substituted derivatives. In marked contrast, no transfer to iron occurs with the azotoluene and azoanisole palladium dimers and $Na_2Fe(CO)_4$[127]. Transfer to another palladium atom was observed (though, interestingly, not in the reaction with $NaFe(CO)_2Cp$). Neutral orange complexes containing two <u>ortho</u> metallated azoarene species were formed.



R = Me,MeO

The neutral species $(Rh(CO)_2Cl)_2$ also undergoes reaction with $((azb)PdCl)_2$. The mononuclear rhodium(I) complex, $((azb)Rh(CO)_2)$ was formed[129].

Ustynyuk and his coworkers demonstrated[138] that transfer to mercury is possible. The nickel complex, ($\underline{h}^5$-cyclopentadienyl)(2-(phenylazo)phenyl)

nickel, was readily cleaved by mercuric acetate or mercuric chloride in the presence of sodium acetate. The products from these reactions were ortho mercurated azobenzenes, $PhN{:}NC_6H_4HgX$, (X=OAc or Cl). The presence of the mercury carbon bond was demonstrated by formation of 2-(phenylazo)phenylbromide by reaction with bromine.

Bridge cleavage and ligand replacement reactions have been observed for many (2-(phenylazo)phenyl) transition metal complexes. Cope's platinum and palladium dimers react with a wide variety of Lewis Bases to form mononuclear complexes $(PhN{:}NC_6H_4)M(L)Cl$ (e.g. M=Pt, L=PR_3[99], CN^-[99], CO[139]) with bidentate C,N' bonded azobenzene groups. The halogen-bridged dimer of ruthenium, $((PhN{:}NC_6H_4)Ru(CO)_2Cl)_2$, has also been shown[140] to undergo bridge splitting reactions to give the mononuclear species, $(PhN{:}NC_6H_4)Ru(CO)_2L(Cl)$, (L=$PPh_3$, $AsPh_3$, $NH_2C_6H_4$-pMe, Py, imidazole). The rhodium dimer, $((PhN{:}NC_6H_4)_2RhCl)_2$, reacts less readily with Lewis Bases[129]. Bridge splitting occurred easily with THF but prolonged reflux was necessary to form $(PhN{:}NC_6H_4)_2Rh(PPh_3)Cl$. No reaction at all was observed with para-toluidine, in contrast to the ruthenium case above.

Kooti and Nixon[141] found that analogous mononuclear species were not formed from the reaction of triphenylphosphine with $(PhN{:}NC_6H_4)_2Rh(\mu\text{-}Cl)_2RhLL'$ (L=L'=PF_3 and L=CO,L'=PF_3). In this case it is thought that the expected phosphine complexes, $(PhN{:}NC_6H_4)_2Rh(PPh_3)Cl$, are produced as intermediates but that the lability of the phosphine results in equilibration to $((PhN{:}NC_6H_4)_2RhCl)_2$ and trans $RhClL(PPh_3)_2$.

Opening of the chelate ring by cleavage of the M-N bond has been observed less frequently than the above bridge cleavage reactions which

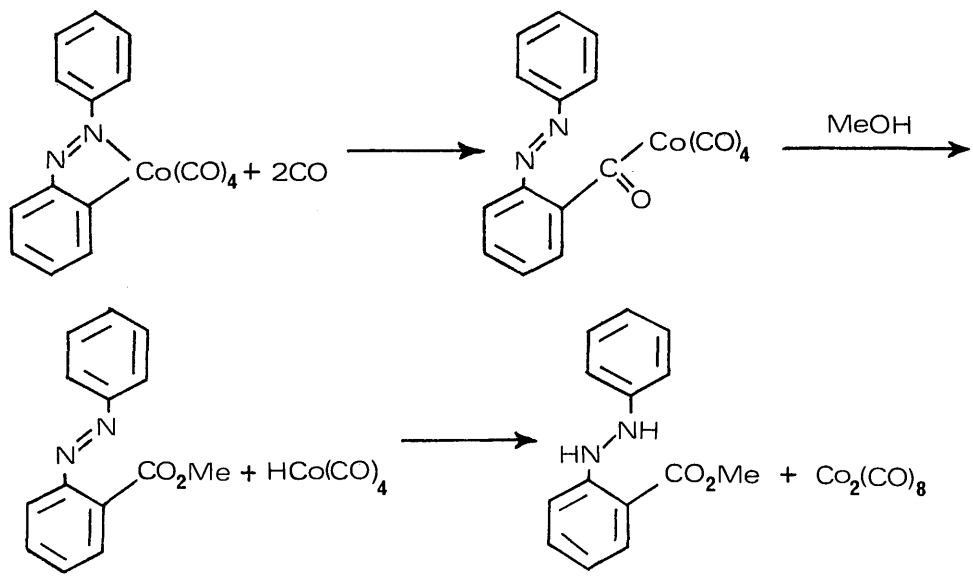
leave the chelate ring intact. The first example of this displacement was the reaction of $((azb)PdCl)_2$ with two moles of triethylphosphine[124]. Orange crystals of $\underline{trans}(C_6H_5N_2C_6H_4)Pd(PEt_3)_2Cl$ were produced and the important features of its X-Ray structure have already been discussed. Bruce and his coworkers have found[140] similar ring opening occurs with $((azb)Ru(CO)_2Cl)_2$ if reacted with a chelating ligand such as 'diphos', which does not replace halide. 2,2'bipyridyl is an exception in that it forms a cationic complex formulated as $[PhN_2C_6H_4Ru(CO)_2(bipy)]^+$ $[PhN_2C_6H_4Ru(CO)_2Cl_2]^-$. It was established that sodium cyclopentadienide also produces ring opening with formation of $(PhN_2C_6H_4)Ru(CO)_2Cp$[140]. The chelate ring reforms with loss of CO on irradiation of this complex with U.V. light.

The nitrogen atom of the phenylazophenyl chelate in (azb)Ru(CO)Cp is not displaced by heating with triphenylphosphine[140]. Only starting materials were recovered. Moreover, irradiation of (azb)Ru(CO)Cp or (azb)Fe(CO)Cp produced substitution of the carbonyl by phosphine showing that CO displacement is favoured over opening of the ring[140]. Since displacement of CO in similar iron complexes is a difficult process, the mechanism of the substitution has been suggested to involve coordination of phosphine with initial displacement of nitrogen. Subsequent displacement of CO by attack of nitrogen would reform the chelate ring structure. This postulate is supported by brief kinetic data on carbonyl replacement by triphenylphosphine in $(azb)Co(CO)_3$[137]. The kinetic results are compatible with a mechanism involving fast displacement of the coordinated nitrogen by phosphine, followed by slow rate determining loss of carbon monoxide by attack of nitrogen.

The final category of reactions undergone by azobenzene complexes is in synthesis of organic products by cleavage of the phenylazophenyl group from the metal. These reactions may be subdivided into carbonylation reactions, nitrogen heterocycle synthesis, halogenation reactions and lithium aluminium hydride cleavage reactions.

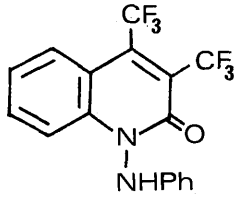
Carbonylation Reactions. The reaction of various ring-substituted azobenzene palladium dimers, $((azb)PdCl)_2$, with CO under pressure in protonic solvents produced no isolable palladium complexes[97]. Instead, 2 aryl-3 indazolinones were isolated in good yield. This reaction is reminiscent of the catalytic transformation of azobenzene to 2 phenyl-3 indazolinone by dicobaltoctacarbonyl[142] and strongly indicates that the latter reaction may well proceed by ortho metallation of azobenzene followed by insertion of carbon monoxide into the cobalt carbon bond.

In contrast, carbonylation of tricarbonyl(2(phenylazo)phenyl)-cobalt in methanol solution produced 2-carbomethoxyhydrazobenzene[137] The mechanism proposed envisages coordination of CO at cobalt resulting in carbonyl insertion and displacement of nitrogen. Attack of methanol would rupture the metal carbon bond with formation of hydrido-cobalt tetracarbonyl which can then serve to reduce the liberated azobenzene derivative.

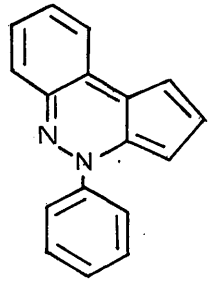


In these reactions organic derivatives with carbonyl residues in the ortho position are formed. In marked contrast are the reactions of carbon monoxide with the rhodium complexes, $((azb)_2RhCl)_2$ and $((azb)_2Rh(-\mu-Cl)_2Rh(CO)_3)$. These complexes yielded[143] the bis azobenzene derivatives linked in the ortho position by a carbon-carbon bond. It may well be that coordination of carbon monoxide causes concomitant carbon-carbon bond formation between the two cis azobenzene groups in preference to displacement of the nitrogen atom from the metal.

Nitrogen heterocycle synthesis. The reaction of $(azb)(Co(CO)_3)$ with hexafluorobut-2-yne produced two products resulting from insertion of the acetylene into the cobalt-carbon bond[145]. The organic product, whose proportional yield increases with increasing reaction time was shown to be an N-anilinoquinolone, XV.



XV



XVI

X-Ray structure determination revealed that the other, metal-containing product is formed by insertion of one acetylene and one carbon monoxide molecule into the cobalt-carbon bond of the starting material. This product is presumably a precursor of the purely organic product.

Ustynyuk and his coworkers isolated 4-phenyl-4H-cyclopenta-[C]-cinnoline, XVI, a non benzenoid aromatic compound, from (h^5-cyclopentadenyl)(2-(phenylazo)phenyl) nickel by two routes: perbenzoic acid oxidation[138] and reaction with 2-haloazobenzenes[115]. Use of the nickel complex containing para-substituted azobenzenes established that the azobenzene residue in the organic product derives from the nickel complex only.

Halogenation Reactions. Fahey demonstrated that catalytic ortho-chlorination of azobenzene could be achieved by bubbling chlorine through a mixture of azobenzene and $PdCl_2$.[117] All five possible ortho-chlorinated products were produced. Reaction of the complex $(azbPdCl)_2$ with excess chlorine or bromine gave initially almost quantitative yields of 2-(phenylazo)phenylhalide. When the chlorination reaction was continued for 60 hours, however, it was found that again a mixture of all five ortho-chlorinated products was present, the tetrasubstituted product predominating. It is clear, therefore, that the ortho-palladation/halogen cleavage cycle repeats itself producing, after longer reaction times, the more highly substituted products.

Interestingly, this does not hold for the bromination reaction which could only be effected stoicheiometrically[117]. The attempted catalytic reaction produced only a complex mixture of products. This was attributed to the failure to remove HBr from the system which would retard the formation of $((azb)PdBr)_2$ and also catalyse the bromination of azobenzene itself. No significant halogenolysis of azobenzene was observed using $PtCl_2$, though this may be ascribed to the slow formation of $((azb)PtCl)_2$

Specific cleavage of (2-(phenylazo)phenyl) mercuric acetate or chloride by bromine has been demonstrated[138]. 2-bromoazobenzene was isolated in high yield from the reaction mixture.

Lithium aluminium hydride cleavage reactions. Many (2(phenylazo)phenyl) transition metal complexes have been reported to react with lithium aluminium hydride to liberate free azobenzene. The reduction by $LiAlD_4$[99] which establishes the position of metallation has already been mentioned. The reaction appears to have complete generality but for the complex $(azb)Mo(CO)_2Cp$. which yields the reduced product, hydrazobenzene[116].

Nixon has reported [141] that azobenzene is reduced to hydrazobenzene by $LiAlH_4$ in the presence of catalytic amounts of $(RhCl(PF_3)_2)_2$, whereas azobenzene itself is unaffected by $LiAlH_4$. A variety of metal halides (including $MoCl_5$) have been found to catalyse this reduction[146]. It may be, therefore, that $(azb)Mo(CO)_2Cp$ is a catalyst for the reduction of azobenzene to hydrazobenzene.

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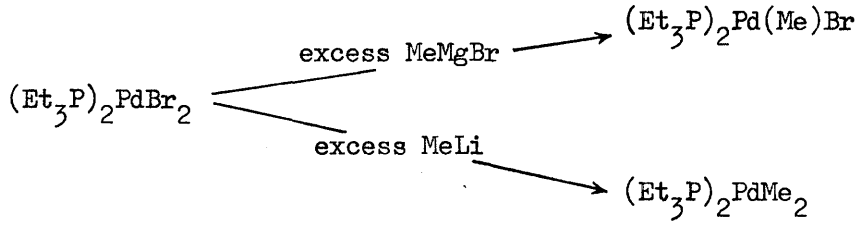
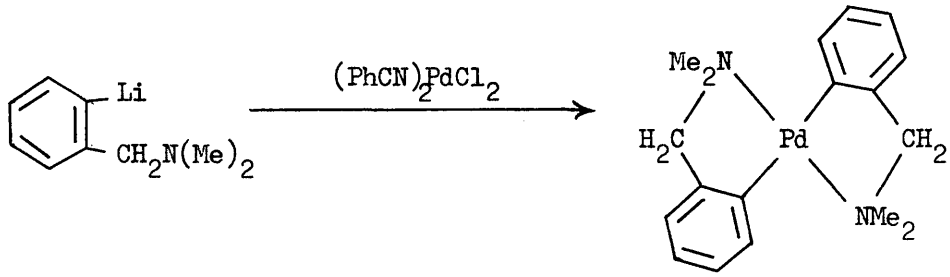
The present study of azobenzene metal complexes and in particular the preparation and synthetic uses of (2-(phenylazo)phenyl)mercurials was prompted by the lack of a high-yield route to Cope's halogen bridged platinum complex, $((azb)PtCl)_2$. Transfer of the organic group from Grignard or organolithium reagents is the most widely used method of preparing simple alkyl or aryl complexes of platinum or palladium e.g.



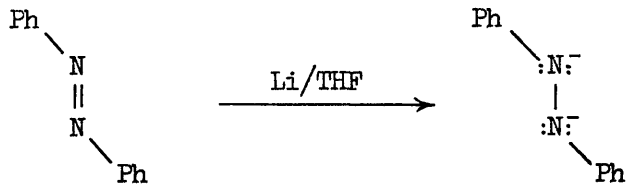
Ref. 29

More specifically, transfer of N,N dimethylbenzylamine from the ortho-lithio derivative to palladium results in a complex containing a chelate C,N bonded ring.



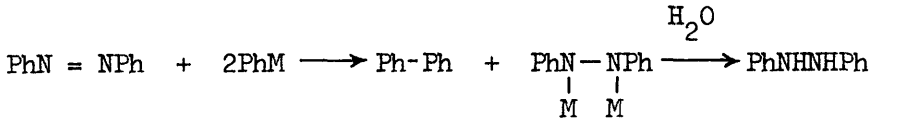
Ref. 147

The preparation of Grignard and organolithium derivatives from azobenzene is ruled out since alkali-metals reduce azobenzene with the formation of the radical dianion.



Ref. 148

Grignard or organolithium reagents also reduce azobenzene.



Ref. 149

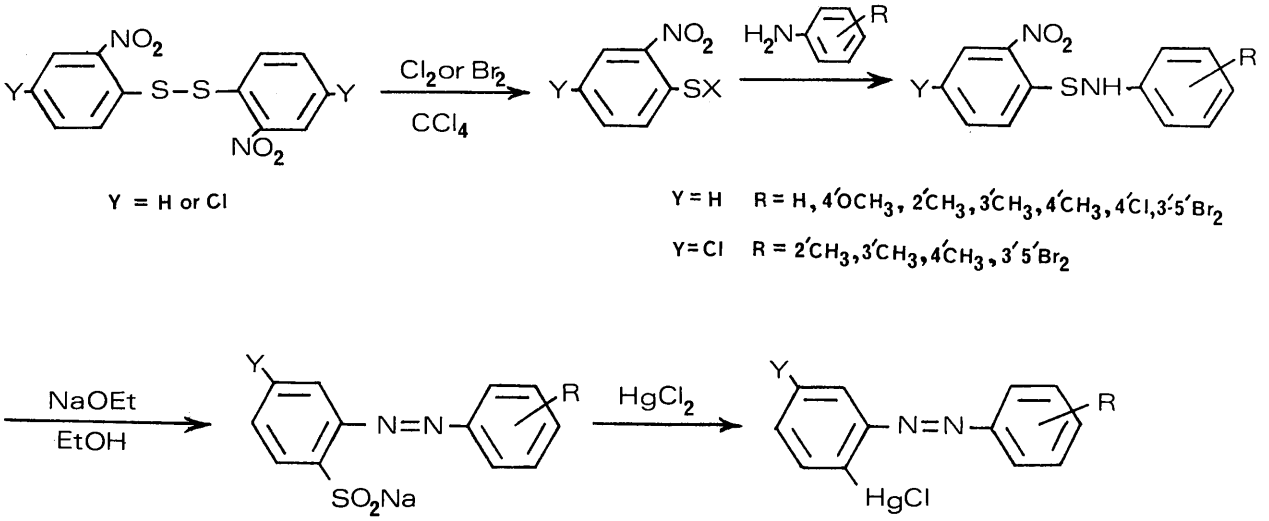
M = MgBr, or Li

Organomercury compounds are known to react with platinum and palladium complexes resulting in transfer of the organic group from mercury [150]. The synthesis of (2-(arylazo)aryl)mercurials was therefore undertaken in the likelihood that they would be the most promising transfer reagent. Since their preparation from the corresponding Grignard or organolithium reagent was prohibited for the reasons mentioned above, an effective synthesis was difficult to find. The synthesis developed incorporated the remarkable rearrangement of 2-nitroarylsulphenanilides to 2-(arylazo)arylsulphinates[151]. This was followed by an extension of the Peter's reaction[152] which was found to produce the desired 2-(arylazo)-arylmercuric halides.

RESULTS AND DISCUSSION.

Preparation of the (2-(arylazo)aryl) mercurials.

The (2-(arylazo)aryl) mercuric halide derivatives were prepared by the four-step synthetic route shown in the scheme below.



This Scheme will be considered in two parts

Preparation of the sodium (2-(arylazo)arylsulphinate derivatives. This preparation involves three steps; formation of arylsulphenyl halides, transformation to arylsulphenanilide derivatives and rearrangement to the 2-(arylazo)arylsulphinate derivatives. The ease of formation of sulphenyl halides from the disulphide and the subsequent conversion to the sulphenanilide has been known for over half a century, since the initial investigations of Zincke and Farr[153]. The chemistry of sulphenyl halides and sulphenanilides has been reviewed[154].

2-nitrobenzenesulphenylchloride and 2-nitro,4-chlorobenzensulphenyl-chloride were prepared from the corresponding disulphides, (which are commercially available) by halogen cleavage according to the literature method[155]. It was found that cleavage of bis(2-nitro,4-chlorophenyl)-

disulphide failed at room temperature in the absence of iodine to activate the reaction. Complete recovery of starting material was achieved. At 50°C this chlorination was observed to proceed faster than with bis(2-nitrobenzene)disulphide presumably because the presence of the 4-chloro substituent facilitates nucleophilic attack by chlorine at sulphur.

The sulphenyl chloride derivatives crystallised as yellow needles from hot carbon tetrachloride but were decolourised with evolution of hydrogen chloride on exposure to air for some weeks. Storing the yellow crystalline products in a desiccator prevented this hydrolysis which is known to be more rapid for the sulphenyl chlorides than bromides[154]. The white product from the hydrolysis is likely to be the sulphenic anhydride.

$$2NO_2\text{-}C_6H_4SCl + H_2O \rightleftharpoons (NO_2C_6H_4S)_2O + 2HCl$$

The conversion to the corresponding sulphenanilides was readily achieved by the reaction with the appropriately substituted anilines in ether. The reaction was performed at 0°C with dropwise addition of amine but in no case was there evidence of an excessively vigorous reaction. Two molar equivalents of the amine were used and occurrence of reaction was indicated by the formation of amine hydrochloride by-product as a white precipitate. With the exception of 2-nitro,4-chlorobenzenesulphen-o-toluidide, 2-nitrobenzenesulphen 3',5'-dibromoanilide and 2-nitro,-4-chlorobenzenesulphen 3',5'-dibromoanilide, all the sulphenanilides have been previously reported. The preparation was successful with all the substituted anilines used except for 2,4,6-tribromoaniline. In this case no precipitate of amine hydrochloride formed at room temperature and evaporation of the ether solvent gave only starting material. The failure of this reagent has, in fact, been observed by other workers[156]. It seems likely that the lack of reaction with this substituted aniline and the few

others which do not react (e.g. o-nitroaniline[151]) is the low basicity caused by the electron withdrawing effects of the ring substituents. In all other cases, yellow or maroon crystalline products which are stable to hydrolysis were formed.

The rearrangement of the sulphenanilide derivatives to the sodium 2-(arylazo)arylsulphinates was achieved in refluxing ethanol/water solution in the presence of sodium hydroxide. The reaction proceeded without exception. In every case the colour of the solution darkened from orange to brown. A more remarkable colour change to intense violet was observed in the initial stages of the rearrangement of all three isomers of 2-nitro,-4-chlorobenzenesulphen-toluidide. This violet colour was not observed with any of the other derivatives, although it is possible that in some cases it may have gone unnoticed. The sodium 2-(arylazo)-arylsulphinates, which are very soluble in ethanol but less so in water, were obtained as glistening orange crystals. Full characterisation was not made but it is observed that the two IR stretching frequency bands, $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$, at about 1560 cm^{-1} and 1330 cm^{-1} respectively (see Table I) which are present in the sulphenanilides are absent in the sulphinate derivatives. The IR spectra of most of these complexes is dominated by two strong bands at about 1025 cm^{-1} and 970 cm^{-1} characteristic of the sulphinate group[157].

The rearrangement of these sulphenanilide derivatives makes use of a reaction first developed by Moore and Johnson who in fact deduced the wrong structure for the rearrangement products.[158] Their formulation was revised by Cava and Blake who correctly identified the products as sodium 2-(arylazo)arylsulphinates.[159] In a closer study of the reaction Brown showed that the kinetics of the transformation can be explained by an 8-step intermolecular route.[151] The generality of the rearrangement,

Table I. $\nu(NO_2)$ for a series of 2-nitrobenzenesulphenanilides.

Compound	$\nu_{asym}(NO_2)$ (cm^{-1})	$\nu_{sym}(NO_2)$ (cm^{-1})
$2\text{-}NO_2C_6H_4SNHC_6H_5$	1559(lit[151],1575)	1334br(lit[151],1345)
$2\text{-}NO_2C_6H_4SNHC_6H_4\text{-}4Cl$	1567	1329br
$2\text{-}NO_2C_6H_4SNHC_6H_4\text{-}4OMe$	1564	1336br
$2\text{-}NO_2C_6H_4SNHC_6H_4\text{-}4Me$	1565	1330br
$2\text{-}NO_2C_6H_4SNHC_6H_4\text{-}3Me$	1561	1335br
$2\text{-}NO_2C_6H_4SNHC_6H_4\text{-}2Me$	1565	1331br
$2\text{-}NO_2C_6H_4SNHC_6H_3\text{-}3,5Br_2$	1555	1330br
$2\text{-}NO_24\text{-}ClC_6H_3SNHC_6H_5$	1552	1330br

.....

Table 2. Characteristic bands for a series of sodium 2-(arylazo)arylsulphinates.

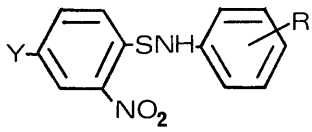
$(C_6H_5N{:}NC_6H_4)SO_2Na$	975sbr	1020sbr
$(4\text{-}MeC_6H_4N{:}NC_6H_4\text{-}4Cl)SO_2Na$	976sbr	1027sbr
$(3\text{-}MeC_6H_4N{:}NC_6H_4\text{-}4Cl)SO_2Na$	974sbr	1027sbr
$(2\text{-}MeC_6H_4N{:}NC_6H_4\text{-}4Cl)SO_2Na$	975sbr	1027sbr

however, is not complete. When the substituted aniline employed bears a <u>para</u> - NO_2 substituent it was found that the rearrangement failed.

The success of the rearrangement reaction for the complete range of substituents on the aniline ring may be correlated with the Hammett σ— constants for these substituents. The Hammett σ— constant is a measure of the effect which the substituent has on the electron density at the reaction site. Generally the more electron-attracting a substituent is, the more positive its σ— value (relative to H = 0.00). Furthermore, it has been found that for multiple substituents the value obtained experimentally is close to the sum of the values for a single substituent. For example, the substituent constant for 3,5-dibromo substitution is 0.720 whereas strict additivity would give a value of 0.782[160].

It would appear from the failure of the rearrangement when ring 2 bears a <u>para</u>-NO_2 group[151] can be accounted for by its high Hammett σ— constant. The NO_2 group is somewhat exceptional in that a separate constant, σ^{-*}, has to be used for reactions involving phenols and anilines. The necessity for dual substituent constants is also found for certain other electron-attracting groups (e.g. CN^-). It seems likely, therefore, that in a comparison of substituent constants for the present reaction the value of σ^{-*} should be chosen for the NO_2 group. Support for this suggestion comes from the successful rearrangement when ring 2 bears 3',5'dibromo substituents. In this case the substituent constant (0.720) closely approaches that of σ— for the 4-nitro group (0.778), but is less close to that of σ^{-*} (1.270)

Hammett σ^- constants for the ring substituents in the sulphenanilides.



Y = H or Cl

Substituent, R	σ^-_{meta}	σ^-_{para}	σ^{-*}_{para}
4-NO_2		0.778	1.270
4-Me		-0.170	
4-Cl		0.227	
4-MeO		-0.268	
3-Me	-0.069		
3,5-Br_2	0.720		

It can be seen that whichever value is used for the NO_2 group it exceeds that of all the other substituents. The implication is, therefore, that while some groups (e.g. CN^-) whose Hammett σ^- (or σ^{-*}) constant approaches that of NO_2 might prevent the rearrangement, the vast majority of substituents will allow it, and this step should be quite versatile.

Conversion to the (2-(arylazo)aryl) mercuric halides. In the final stage of the reaction sequence the sodium (2-arylazo)arylsulphinates were easily converted to (2-(arylazo)aryl) mercuric halides by reaction with mercuric halide in water or ethanol. Ethanol is more convenient since water has the practical disadvantage that the insolubility of the product leads to loss of stirring efficiency. Even in refluxing ethanol the flocculent orange product precipitates out, in most cases.

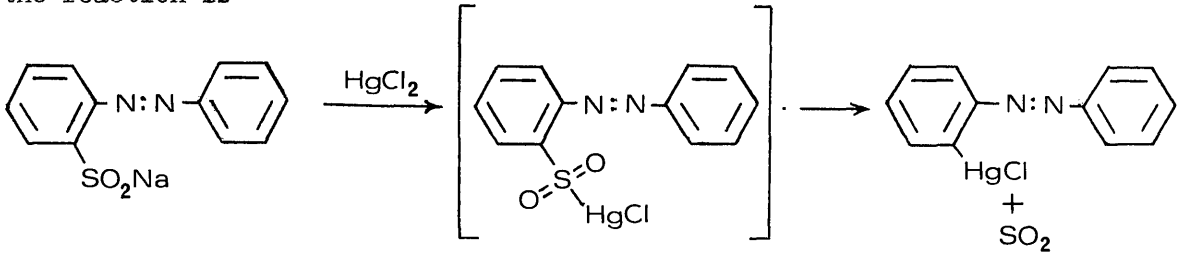
The evolution of sulphur dioxide during the reaction was inferred from the pungent smell at the neck of the reaction vessel and the red colour produced with wet litmus paper.

The (2-(arylazo)aryl) mercuric halides are all orange or orange-red, air stable, crystalline solids which have low solubility in most organic solvents. Recrystallisation from benzene results in the formation

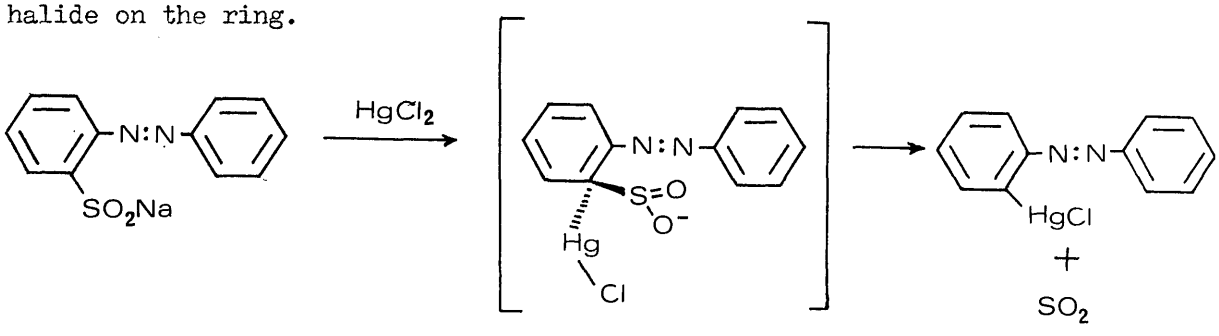
of glistening clusters of needle-shaped crystals as illustrated by the photographs of (2-(phenylazo)phenyl) mercuric iodide and 2-(4'-methoxy-phenylazo)phenylmercuric chloride.

This reaction is an extension of that first developed by Peters in 1905 for the synthesis of para-tolylmercuric chloride from para-tolylsulphinic acid and mercuric chloride.[152] The reaction has recently been extensively studied by Deacon and his coworkers[161]. They have presented evidence that the Peter's Reaction proceeds by way of an intermediate chloro(arenesulphinate) mercury (II) complex. These intermediates have been isolated in some cases and on the basis of their IR spectra are thought to be S-bonded. Heating in aqueous solution or in vacuo leads to the formation of arylmercuric halides.

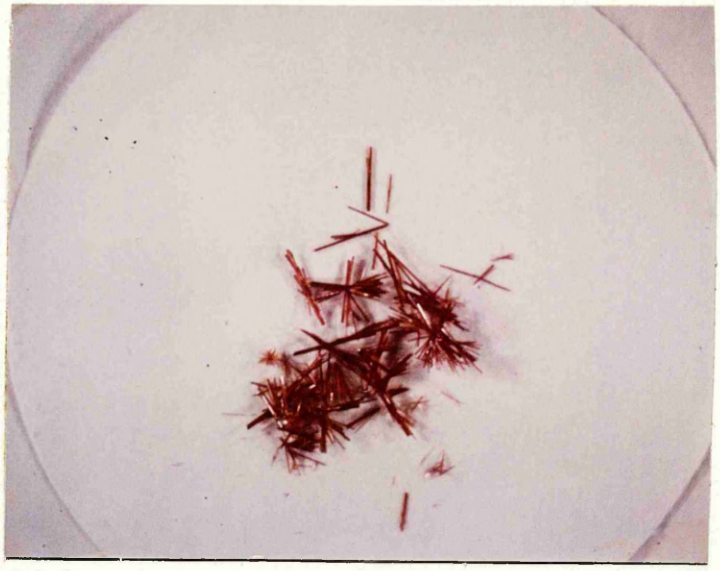
No attempt has been made to isolate such intermediates in the present case, but on the basis of these results a likely mechanism of the reaction is



An alternative mechanism which cannot be excluded in the absence of any isolated intermediate is that of direct electrophilic attack by mercuric halide on the ring.



The by-product of the reaction is sodium chloride. If the Peter's



SCALE : 4 cm

2-(4′-METHOXYPHENYLAZO) PHENYL MERCURIC CHLORIDE

SCALE : 4 cm

2-(PHENYLAZO) PHENYL MERCURIC IODIDE

Reaction is performed using the sulphinic acid rather than its sodium salt, hydrogen chloride is produced.

Sulphur dioxide extrusion in other systems has lead to formation of a variety of metal-carbon bonds.[162] The reverse reaction, SO_2 insertion, has also received much recent study and has been reviewed[163]

$$MSO_2R \rightleftharpoons MR + SO_2$$

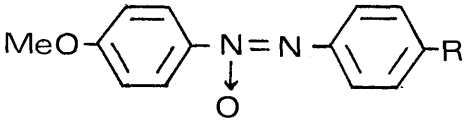
The formation of the (2-(arylazo)aryl) mercuric chlorides was accompanied by the production of significant amounts of an insoluble grey powder. This was identified as mercurous chloride by its melting point and the following spot tests which differentiate between mercury (I) and mercury(II) chloride.

Reagent	Mercuric Salts	Mercurous Salts
KI	Red precipitate which dissolves on adding excess KI $HgCl_2 + 2KI \longrightarrow HgI_2 + 2KCl$ $HgI_2 + 2KI \longrightarrow K_2(HgI_4)$	Yellowish-green precipitate
KOH	Yellow-orange precipitate $HgCl_2 + OH^- \longrightarrow \underbrace{HgO}_{\text{Yellow or red form depending on particle size}}$	Black precipitate $Hg_2Cl_2 + 2OH^- \longrightarrow \underbrace{Hg + HgO + H_2O}_{\text{black precipitate}}$

A separate experiment established that passing sulphur dioxide through a refluxing ethanol solution of mercuric chloride for the same length of time as the sulphinate reaction, resulted in very little reduction (<3%). It was also found that, in cases where equimolar amounts of mercuric chloride and sodium 2-(arylazo)arylsulphinate had been used, the latter was completely consumed since no more product was obtained on

adding excess mercuric chloride at the end of the reaction. This implies that some of the sulphinate has undergone a transformation to a different product than (2-(arylazo)aryl) mercuric chloride. These two observations indicate that the reduction is facilitated by some reaction-intermediate, perhaps the chloromercurisulphinate complex. The reduction to mercurous chloride has been noted previously for the Peter's reaction but ascribed to reduction by the sulphurous acid formed.[164] It was also suggested that some inorganic mercury was present in the form of the mercuric salt of the sulphonic acid, produced by oxidation of some of the sulphinic acid. This may also be the fate of some of the sodium 2-(arylazo)arylsulphinate in the present reaction.

The melting points of some of the (2-(arylazo)aryl) mercuric halides are not sharp even for analytically pure samples. A possible explanation might be the formation of liquid crystals as some related derivatives, for example XVIIA & B, have been observed to display this phenomen.[165]



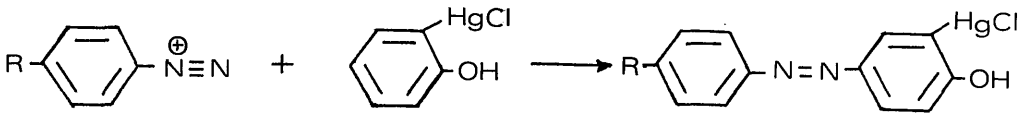
XVIIA & B R = Et; R = C_4H_9

The general requirements for molecules to form liquid crystals are that they should be rod shaped, should have one or more aromatic ring and have multibond linkages (such as -CH=N-, -CH=CH-, or -N=N-). All these requirements are met by the present compounds, and this explanation is favoured.

Nevertheless, the possibility that spontaneous symmetrisation caused the broad melting range cannot be excluded. Symmetrisation of RHgX by ammonia is well established and probably proceeds by way of

$RHgBr \cdot NH_3$[166]. It is therefore feasible that the more distant atom of the azo-linkage may play a similar role in producing spontaneous symmetrisation.

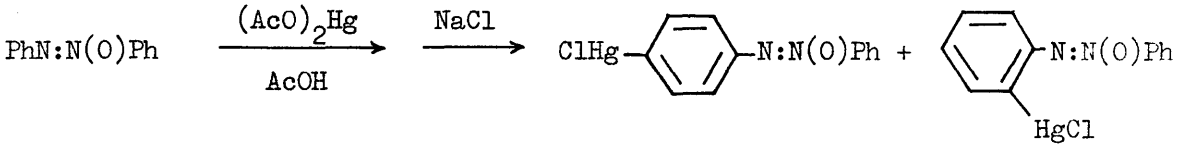
Few reports of mercury derivatives of azobenzene appear in the literature. Ustynyuk and his coworkers isolated (2-(phenylazo)phenyl)-mercuric chloride (for which a different melting point is reported in this work) and (2-(phenylazo)phenyl) mercuric acetate from the cleavage of $\underline{h}^5$-cyclopentadienyl(2-(phenylazo)phenyl) nickel by $HgCl_2$ and $Hg(OAc)_2$ respectively.[138] Two hydroxyl-bearing derivatives were prepared in moderate yields from the reaction of 2-(chloromercuri)phenol with diazotized amines.[112]



R = H, NO_2

Since the publication of some of this present work on (2-(arylazo)-aryl) mercurials, Rausch et.al.[167] reported the synthesis of some chloromercuri-derivatives of azobenzene. These were isolated from refluxing methanol solutions of azobenzene (or substituted azobenzenes) and mercuric acetate by addition of lithium chloride. Incorporation of mercury at the carbon atoms adjacent to the azo link took place in every case. For example, a mixture of products was obtained from the reaction with azobenzene itself. (2-(phenylazo)phenyl) mercuric chloride, the only monosubstituted product, was isolated in 40% yield from an inseparable mixture of two disubstituted derivatives. Likewise, mercuration of 2-(phenylazo)phenyliodide gave low yield of two separable mercurials: (2-(2'-iodophenyl)phenyl) mercuric chloride and (2-(phenylazo)3-iodophenyl)-mercuric chloride.

Similar work on the mercuration of azoxybenzenes had previously been carried out by Japanese workers. Although yields were low the only isolated products were those resulting from mercuration of the ring not adjacent to the oxygen-bearing nitrogen atom.[168]



In contrast to the mercuration of azobenzene, the chloromercuri-substituent was introduced in both ortho and para positions. Both these observations cast doubt on the conclusion drawn by Rausch that an azo nitrogen directs, by coordination, the mercury into the ortho position of the benzene ring (analogous to the proposed mechanism for ortho-palladation of azobenzene). In azoxybenzene only one nitrogen is available to direct the mercuration by this means. This,however, would result in mercuration of the more distant ring, the opposite to the observed result. Furthermore, the formation of a para-chloromercuri group indicates that in this case, at least, some of the reaction proceeds by direct electrophilic attack at the para position.

In contrast to the above reactions it was found in the present study that no mercuration resulted from ethanol solutions of azobenzene and mercuric chloride even after prolonged reflux. This distinction is not surprising since mercuric halides are among the least active mercurating agents while mercuric acetate is one of the most effective[15].

The great advantages of the present synthetic route to (2-(arylazo)aryl) mercuric halides are that it affords specific substitution by mercury at the required position and that it carries the potential for specific and predictable unsymmetrical substitution of both rings. Monosubstitution at the ortho position of one ring is afforded by

the $\underline{h}^5$-cyclopentadienyl(2-(phenylazo)phenyl) nickel route, but not by direct mercuration. Since the electronic effect of mercury in a benzene ring is weak[169], mercuration of several positions in the ring is possible. Indeed, for one recently reported case complete mercuration was achieved[169]. Specific unsymmetrical substitution of the two rings is not possible in either of these two methods since the position of the chloromercuri group relative to the other ring substituents is unpredictable. In many cases more than one isomer may form and these may well be inseparable.

A synthetic route based on the use of diazotized anilines, mentioned above, would be limited to derivatives bearing <u>para</u>-OH or $-NH_2$ groups for which the diozotization reaction holds. In addition, the diazotization step is not always simple.

Although the sulphinate route consists of a multi-step process the yields at each stage are high and all the materials are easily handled. The synthesis of $\underline{h}^5$-cylopentadienyl(2-(phenylazo)phenyl) nickel, though a one step process, occurs in very low yield. Likewise, the direct mercuration route requires the initial preparation of substituted azobenzenes (normally from the appropriately substituted nitrosobenzene and aniline derivatives) and is followed by a step of highly variable yield which may involve a difficult separation of several products.

<u>Reactions of (2-(arylazo)aryl) mercurials.</u>

<u>Symmetrisation.</u> (2-(phenylazo)phenyl) mercuric chloride reacted with triphenylphosphine in acetone to produce the diorganomercurial; bis(2-(phenylazo)phenyl) mercury(II).

$$2(C_6H_5N{:}NC_6H_4)HgCl + 2Ph_3P \longrightarrow (C_6H_5N{:}NC_6H_4)_2Hg + (Ph_3P)_2HgCl_2$$

Bis(triphenylphosphine) mercuric chloride[170] was characterised as the by-product of the reaction. Isolation of bis(2-(phenylazo)phenyl) mercury was achieved by extraction with ether which takes advantage of the greater solubility of bis(2-(phenylazo)phenyl) mercury than bis(triphenylphosphine)-mercuric chloride in this solvent. Recrystallisation from ethanol produced orange crystalline clusters.

It was found that use of an ion exchange column packed with Amberlyst A26 resin provided a more convenient method of symmetrisation. Conversion to the iodide form of the resin gave better results. The convenience of the method is twofold. Firstly, the elution of the product can be easily followed by the distinctive intense orange colour of the phenylazophenyl moiety. Secondly, the chromatographic technique provides the product in a high degree of purity and dispenses with the separation of products by fractional crystallisation which is necessitated after the phosphine symmetrisation route.

Tertiary phosphines are well recognised symmetrising agents. In general, one role at least of symmetrising agents is to remove the inorganic mercury salt (by complexation, precipitation or reduction) thereby forcing the equilibrium to the right.

$$2RHgX \rightleftharpoons R_2Hg + HgX_2$$

The symmetrisation of meta-tolylmercuric chloride by triphenylphosphine has been shown to be accompanied by an increase in conductivity corresponding to the formation of $(\underline{m}\text{-}MeC_6H_4HgPPh_3)^+Cl^-$[171]. A subsequent fall in conductivity is accompanied by the production of $(Ph_3P)_2HgCl_2$. The formation of bis(2-(phenylazo)phenyl) mercury may well follow a similar reaction course.

The symmetrisation found to occur using an ion-exchange column marks an interesting extension to the use of chromatographic materials in

symmetrisation reactions. A similar reaction has recently been reported using KI adsorbed on an alumina column.[172] Iodide is another recognised symmetrising agent and in both cases the reaction probably occurs by nucleophilic attack by I^- at mercury. This would lead to increased electron density on the phenylazophenyl group (R) which would enhance its ability as an electrophilic substrate to a second $(C_6H_5N{:}NC_6H_4)HgCl$ molecule

$$RHgX + I^- \rightleftharpoons R^{\delta-} — \underset{\uparrow}{Hg}(I^-) — X$$

Attack of a second molecule leads to an intermediate complex which may decompose via a four-centre transition state to give the observed products.

$$R — \underset{\uparrow}{Hg}(I^-) — X \xrightarrow{RHgX} R — Hg\cdots X \longrightarrow R_2Hg + (I)HgX_2$$

$$R\cdots Hg — X \quad (I^-)$$

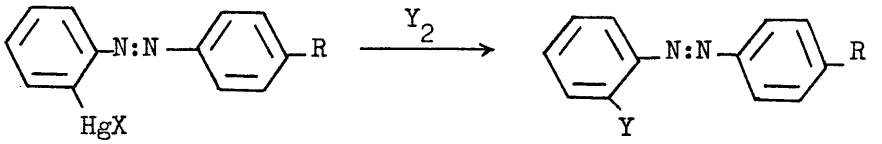
The mercuric halide was not recovered from the column and must remain firmly bound. Indeed, it is an essential facet of this method that strong absorption of HgX_2 occurs to allow separation of the products.

In its chloride form, the ion exchange resin was less effective which is in agreement with the known relative nucleophilicity and symmetrising ability of chloride and iodide. The complete symmetrisation obtained with (2-(phenylazo)phenyl) mercuric chloride is encouraging from the established decreasing ease of symmetrisation, $RHgI > RHgBr > RHgCl$[172]. It seems likely, therefore, that complete symmetrisation could also be achieved by this method, using the other (2-(phenylazo)phenyl) mercuric halides.

Use of (2-(arylazo)aryl) mercurials in synthetic organic chemistry.

(i) Reaction with halogens. Facile halogen cleavage of the mercury-

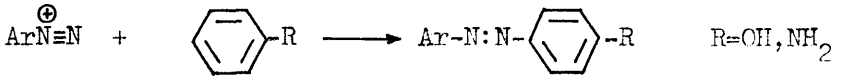
carbon bonds of the (2-(arylazo)aryl) mercuric chloride derivatives has been established. Refluxing ethanol solutions of (2-(4'R-phenylazo)-phenyl) mercuric chloride (R=H, Me, MeO or Cl) reacted with iodine to give the corresponding 2-(4'R-phenylazo)phenyliodide derivatives.



X = Cl R = Me Y = Cl,Br,I
X = Cl R = MeO,Cl Y = I
X = I R = H Y = I

Mercuric iodide was isolated and identified from the reaction of (2-(phenylazo)phenyl) mercuric iodide with iodine. Cleavage of the Hg-C bond of (2-(4'-methylphenylazo)phenyl) mercuric chloride by chlorine and bromine proved an equally straightforward process. In all cases the products were orange crystalline solids whose very high solubility in organic solvents contrasts with that of the mercurials.

The specific Hg-C bond cleavage, demonstrated by NMR (vide infra) constitutes a useful route to these unsymmetrically substituted azobenzene derivatives. Alternative routes to these compounds are by the two main syntheses of azo compounds; coupling of aromatic diazonium compounds with phenols and anilines, and the condensation of nitroso compounds with anilines



$ArNO + Ar'NH_2 \longrightarrow Ar\text{-}N{:}N\text{-}Ar'$

These reactions have certain limitations, apart from experimental difficulties. The coupling capacity of phenols and anilines is affected by ring substituents and ortho coupling is also possible. Furthermore, the stability of the diazonium compounds is influenced by several factors

including ring substuents. The condensation reaction has more widespread use, but the nitroso compounds are not always easily prepared and the method gives poor yields in the case of ortho-methyl substituted compounds[173].

Perhaps as a consequence of these factors, only 2-(phenylazo)-phenyliodide and 2-(4'-methylphenylazo)phenyl bromide had previously been reported. The large majority of disubstituted azobenzenes which do appear in the literature are of a symmetrical nature. This synthesis therefore represents a significant extension to the field.

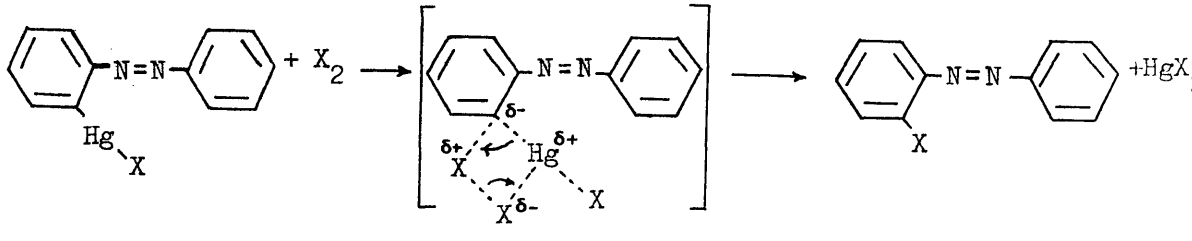
The smooth cleavage of the Hg-C bond of organomercurials, producing mercuric halide and alkyl or aryl halides, has long been known.

$$RHgX + X_2 \longrightarrow RX + HgX_2$$

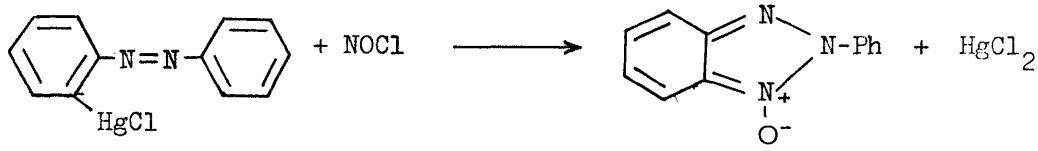
or

$$R_2Hg + 2X_2 \longrightarrow 2RX + HgX_2$$

Both radical and ionic mechanisms have been proposed, depending on the experimental conditions employed[174]. In the present case where a polar solvent (ethanol) was used the reaction probably proceeds by an ionic mechanism. In polar solvents the halogen molecule will be polarized, lose its ability to dissociate homolytically and provide a source of electrophilic halogen. Moreover, the Hg-C bond too is probably polarised and radical formation inhibited. The course of the present reaction may be described as proceeding by way of a four-centre transition state.



(ii) Reaction with nitrosyl chloride. The product isolated in high yield from the reaction (2-(phenylazo)phenyl) mercuric chloride and nitrosyl chloride was 2-phenylbenzotriazole-1-oxide.

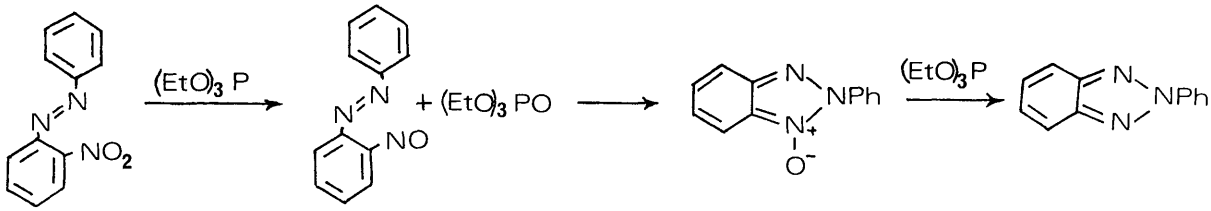


The reaction represents one of the simplest routes to this compound whose history dates back to 1860.[175] This synthesis has the potential for specific substitution at either aromatic ring.

Organometallic compounds and in particular organomercurials are known to react with nitrosyl halides to produce C-nitroso derivatives. Nitrosobenzene has been prepared by passing nitrosyl chloride through a solution of phenylmagnesium bromide[176] and by the reaction of nitrosyl bromide with diphenyl mercury[177]. The long unknown 1-nitrosoacetylenes were first synthesised by this reaction[178]

$$(RC\equiv C)_2Hg + NOCl \longrightarrow RC\equiv CNO \qquad R=Me(CH_2)_3-,\ (Me)_3CH-$$

In the present reaction the C-nitroso compound is presumably produced as an intermediate, prior to cyclisation. This adds weight to the argument that the same intermediate may be involved in other routes to 2-phenylbenzotriazole-1-oxide. For example, its isolation from the sodium sulphide reduction of 2-nitroazobenzene is thought to involve this intermediate[188]. In the synthesis of 2-phenylbenzotriazole from 2-nitroazobenzene and triethylphosphite, a similar mechanism followed by removal of oxygen may operate rather than the postulated cyclisation of an intermediate nitrene[189].

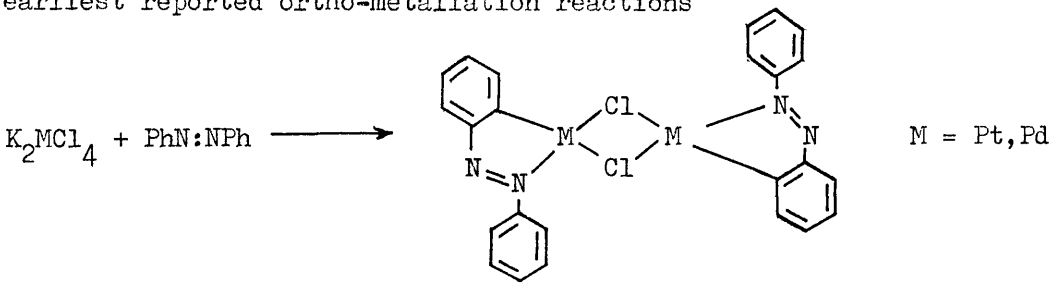


In keeping with this mechanism, the removal of oxygen from aromatic groups and from 2-phenylazobenzotriazole-1-oxide by phosphines has been established. The formation of $Ph_2MeP(O)$ from Ph_2MeP and nitrobenzene (see Chapter II) is probably an example of this process.

Preparation of (2-(arylazo)aryl) complexes of other metals.

From Azobenzene.

The preparation of the halogen bridged dimers, di-μ-chloro-di(2-(phenylazo)phenyl) diplatinum and palladium represents one of the earliest reported ortho-metallation reactions[99]



These reactions have been repeated in this study.

Potassium chloropalladite and palladous chloride both reacted with azobenzene to give good yields of the bridged dimer, as reported[97,99]. The $PdCl_2$ reaction gave a crude orange product which was seen from its IR spectrum to be a mixture of more than one compound. (Particularly conspicuous was a band at 331cm^{-1} not present in the spectrum of the bridged dimer). Recrystallisation of this material from benzene gave two distinct products; orange glistening crystals and maroon micro-crystalline material. These were identified as bis(azobenzene) palladium dichloride and di-μ-chloro-di(2-(phenylazo)phenyl) palladium, respectively. The non-metallated product, with azobenzene bonded through the N atom only, has previously been prepared from the reaction of azobenzene with bis(benzonitrile) palladium dichloride[135] but had not previously been isolated

from direct interaction with palladium dichloride. Its isolation from this reaction is good evidence for the suggestion that it is a precursor of the ortho-metallated product. In accord with this proposal the transformation of $(C_6H_5N_2C_6H_5)_2PdCl_2$ to $(C_6H_5N_2C_6H_4)_2Pd_2Cl_2$ in refluxing ethanol is documented [135].

By comparison, the preparation of di-μ-chloro-di(2-(phenylazo)-phenyl) diplatinum from azobenzene and K_2PtCl_4 is reported to proceed more slowly and in lower yield.[99] Repetition of this reaction verified these observations. Dioxane/water or methanol/water mixtures were used as solvents and the reaction involved a gradual colour change from orange to a dark maroon solution. The product was isolated by removal of solvent and at this stage the presence of HCl was detected by its pungent odour and the formation of white fumes with ammonia.

The reaction of azobenzene with platinous chloride had not been reported. The reaction in methanol at room temperature proceeded very slowly compared to the palladous chloride case. That the reaction was proceeding was seen by the colour change to dark maroon. After 6 weeks reaction time the majority of platinum chloride was recovered unreacted. A small amount of di-μ-chloro-di(2-(phenylazo)phenyl)diplatinum was isolated and again the presence of HCl was detected. The different rates of reaction between $PdCl_2$ and $PtCl_2$ may be partly explained by the greater solubility of the former in methanol but the primary cause is thought to be the different affinities of palladium and platinum for azobenzene (vide infra).

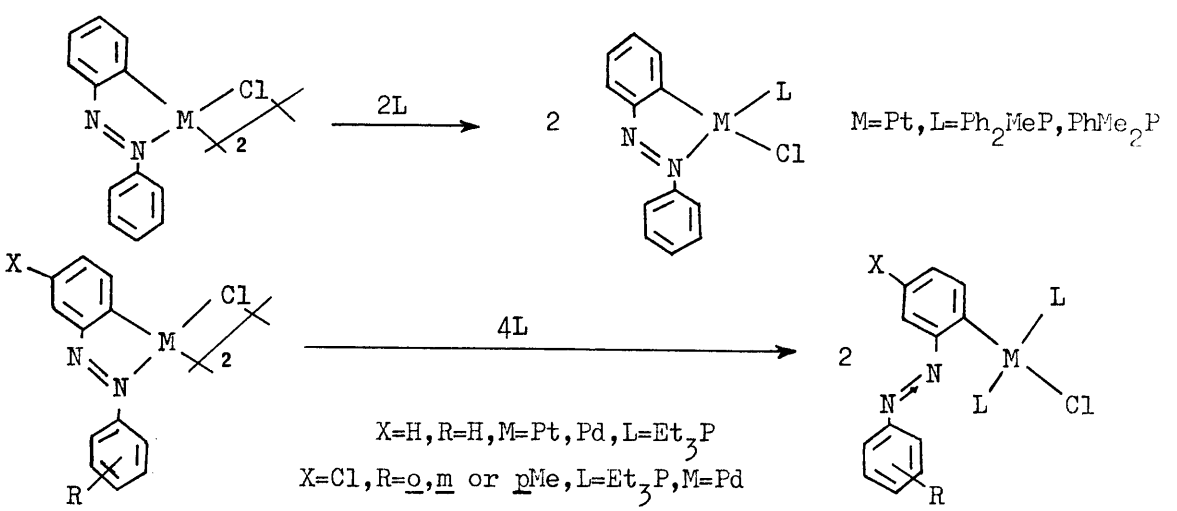
It has been found that the presence of base helps to promote the internal metallation of secondary benzylamines [89]. In an attempt to find a superior route to di-μ-chloro-di(2-(phenylazo)phenyl) diplatinum the reaction of bis(benzonitrile) platinum dichloride and azobenzene in

the presence of triethylamine was studied. It has been established that $(PhCN)_2PtCl_2$ and azobenzene do not react in dichloromethane solution.[131] The presence of triethylamine does bring about a reaction involving a colour change from orange to dark maroon. A white precipitate which was not identified, though may have been amine hydrochloride, formed but was consumed as the reaction proceeded. It is clear that, since very little azobenzene was recovered from the reaction, azobenzene does react under these conditions. No products were identified from the reaction though if formation of $((azb)PtCl)_2$ did take place conversion to $(azb)PtCl(NEt_3)$ may have occurred.

Bridge splitting reactions of this kind are well known for these complexes[99] and in the present work several phosphine complexes have been prepared by this method.

Preparation of (2-(arylazo)aryl) phosphine complexes by bridge cleavage.

Addition of phosphine to $((azb)MCl)_2$, M=Pt or Pd resulted in cleavage of the chlorine bridges and formation of mononuclear complexes where the chelate ring remains intact. Addition of 4 moles of phosphine not only cleaves the bridge but also displaces the azo nitrogen atom.



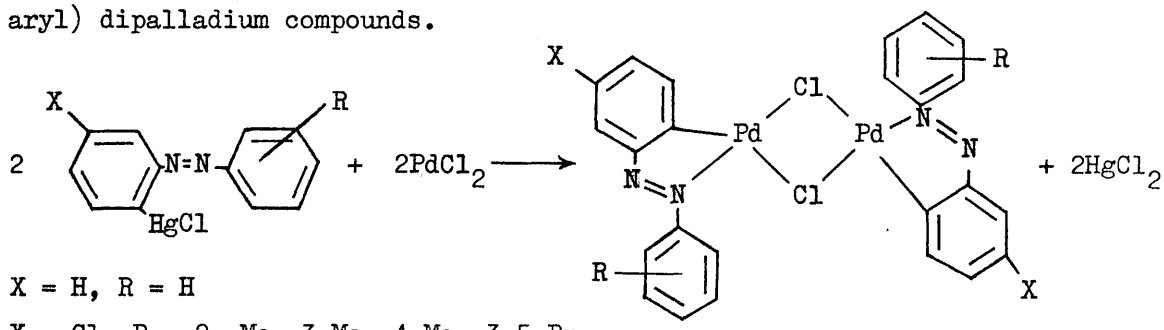
The stereochemistry of these complexes determined by NMR (vide infra) is as shown.

Transfer of the (2-(aryazo)aryl) group from mercury to other metals.

In a bid to find a superior route to the platinum and palladium dimers, the interaction of the (2-(arylazo)aryl) mercurials with platinum and palladium chloride was examined.

Reaction of the (2-(arylazo)aryl) mercuric chloride complexes with $PdCl_2$.

Reaction of several of the (2-(arylazo)aryl) mercuric chloride complexes with palladous chloride in methanol, at room temperature, gave products which were identified as the corresponding di-μ-chloro-di(2-(arylazo)-aryl) dipalladium compounds.

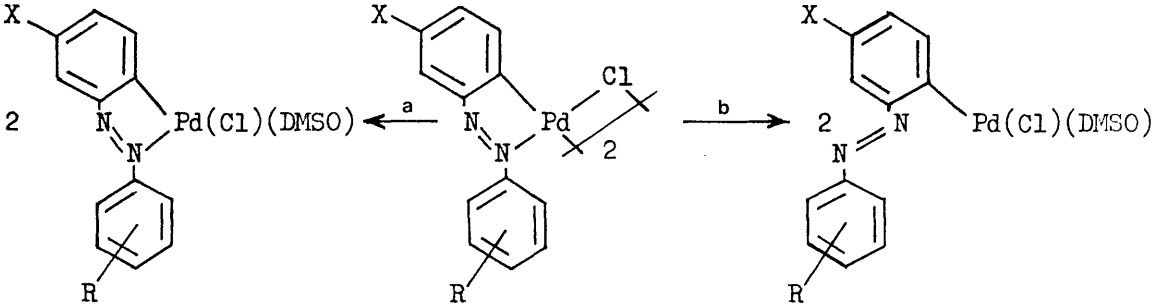


X = H, R = H

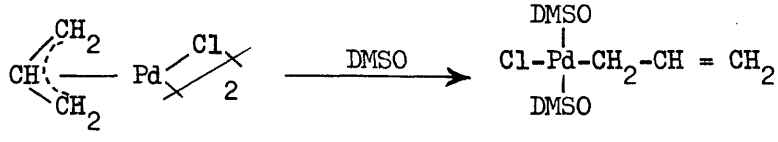
X = Cl, R = 2- Me, 3-Me, 4-Me, 3,5-Br_2

The yields from the reaction are quantitative and mercuric chloride by-product was identified from the water extract of the crude reaction product. The products are isolated as maroon crystalline solids from benzene. Their solubility is very low in nearly all solvents. Di-μ-chloro-di(2-(3',5'-dibromophenylazo)4-chlorophenyl) dipalladium, for example, is almost insoluble in benzene. Analytically pure samples of this complex were obtained by washing the product with hot benzene.

In contrast, these complexes are all remarkably soluble in dimethyl sulphoxide. The enhanced solubility in this solvent may be due to bridge cleavage analogous to that observed with phosphines or amines.



Support for this explanation comes from the effect of DMSO on the ^{1}H NMR spectrum of π -allyl palladium chloride complexes[179]. This effect is rationalised on the basis of chlorine bridge cleavage and $\pi \rightarrow \sigma$ rearrangement of the allyl group produced by coordination of DMSO.



Isolable dimethyl sulphoxide complexes of palladium are known and the Crystal Structure of <u>trans</u> $PdCl_2(DMSO)_2$ has been determined by Cotton <u>et,al.</u>[180]

The chemical shift of the methyl signals in the ^{1}H NMR spectrum (vide infra) of di-μ-chloro(2-(2'-methylphenylazo)phenyl) dipalladium indicate that the palladium-nitrogen bond is not ruptured by DMSO. It remains unresolved whether bridge splitting by one DMSO group has occurred (reaction 'a'), It is highly likely, however, that the enhanced solubility in DMSO over all other solvents employed results from its greater ability to solvate the vacant coordination sites of palladium.

On the basis of the successful transfer of the 2-(phenylazo)-phenyl group from mercury to palladium it seemed likely that an extension of this reaction to platinum would provide the desired quick, high-yield route to $((azb)PtCl)_2$.

<u>Reaction of bis(2-(phenylazo)phenyl) mercury with $PtCl_2$</u>. Under the same conditions as the palladium reaction bis(2-(phenylazo)phenyl) mercury and platinous chloride did not react. Refluxing in ethanol gave extensive decomposition. Platinum metal, mercury metal, azobenzene and (2-(phenylazo)phenyl) mercuric chloride were the only products characterised though not accounting for the total product. No$((azb)PtCl)_2$ was produced

and the reaction was not further investigated.

From the isolation of (2-(phenylazo)phenyl) mercuric chloride it appears that transfer of the 2-(phenylazo)phenyl group to platinum may indeed take place but is followed by decomposition at elevated temperature. It is relevant to point out that finely divided platinum has been reported to decompose diarylmercurials[181], so the decomposition may be autocatalytic. Furthermore, platinum dichloride has been reported to catalyse the lithium aluminium hydride reduction of azobenzene to hydrazobenzene[146]. Coupling of two 2-(phenylazo)phenyl groups may have occurred, as the elimination of the bis-azobenzene compound has been observed for $(azb)_2\ Ru{\cdot}Cl_2{\cdot}\ Ru(CO)_3$ in the presence of carbon monoxide.[143] Neither hydrazobenzene nor the bis-azo compound were identified amongst the decomposition products although small amounts may have gone undetected.

Reaction of bis(2-(phenylazo)phenyl) mercury with $(Et_3P)_2MCl_2$ (M=Pd,Pt).

The transfer of organic groups from mercury to bis(phosphine) platinum and palladium dihalide complexes has been reported.[150] It was therefore of interest, more especially because of the failure of the transfer reaction with platinum dichloride, to examine the interaction of bis(2-(phenylazo)-phenyl) mercury with dichloro-bis(triethylphosphine) platinum and palladium. Transfer of the 2-(phenylazo)phenyl group was achieved in both cases, but the yield in the platinum case was markedly inferior than with palladium.

$$(C_6H_5N{:}NC_6H_4)_2Hg + (Et_3P)_2MCl_2 \longrightarrow \underline{trans}\ (C_6H_5N{:}NC_6H_4)M(PEt_3)_2Cl$$

M = Pd or Pt

The products are the orange crystalline complexes, trans-chloro(2-(phenylazo)phenyl)bis(triethylphosphine) platinum and palladium. These were also prepared by the action of Et_3P on the dimers $((azb)MCl)_2$.

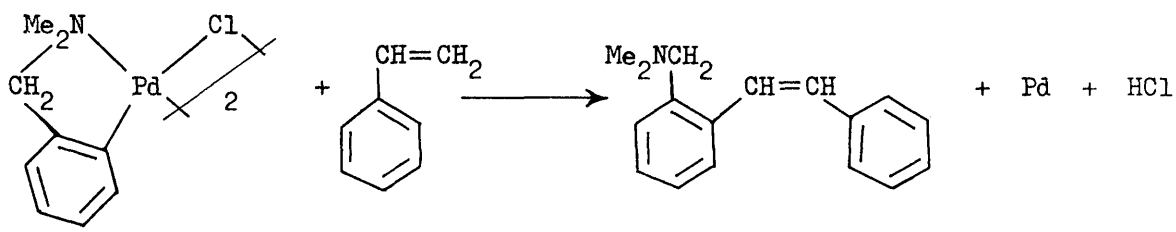
The ready transfer of 2-(arylazo)aryl groups from mercury to palladium marks a useful extension to the synthesis of di-μ-chloro-di(2-(arylazo)aryl) dipalladium complexes. The transfer is probably analogous to that which occurs from arylmercuric halide to palladium chloride in the palladium catalysed arylation of olefins[182].

$$PdX_2 + RHgX \rightleftharpoons RPdX + HgX_2$$

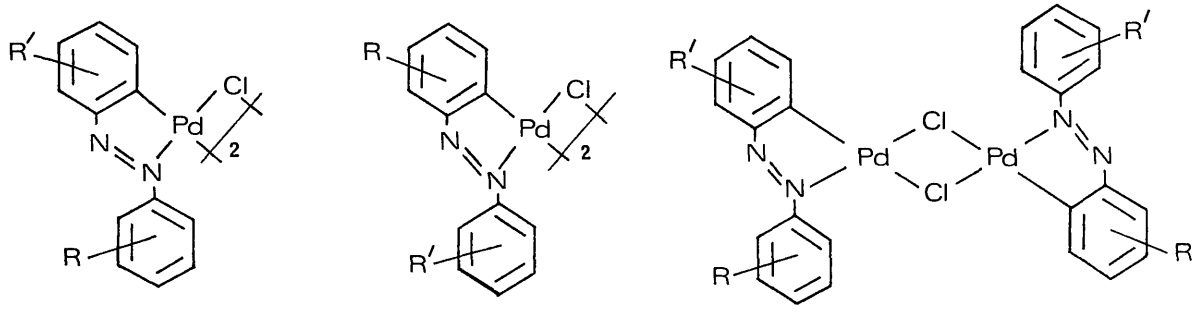
$$RPdX + \begin{matrix} H \\ \diagdown \\ C=C \\ \diagup \end{matrix} \longrightarrow \begin{matrix} H \\ | \\ R-C-C-PdX \\ | \quad | \end{matrix} \longrightarrow \begin{matrix} R \\ \diagdown \\ C=C \\ \diagup \end{matrix} + (HPdX)$$

The key step consists of transfer of the organic group, R, from mercury to palladium. Coordination of olefin to palladium, insertion into the R-Pd σ- bond, and decomposition of the intermediate produced yields the substituted olefin and metal hydride. In the present case, the reaction stops after initial transfer of the 2-(arylazo)aryl group. It is not known whether coordination of one of the azo nitrogen atoms to palladium occurs prior to formation of the palladium-carbon bond as postulated for the direct palladation of azobenzene itself.

An attempt to extend the olefin arylation reactions to the addition of the 2-(phenylazo)phenyl group to styrene failed. The only product of the reaction was $((azb)PdCl)_2$. This is in keeping with Heck's report[182] that if the aryl group contains a substituent with a strong donor-atom (e.g. an amine group) then the catalytic addition to olefins fails and an isolable organopalladium compound is the end product. Despite this, the transfer of ortho-$C_6H_4CH_2NMe_2$ from palladium to styrene in acetic acid has been reported[183].



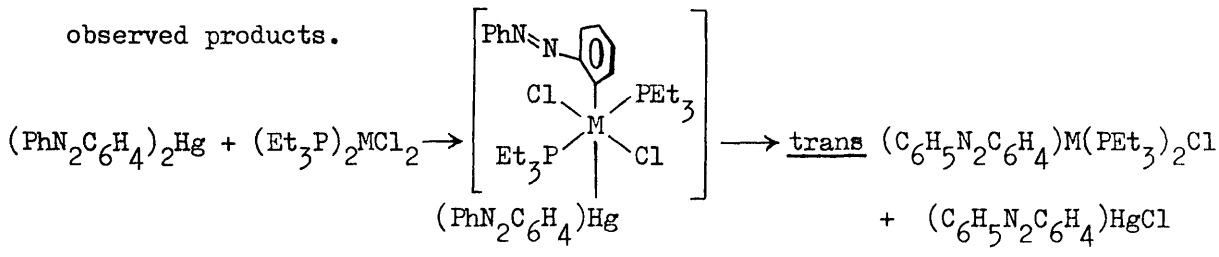
The advantages of the synthesis of substituted $((azb)PdCl)_2$ derivatives by the mercurial route are those that apply to the preparation of the mercurial itself. Takahashi and Tsuji have shown that three isomers for assymetrically substituted azobenzene complexes are possible.[97]



Degradation experiments indicated the ratio of isomers present depends on the azobenzene ring substituents. Similar results have been found with manganese[137]. Synthesis <u>via</u> the mercurial should yield specific isomers since the carbon atom bonded to mercury should also be that bonded to palladium after the transfer. That this process is indeed specific is indicated by the IR and NMR spectra of the compounds produced. (vide infra).

The failure of the platinum dichloride reaction is not understood and is surprising in the light of the greater thermal stability of organoplatinum complexes compared to organopalladium complexes.

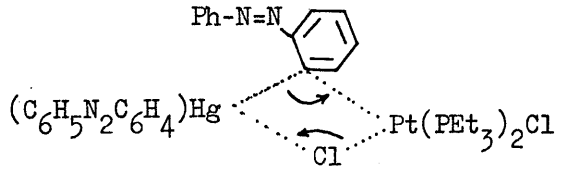
The formation of chloro-(2-(phenylazo)phenyl)bis(triethylphosphine) platinum and palladium is likely to proceed by oxidative addition of the diorganomercurial to the square planar Pt(II) and Pd(II) phosphine complexes. Reductive elimination of organomercuric halide from the Pd(IV) and Pt(IV) intermediates would result in the formation of the observed products.



M = Pd,Pt.

This mechanism has been proposed for the transfer of organic groups from mercury to phosphine complexes of platinum palladium and nickel[150] and has also been invoked by Russian workers to explain the formation of alkylplatinum species from alkylmercuric halides and K_2PtCl_4.[184]

A mechanism involving bimolecular electrophilic substitution cannot, however, be discounted. This mechanism, possibly involving the type of four-centre transition state shown below, is often encountered in mercury chemistry[174] and has been discussed for the symmetrisation and halogen cleavages reactions.



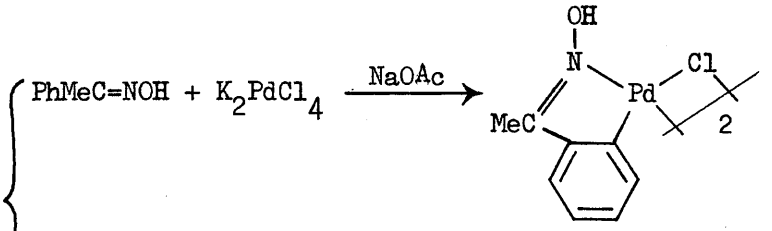
Although successful transfer of the 2-(phenylazo)phenyl group took place with both the palladium and platinum phosphine complexes, the yield with the latter was much lower and the production of some mercury and azobenzene was noted. The production of mercury has been observed by Cross and Wardle[150] for the reaction between cis $(Bu_3P)_2PtCl_2$ and Me_2Hg, but the present behaviour difference between platinum and palladium was not expected on the basis of that work. It again highlights the difference which seems to exist in the formation of platinum and palladium complexes of azobenzene. These differences are summarised below.

Reaction	Remarks	
	Palladium (M=Pd)	Platinum (M=Pt)
MCl_2+PhN:NPh	Fast, quantitative yield of $(azbPdCl)_2$	Very slow, very low yield of $(azbPtCl)_2$
K_2MCl_4+PhN:NPh	Fast, Quantitive yield of $(azbPdCl)_2$	Very slow, low yield of $(azbPtCl)_2$
$(PhCN)_2MCl_2$+PhN:NPh	Quantitative yield of $(PhN:NPh)_2PdCl_2$	No reaction
$(C_6H_5N:NC_6H_4)_2Hg+MCl_2$	Quantitative yield of $(azbPdCl)_2$ at room temperature	No reaction at room temperature, decomposition at higher temperatures.
$(C_6H_5N:NC_6H_4)_2Hg+(Et_3P)_2MCl_2$	Clean reaction, good yield of $(C_6H_5N:NC_6H_4)$-$Pd(PEt_3)Cl$	Some decomposition, poor yield of $(C_6H_5N:NC_6H_4)$-$Pt(PEt_3)_2Cl$

The reason for this behaviour difference of platinum and palladium is not understood and indeed there may be no unifying explanation. The failure of platinum to form simple N-bonded complexes of azobenzene can be ascribed to the low basicity of azobenzene which arises from the interaction of the lone pairs on the nitrogen atoms interacting with the π-electron systems of the phenyl rings.[185] The slow ortho-metallation reaction may therefore be a reflection of the low tendency to form the N-bonded platinum complex which is the likely precursor. This cannot be the full explanation as it does not account for the other unidentified product/s of the reaction. It is of relevance to restate that in the complex originally formulated with an olefin-type bond from the azo group to platinum, the azobenzene molecule is now known to have been reduced. Both $(PhNH\cdot NH_2Ph)^+PtCl^-$[131] and $(PhN:NHPh)^+PtCl^-$[132] have been proposed

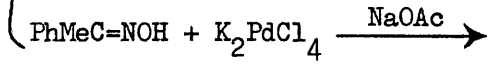
for this product. The ease of reduction of azobenzene in these transition metal systems is further emphasised by the production of aniline in some cases[129].

The behaviour difference between platinum and palladium is not restricted to azobenzene and has been observed in reactions with similar organic substrates.

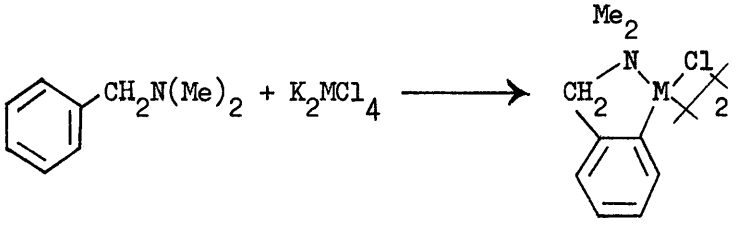


Quantitative yield

Ref. 186



Intractible black material which deposited platinum metal on dissolving in CH_2Cl_2

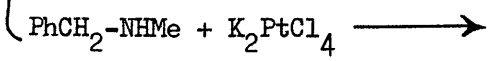


M=Pd, Quantitive yield

Ref. 89

M=Pt, Slower reaction and inferior yield.

Ref. 89



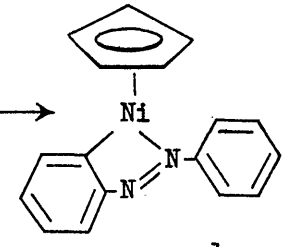
Intractible black material.

The explanation of the failure of the mercurial reaction with $PtCl_2$ is also unclear. It seems probable that the reaction passes through some unstable intermediate which leads to decomposition whereas this decomposition is prevented in the palladium case. The reason may again be the lower affinity of the azobenzene nitrogen atoms for platinum. With palladium ready coordination of nitrogen is likely and this may have

the effect of blocking coordination sites which remain available for decomposition pathways in the platinum case.

Reaction of bis(2-(phenylazo)phenyl) mercury with Cp_2Ni. The reaction between bis (2-(phenylazo)phenyl) mercury and nickelocene in refluxing benzene produced high yields of (2-(phenylazo)phenyl) ($\underline{h}^5$-cyclopentadienyl)-nickel(II)

$$(PhN_2C_6H_4)_2Hg + (\underline{h}^5\text{-}C_5H_5)_2Ni \longrightarrow$$



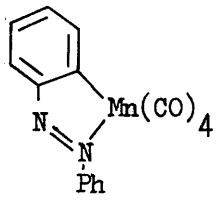
The expected by-product, (2-(phenylazo)phenyl)($\underline{h}^1$-cyclopentadienyl) mercury was not isolated, but cyclopentadienyls of mercury are known to be unstable[187] and unsymmetrical diorganomercurials slowly symmetrise.[190] Some bis(2-(phenylazo)phenyl) mercury was in fact isolated from the reaction mixture though this could have been unreacted starting material.

(Azb)Ni(Cp) has previously been prepared from the reaction of azobenzene [118] or 2-(phenylazo)phenylhalides[115] and nickelocene but in inferior yield. All these routes probably proceed via a mechanism involving coordination of nitrogen to nickel and $\pi \rightarrow \sigma$ conversion of a cyclopentadienyl ligand. The next steps will differ and involve cleavage of the Ni-($\underline{h}^1$-C_5H_5) bond by either mercurial or halide. There are precedents for both using triphenylphosphine as nucleophile. Organic halides lead to ($\underline{h}^5$-C_5H_5)(Ph_3P)NiX[191], whereas dimethylmercury produces ($\underline{h}^5$-C_5H_5)(Ph_3P)NiMe.[192]

Reaction of (2-(phenylazo)phenyl) mercuric iodide with $Mn(CO)_5Cl$. (2-(phenylazo)phenyl) mercuric iodide and pentacarbonyl manganese chloride when reacted in refluxing benzene produced good yields of (2-(phenylazo)-

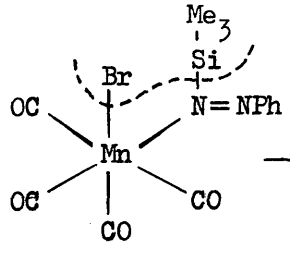
phenyl)(tetracarbonyl) manganese (I).

$$PhN_2C_6H_4HgI + Mn(CO)_5Cl \longrightarrow$$



The formation of organomanganese carbonyl compounds from pentacarbonylmanganese halides and other organometallic reagents has received little attention, though transfer of an organic group to manganese from, for example, C_6F_5MgBr[193] and allyltrimethyltin[194] is documented. $(Azb)Mn(CO)_4$ has been prepared previously using azobenzene itself[116] though yields are actually lower than by the present method. There is evidence that the reaction between azobenzene and $MeMn(CO)_5$, which gives high yields of $(azb)Mn(CO)_4$, proceeds via initial nucleophilic attack at the ortho position of the aromatic ring[116]. This mechanism may operate in the present case, but the possibility of CO displacement by a nitrogen donor atom followed by mercuric halide elimination cannot be discounted. This mechanism would be in accord with the proposed route for the formation of a novel manganese complex with bridging aryldiazo ligands.[195]

$$PhN{=}NSiMe_3 + Mn(CO)_5Br \longrightarrow$$



$$\longrightarrow$$

$$PhN{=}N\text{-}Mn(CO)_4 \longrightarrow (PhN{=}N\text{-}Mn(CO)_4)_2$$

SPECTROSCOPIC EXAMINATION OF COMPLEXES.

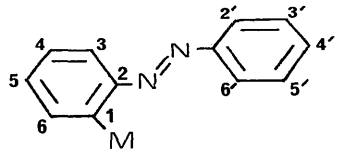
NMR Spectra.

^1H NMR has been used, along with IR spectroscopy, to establish the ring substitution pattern of the (2-(arylazo)aryl)-mercury, -palladium and -iodine derivatives described in this Chapter. Complete or partial analysis of the ^1H NMR spectra of a few azobenzene transition metal complexes have been reported[116,138,140] The 100 MHz spectrum of $(C_6H_5N_2C_6H_4)Mn(CO)_4$[116] is one example. It is found in the present work that even at 60 MHz easy and complete assignment of all the protons of the ortho-metallated ring is possible.

The spectra of the (2-(arylazo)aryl) mercury compounds are more difficult to analyse since the chemical shifts of the aromatic protons span a smaller range. Low solubility of these derivatives further complicates the issue. Nevertheless, complete analyses proved possible for the 220 MHz spectra of some of the more highly substituted derivatives. Line diagrams of examples are shown in Figures 2, 3 and 4. Comparison with these spectra and also with the better resolved palladium and iodine derivatives, discussed below, allowed at least partial interpretation of the more difficult spectra. Data is presented in Table 3. The coupling constants between ortho protons (ca.8Hz) and meta protons (ca.2.5Hz) are quite normal[196] as are the values of $^3J(^1H\text{-}^{199}Hg)$ (ca.200Hz) ($^{199}Hg, I=\frac{1}{2}$, 16.84 %).[197]

The peak patterns of the (2-(arylazo)aryl) mercurials shown in the line diagrams are characteristic of the various ring substitution patterns. This establishes the retention of substituent group positions throughout the synthetic sequence. For the (2-(4'R-phenylazo)phenyl)-mercury complexes (R = MeO-, Cl-, Me-) complete analysis was not possible. In these cases it was found that the spectra of the very soluble

Table 3. Proton NMR spectra

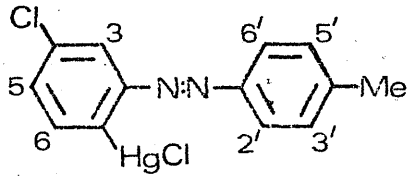


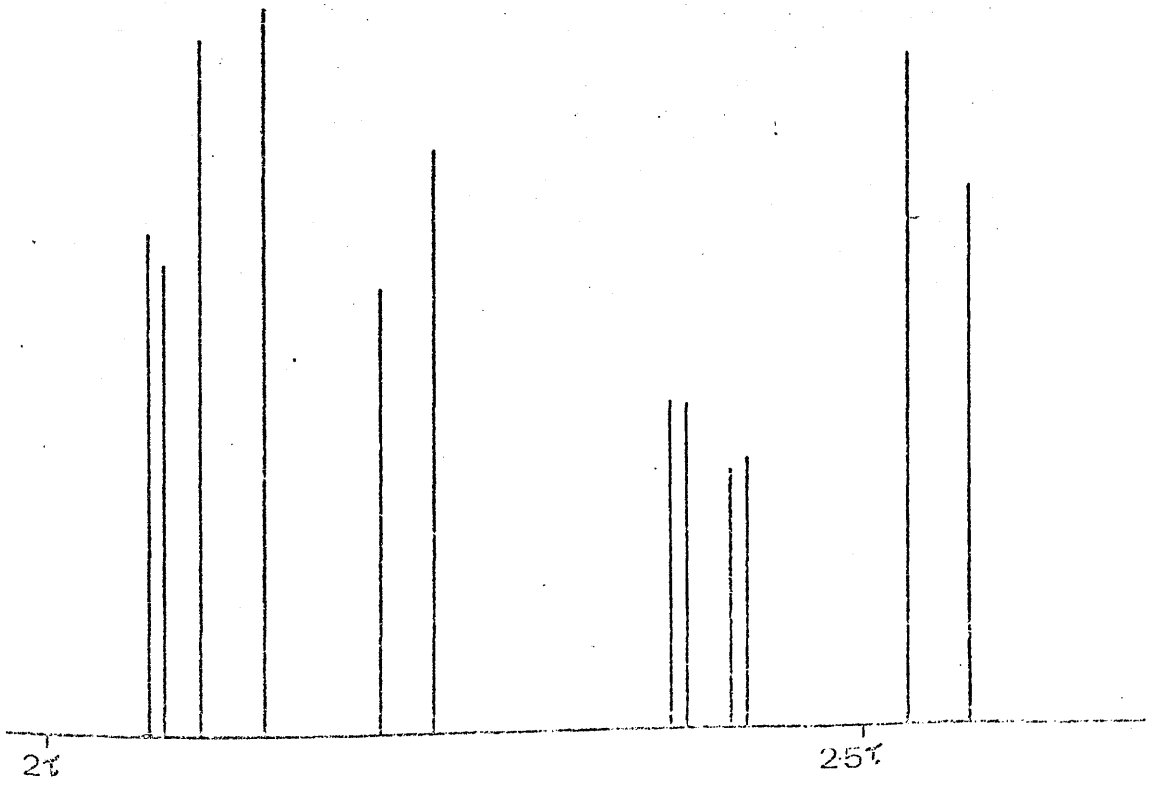
Compound	Chemical Shifts (τ)										Solvent	Temperature (°C)
	H_3	H_4	H_5	H_6	$H_{2'}$	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{6'}$	Me		
(4'Me-$C_6H_4N_2C_6H_3$-4Cl)HgCl[a,g]	2.06d	-	2.41dd	2.21d	2.10d	2.55d	-	2.55d	2.10d	7.58s[c]	$(CD_3)_2SO$	+61
(3'Me-$C_6H_4N_2C_6H_3$-4Cl)HgCl[a,h]	2.04d	-	2.40dd	2.19d	2.18[f]	-	2.55dt	2.48t	2.19[f]	7.57s[c]	$(CD_3)_2SO$	+61
(2'Me-$C_6H_4N_2C_6H_3$-4Cl)HgCl[a,i]	2.14d	-	2.42dd	2.18d	-	e	e	e	e	7.29s[c]	$(CD_3)_2SO$	+61
(3',5'Br_2-$C_6H_3N_2C_6H_3$-4Cl)HgCl[a]	2.07d	-	2.37dd	2.17d	1.87d	-	1.97t	-	1.87d	-	$(CD_3)_2SO$	+61
(3',5'Br_2-$C_6H_3N_2C_6H_4$)HgCl[a]	1.99dd	2.38td	2.42td	2.20dd	1.88d	-	1.97t	-	1.88d	-	$(CD_3)_2SO$	+61
(4'Me-$C_6H_4N_2C_6H_3$-4Cl)$_2Pd_2Cl_2$[b]	1.97d	-	2.69dd	2.22d	2.23d	2.62d	-	2.62d	2.23d	7.58s	$(CD_3)_2SO$	+70
(3'Me-$C_6H_4N_2C_6H_3$-4Cl)$_2Pd_2Cl_2$[b]	1.97d	-	2.70dd	2.24d	e	-	e	e	e	7.58s	$(CD_3)_2SO$	+70
(2'Me-$C_6H_4N_2C_6H_3$-4Cl)$_2Pd_2Cl_2$[b]	1.87d	-	2.58dd	2.21d	-	e	e	e	e	7.62s	$(CD_3)_2SO$	+70
(4'Me-$C_6H_4N_2C_6H_3$-4Cl)Pd$(PEt_3)_2$Cl[b]	2.46d	-	3.02dd	2.51d	2.07d	2.72d	-	2.72d	2.074	7.58s	CCl_4	+35
(3'Me-$C_6H_4N_2C_6H_3$-4Cl)Pd$(PEt_3)_2$Cl[b]	2.52d	-	3.06dd	2.55d	2.73d	-	2.85d(br)	e	e	7.56s	CCl_4	+35
(2'Me-$C_6H_4N_2C_6H_3$-4Cl)Pd$(PEt_3)_2$Cl[b]	2.65d	-	3.04dd	2.55d	-	e	e	e	e	7.23s	CCl_4	+35

[a] Recorded at 220 MHz. [b] Recorded at 100 MHz. [c] Values for the analogous complexes[b] with H in position 4: 4'Me, 7.64s; 3'Me, 7.57s; 2'Me, 6.19s [e] Overlap of signals prevents assignment. [f] Partially obscured by H_6

[g] $^3J(^1H\text{-}^{199}Hg)$,203Hz [h] $^3J(^1H\text{-}^{199}Hg)$,201Hz [i] $^3J(^1H\text{-}^{199}Hg)$,199Hz

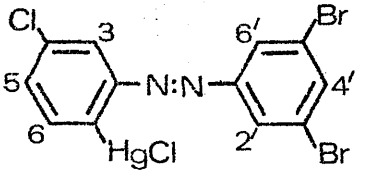
Figure 2. Line Diagram of ^{1}H NMR Spectrum[a] of

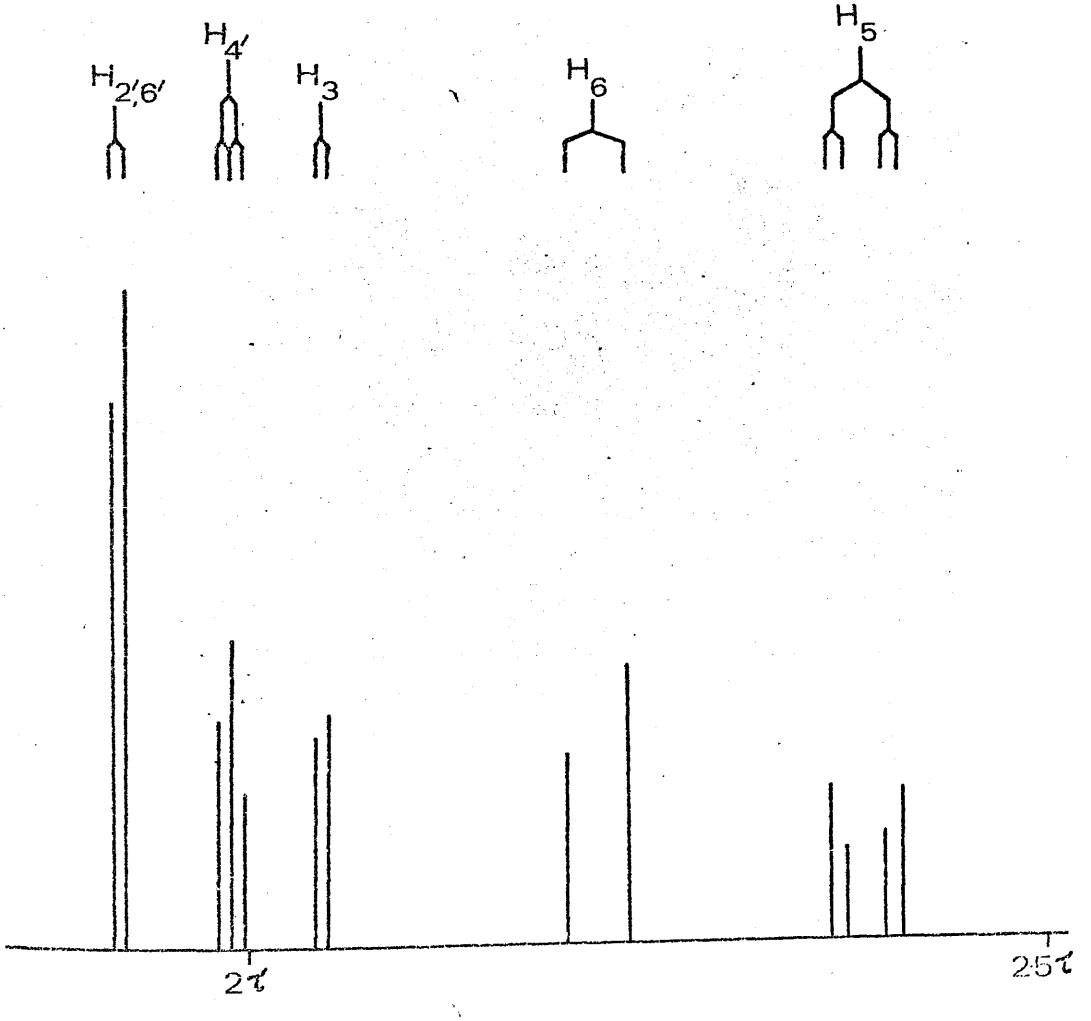




[a] Recorded at 220 MHz in DMSO solution at 61°C.

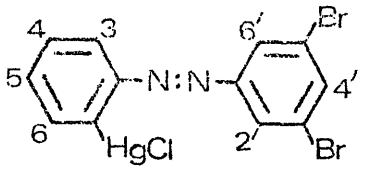
Figure 3. Line Diagram of ^{1}H NMR Spectrum[a] of

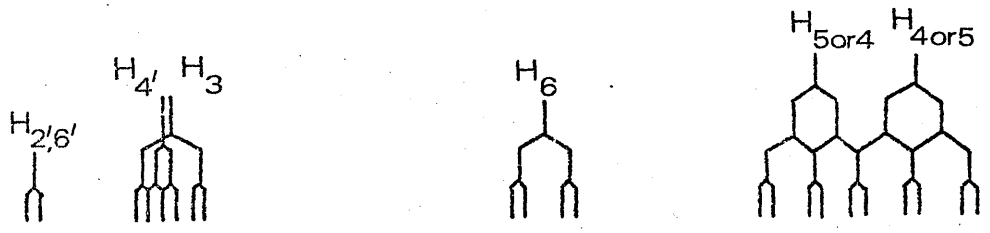


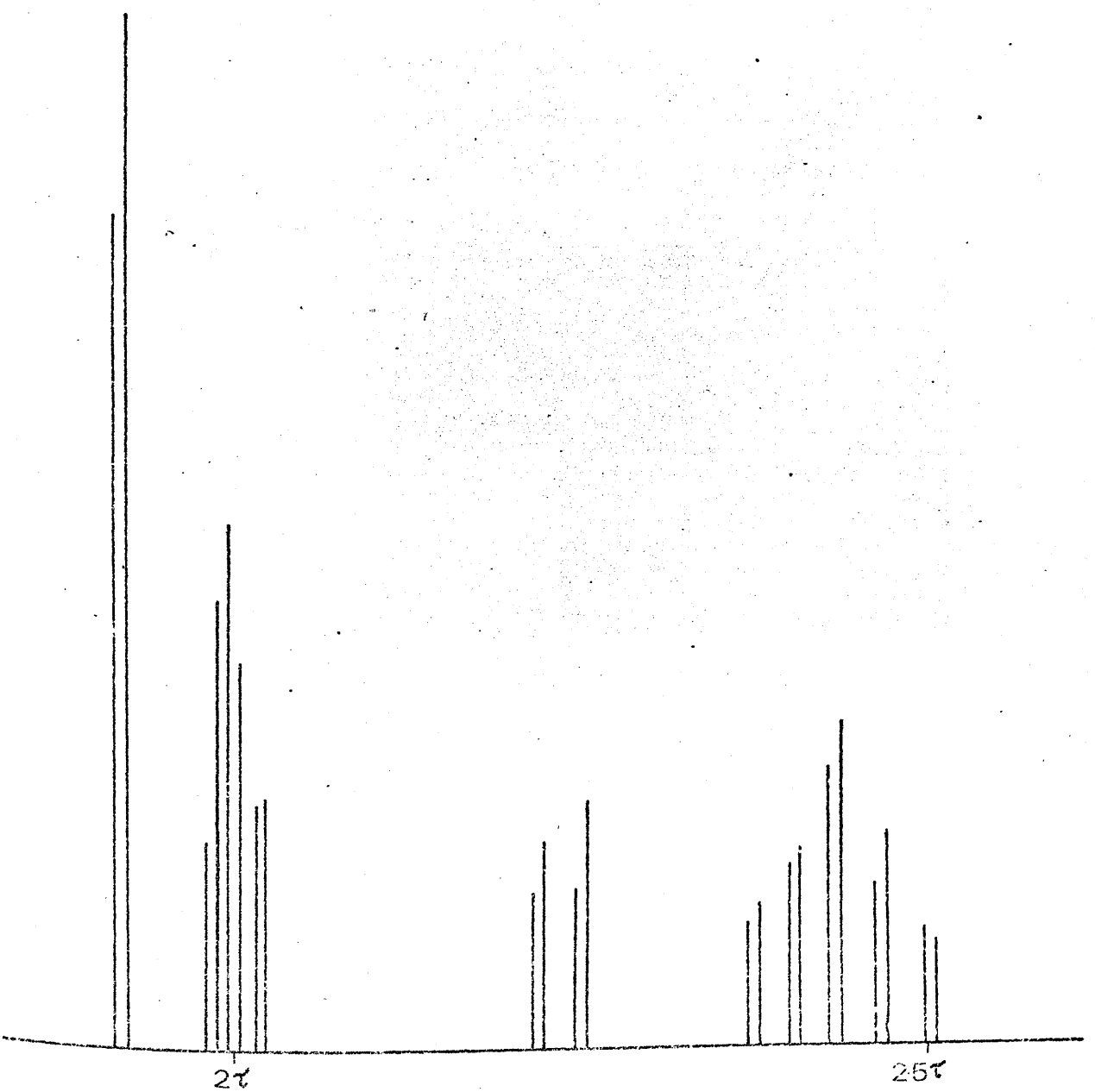


[a] Recorded at 220 MHz in DMSO solution at 61°C.

Figure 4. Line Diagram of ^{1}H NMR Spectrum[a] of







[a] Recorded at 220 MHz in DMSO solution at 61°C.

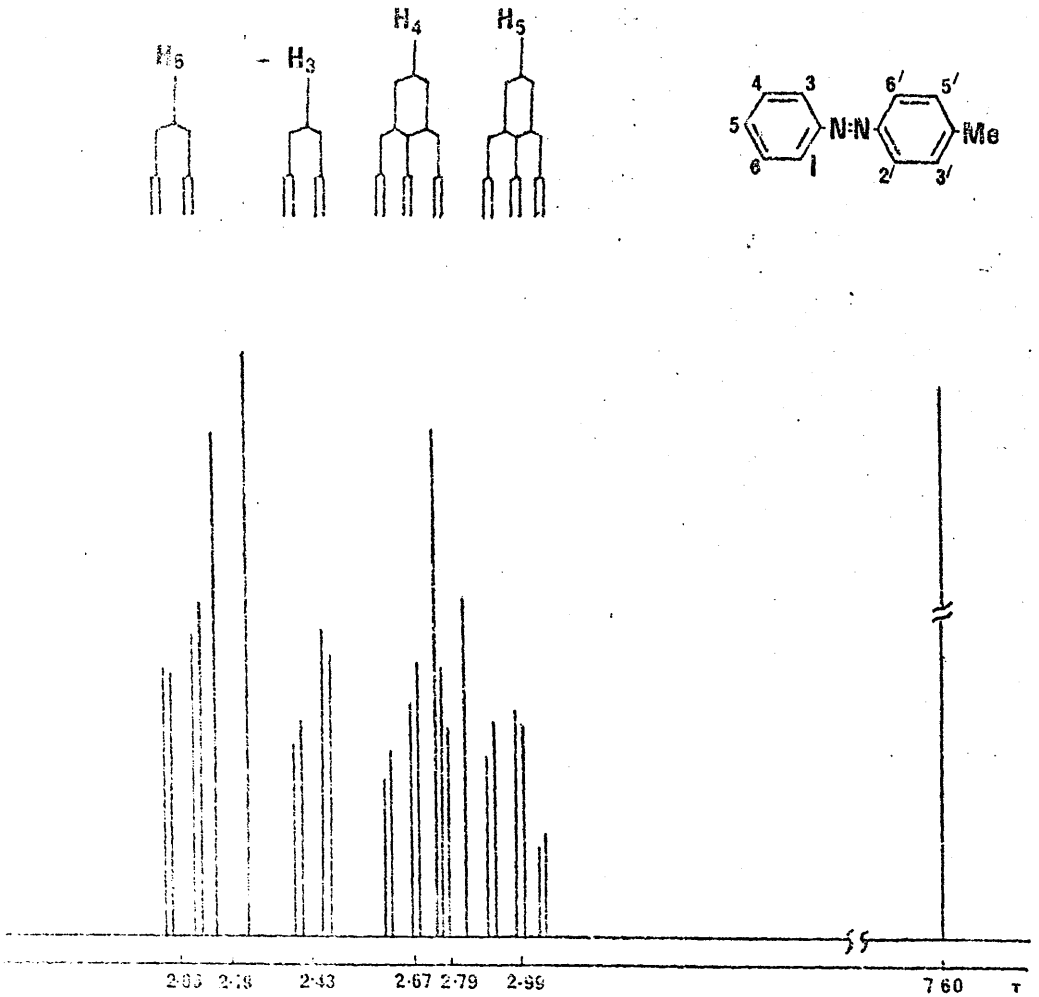
2-(4'R-phenylazo)phenyliodide derivatives were easily interpretable. Line diagrams of these spectra, Figures 5 and 6 show two triplets of doublets (J_{ortho} ca. 8Hz, J_{meta} ca 2.5Hz) and two doublets of doublets (J_{ortho} ca. 8Hz, J_{meta} ca 2.5Hz) characteristic of an ortho disubstituted benzene ring, again confirming the retention of the substitution pattern of that ring. The similar appearance of the spectrum of ortho-iodoaniline (Figure 6) supports this conclusion.

Interestingly, the greater spread of chemical shift produced by replacing the chloromercuri group by iodine is not found on replacement by bromine or chlorine. This may be ascribed to the greater magnetic anisotropy of iodine compared to the other halogens. The same effect has been observed for monohalobenzenes.[213] Nevertheless, it is found that the A_2B_2 quartet pattern arising from the para disubstituted ring is easily recognised in all cases. The low field limb of this quartet is assigned to the protons adjacent to the azo link, on the basis of the electron withdrawing nature of the phenylazo group[133]. Further justification of this assignment comes from the insensitivity of these protons to changing the substituent in the 4' position.

Replacing the 4'Me substituent by 4'-MeO and 4'-Cl groups has the expected effect on the chemical shift of the A_2B_2 quartet. The effect on the 2', 6'-protons is very small - downfield in both cases. The chemical shift change is much more pronounced with the 3', 5'-protons. A downfield shift is produced by chlorine, as expected for a more electronwithdrawing substituent while an equally marked upfield shift is produced by the electron releasing methoxyl group. These effects are again in line with the changes observed in the spectra of monosubstituted benzenes[213]. Surprisingly a downfield shift has been reported in a similar azobenzene derivative.[198]

It is noted that in the (2-(arylazo)4-chlorophenyl) complexes

Figure 5. Line Diagrams of ^1H NMR Spectra of 2-(4'-Methylphenylazo)phenyliodide and 2-(4'-Methoxyphenylazo)phenyliodide.



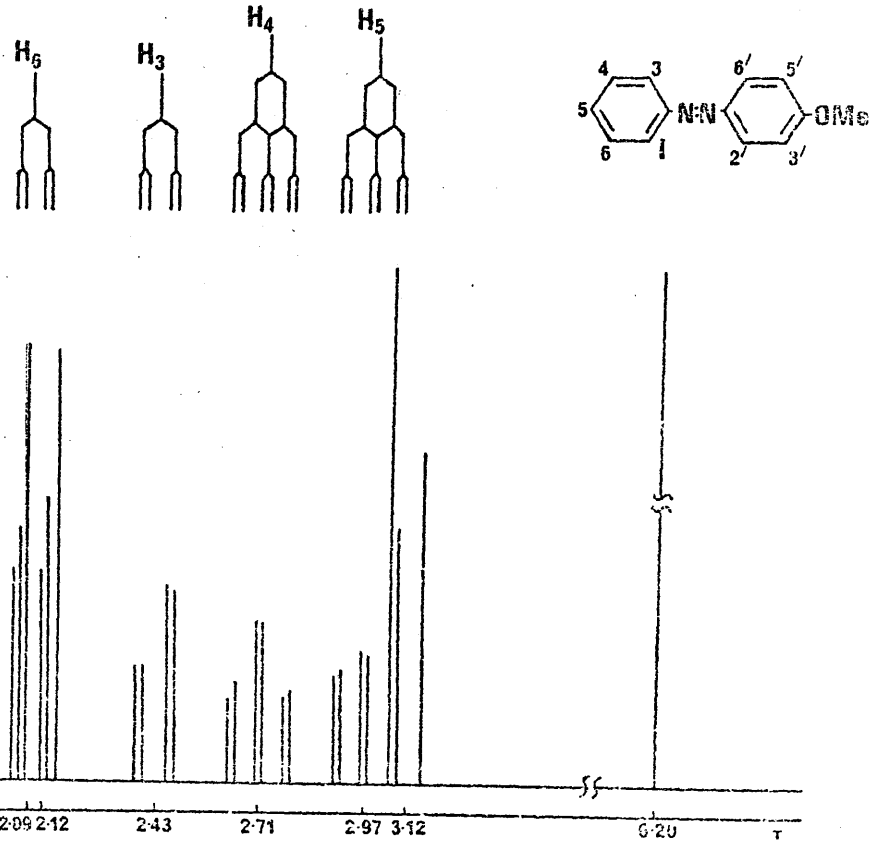
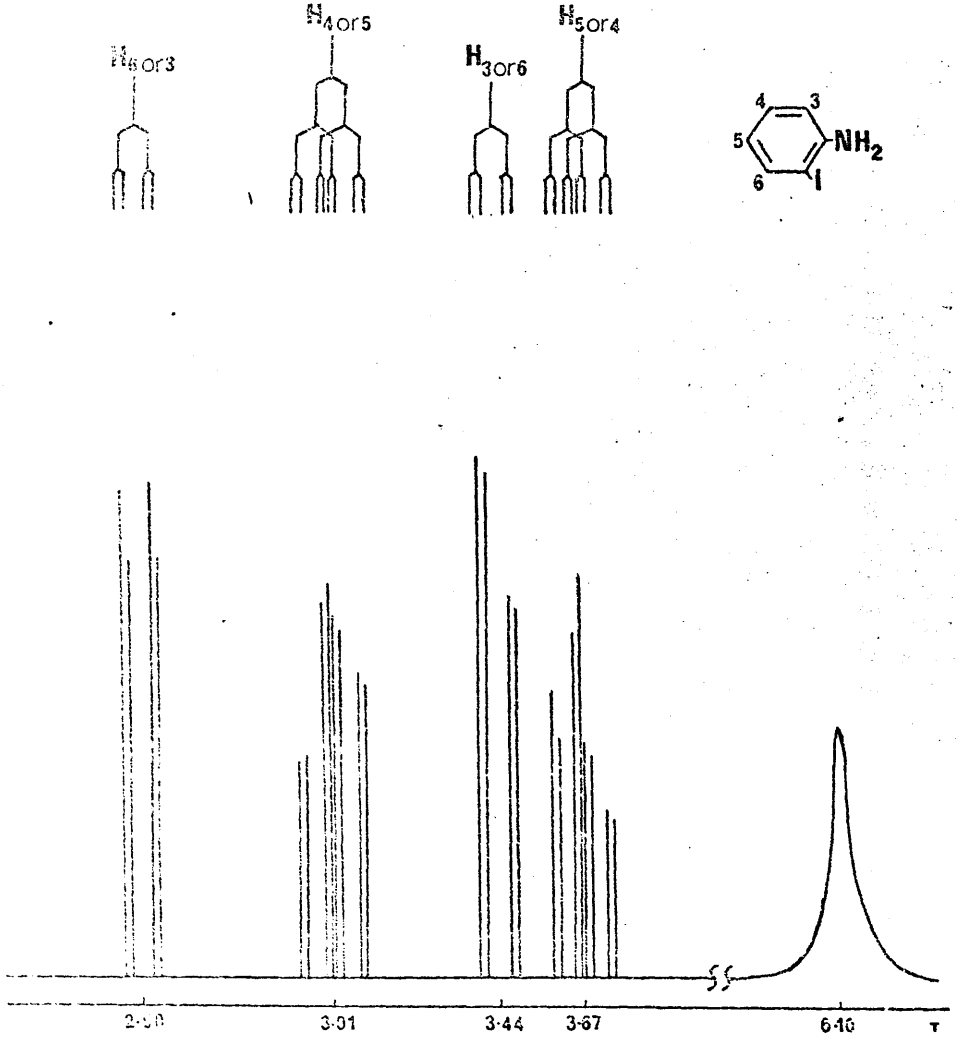
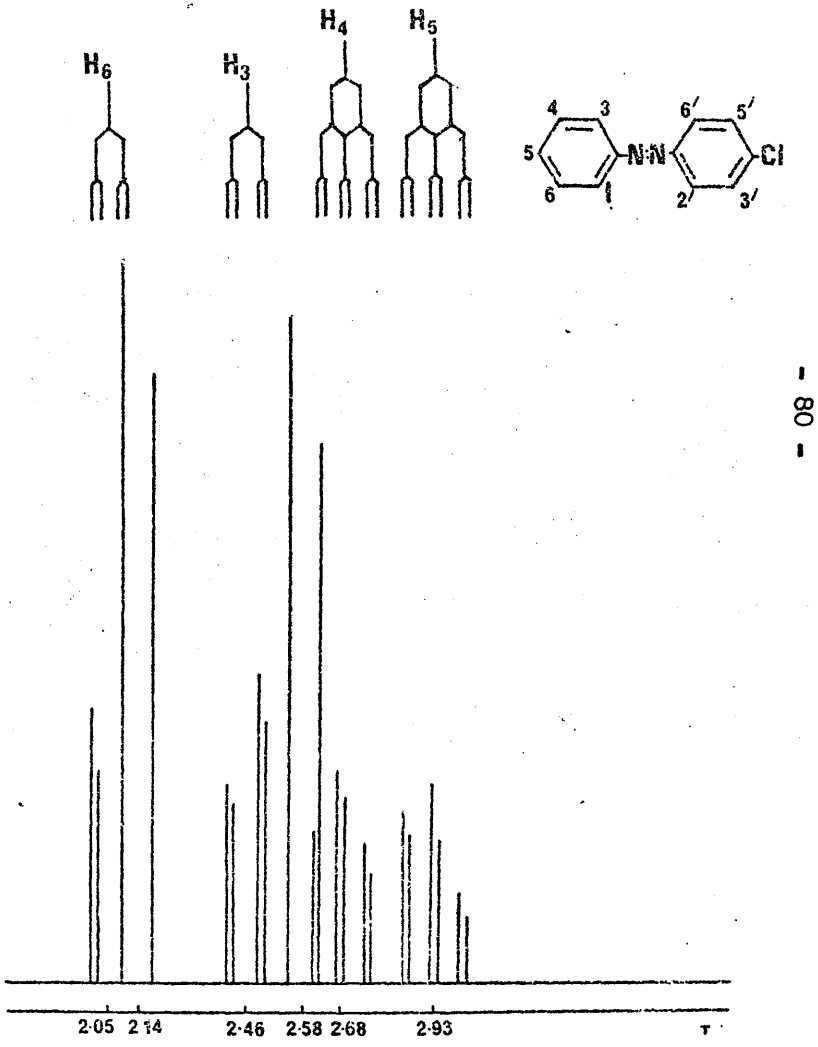


Figure 6. Line Diagrams of ^{1}H NMR Spectra of ortho-Iodo-aniline and 2-(4'-Chlorophenylazo)phenyliodide.

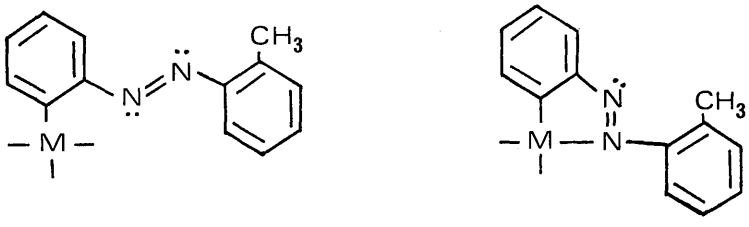




the proton between chlorine and nitrogen, H_3, is shifted well to low field compared to the other aromatic protons. This proton adjacent to nitrogen has also been found to occur at lowest field in $\underline{h}^5$-cyclopentadienyl(2-(phenylazo)phenyl) nickel.[138] A different assignment for this complex ascribes the low field resonance to the proton adjacent to the metal.[116] This assignment is also suggested for Mn, Re, Fe, Mo and Ru complexes.[116,140]

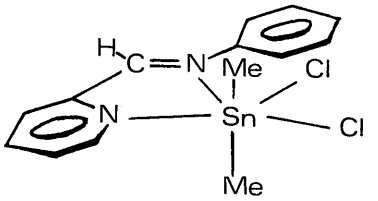
The main difference between the chelate and monodentate (2-(arylazo)aryl) palladium complexes is that all the protons signals of Ring 1 are shifted upfield in the latter case. This shift is most pronounced for the proton adjacent to the nitrogen. Curiously, the opposite effect has been observed before for ruthenium complexes and ascribed to the extra shielding of the azo group in the chelate complexes.[140]

In comparing the spectra of ortho-, meta- and para-methyl substituents in ring 2, a significant downfield shift of the methyl resonance of ortho-derivatives is noted when the ligand is monodentate and carbon-bonded only. This shift is not found in the bidentate (C,N'-bonded) complexes. With a trans-planar structure for the azobenzene moiety, the configuration of the monodentate derivatives is likely to be that depicted below.

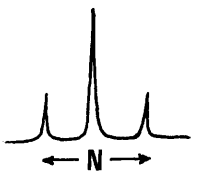


The downfield shift of the ortho-methyl protons probably arises from the magnetic anisotropic effect of the lone pair on nitrogen. Molecular models confirm that this interaction of the methyl group and the lone pair is indeed reasonable. In the bidentate derivatives this lone pair is not available. In the spectra of picolinaldimine-tin

adducts the same explanation has subsequently been offered to account for the observed chemical shift of the aromatic protons on coordination of the imine nitrogen.[199]



The <u>trans</u> configuration of the chloro-(2-(arylazo)aryl)bis-(triethylphosphine) platinum and palladium complexes has been established from the pattern of the methyl signals in the ^1H NMR spectrum. This differentiation between <u>cis</u> and <u>trans</u> phosphine on the basis of their ^1H NMR spectra results from the phenomenon of Virtual Coupling. Jenkins and Shaw established that for complexes which contain two phosphines bearing a methyl or methylene group attached to phosphorus, the <u>trans</u> isomers exhibit a triplet structure and <u>cis</u> compounds appear as a doublet.[200] The doublet arises in the expected way from coupling to the adjacent phosphorus atom only. The origin of the deceptively simple triplet for the <u>trans</u> isomer is more complicated. Harris considered the theoretical aspects of the $X_nAA'X'_n$ system (A = P, X = H in the present case) for J(X - X') equal to zero.[201]

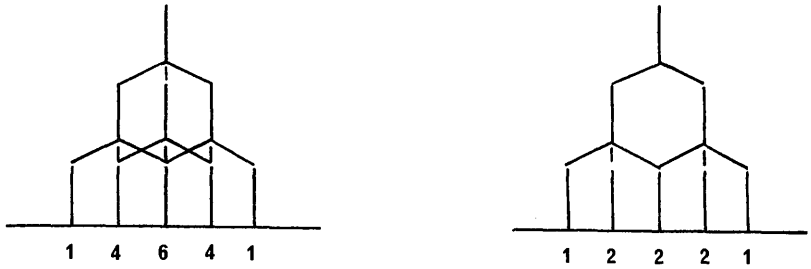


$$N = J_{HP} + J_{HP'}$$

The 'triplet' is one of the limiting cases of this spin system and arises when $|JAA'| \gg |JAX - JAX'|$. In the phosphine complexes <u>trans</u>-$(Me_nPh_{3-n}P)_2PtX_2$, J(H-H') = 0, J(H-P) $\simeq$ 10Hz, J(H-P') = 0 and J(P-P') $\gg$ 10Hz thus satisfying the conditions required for observation of a 'triplet' in the ^1H n.m.r. spectrum. The centre line, since it arises from a superposition of several transitions, is often broader than the outer lines

of the triplet.

The triethylphosphine complexes are slightly more complicated.[202] The methyl resonances approximate to a 1:4:6:4:1 quintet. This arises from coupling of the methyl protons with the methylene protons to give a triplet which is further split by virtual coupling into a quintet.



In the chloro-(2-(arylazo)aryl)bis(triethylphosphine) palladium derivatives this quintet is centred at ~9.0τ. The methylene signal ~8.5τ cannot be simply interpreted.

If the two phosphorus nuclei had been disposed in a cis configuration where Virtual Coupling is not expected, the methyl proton resonance would have appeared as a 1:2:2:2:1 quintet. This arises from coupling of the methyl protons with phosphorus to give a doublet which is further split by the methylene protons into two overlapping triplets.

IR Spectra.

The IR spectra of aryl mercurials have received little attention, although an analysis of the spectra of phenyl mercury complexes has been made[203]. Furthermore, the spectra of azobenzene derivatives has generally not been related to elucidation of substitution patterns.

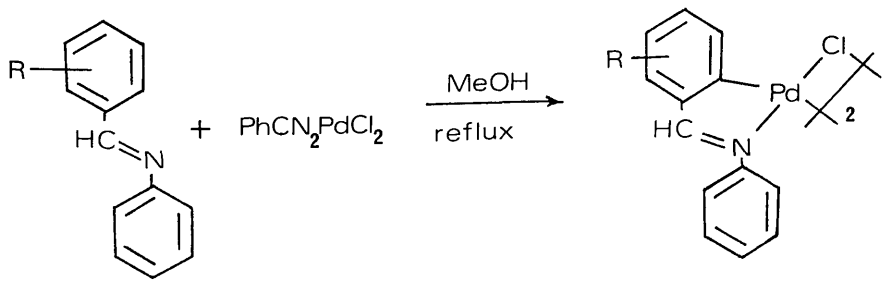
The ring substitution pattern of most of the 2-(arylazo)aryl derivatives can be confirmed by the carbon-hydrogen out of plane deformations near 750cm^{-1}. These absorptions are characteristic of the substitution

patterns involved[157] though an extra absorption band is observed near 710cm^{-1} for the 1,2- substituted aromatics in the present compounds. Masking of some of these absorptions occurs in the spectra of phosphine complexes and in the chlorine substituted compounds the C-Cl stretch (assigned to a band near 710cm^{-1}) is a further complication. In general, however, the recognition of substitution patterns from this IR region is a simple process. This complements the NMR studies in that the more substituted derivatives are easier to interpret from their NMR spectra but less easy from their IR spectra and vice versa.

The spectra were compared using a light box and the relevant bands are listed in Table 4 . Those 2-(arylazo)aryl complexes containing monosubstituted rings give rise to two bands which correspond well with those at 772cm^{-1} and 684cm^{-1} for azobenzene itself.[204] As with NMR, those compounds containing a <u>para</u>-disubstituted ring are especially easy to recognise. A single strong band near 820cm^{-1} dominates the spectrum as is found also with <u>para</u>-hydroxyazobenzene (837cm^{-1})[204] and <u>para</u>-aminoazobenzene (834cm^{-1})[204].

Several workers have used the C-H out of plane deformation modes as a means of establishing the <u>ortho</u>-metallation of various ligands. Apart from the phosphite complexes, the relevant bands appear in the region 770-735cm^{-1}, characteristic of <u>ortho</u>-disubstitution[157]. The phosphites show a band for this substitution pattern near 800cm^{-1}. Examples of these assignments are displayed in Table 5.

Molnar and Orchin[205] have used this region of the IR spectrum to determine which ring becomes bonded to palladium in the ortho-metallation of benzylideneaniline, which is isolelectronic with azobenzene,



From the presence of a band at 690cm^{-1} they concluded that ortho metallation involves the ring attached to the carbon of the azomethine group.

Shaw reports[91] the presence of a band at ca. 1560cm^{-1}, indicative of ortho- metallation of the aromatic ring in Bu^t_2PhP. In accord with this, the 2-(phenylazo)phenyl chelate complexes of platinum, palladium and manganese all show a low intensity band at 1550cm^{-1} not present in azobenzene. Interestingly, the carbon-only bonded 2-(phenylazo)phenyl derivatives of mercury, platinum or palladium have no band at 1550cm^{-1} despite the same ring substitution pattern. The weakness of these bands, however, makes them of low diagnostic value relative to the 750cm^{-1} region.

Other workers[60,208] have shown that a strong band at ca 1100cm^{-1} is indicative of ortho-metallation of ruthenium phosphite complexes. This region of the IR spectrum is often complicated by other peaks and this assignment is probably of most use when spectra of the corresponding metallated and non-metallated complexes can be compared.

The metal-halogen stretch of the chloro(2-(arylazo)aryl)phosphine palladium and platinum complexes supports the formulation as trans isomers made by NMR. These values are typical of a chlorine atom trans to an aromatic group[91]. The mercury-halogen stretches in the (2-(arylazo)aryl)-mercuric halides have also been observed and are normal for arylmercuric halides[209]. This data is presented in Table 6.

A Far-IR study of palladium(II) halogen complexes with C⁀N chelating ligands has been reported[210] and includes several halogen-bridged azobenzene complexes. Two bands for ν(Pd-X) were detected in each compound. On the basis of the higher trans influence of a σ-bonded carbon over a nitrogen donor ligand, the higher frequency band was attributed to the stretching vibration ν(PdX) trans to N, and the lower frequency band to ν(PdX) trans to carbon. For $((azb)PdCl)_2$ these modes

Table 4. C-H out-of-plane deformation modes for (2-(arylazo)aryl) metal complexes (cm^{-1})[a].

Compound	Ring Substitution Pattern: 1		1,2	1,3	1,4	1,3,5	1,2,4	
$(C_6H_5N_2C_6H_4)HgCl$	774vsbr	684s	765sh					
$(C_6H_5N_2C_6H_4)HgBr$	771s	682s	765sh					
$(C_6H_5N_2C_6H_4)HgI$	777s	678s	761s					
$(2'Me\text{-}C_6H_4N_2C_6H_4)HgCl$			761s					
$(3'Me\text{-}C_6H_4N_2C_6H_4)HgCl$			762s	785s 683s				
$(4'Me\text{-}C_6H_4N_2C_6H_4)HgCl$			761s		822vs			
$(4'MeO\text{-}C_6H_4N_2C_6H_4)HgCl$			763s(769sh)		830vs			
$(4'Cl\text{-}C_6H_4N_2C_6H_4)HgCl$			763sbr		834vs			
$(3',5'Br_2\text{-}C_6H_3N_2C_6H_4)HgCl$			760s(769sh)			857s 746s		
$(2'Me\text{-}C_6H_4N_2C_6H_3\text{-}4Cl)HgCl$			760s				885m or 869m	822s
$(3'Me\text{-}C_6H_4N_2C_6H_3\text{-}4Cl)HgCl$				782s 680s			880s	815s
$(4'Me\text{-}C_6H_4N_2C_6H_3\text{-}4Cl)HgCl$					821vsbr		880s or 869m	815sh
$(2'Me\text{-}C_6H_4N_2C_6H_3\text{-}4Cl)_2Pd_2Cl_2$			770s				882s or 865m	815s
$(3'Me\text{-}C_6H_4N_2C_6H_3\text{-}4Cl)_2Pd_2Cl_2$				776s 685s			880sh or 869m	804s
$(4'Me\text{-}C_6H_4N_2C_6H_3\text{-}4Cl)_2Pd_2Cl_2$					811s		879m or 869m	811s
$(2'Me\text{-}C_6H_4N_2C_6H_3\text{-}4Cl)Pd(PEt_3)_2Cl$			775s				888m	821s
$(3'Me\text{-}C_6H_4N_2C_6H_3\text{-}4Cl)Pd(PEt_3)_2Cl$				799s 694s			884m	815s
$(4'Me\text{-}C_6H_4N_2C_6H_3\text{-}4Cl)Pd(PEt_3)_2Cl$					830vsbr		881m or 861m	obscured

[a]KBr disc, br = broad, sh = shoulder, m = medium, s = strong, vs = very strong.

Table 5.

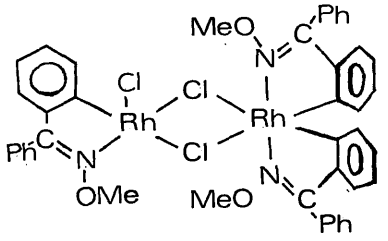
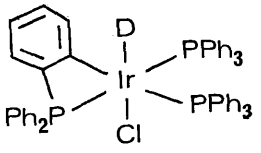
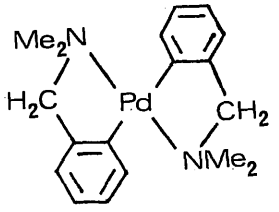
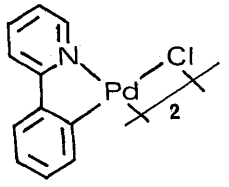
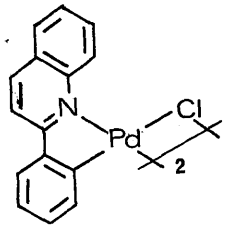
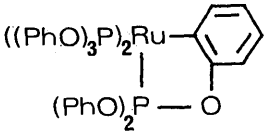
Ortho-Metallated Complex	C-H Out of Plane Deformation Modes for ortho-substitution	Reference
	$728cm^{-1}$	55
	$728cm^{-1}$	98
	$750cm^{-1}$	147
	$737cm^{-1}$	206
	$738cm^{-1}$	206
	$800cm^{-1}$	207
$RuX(P(OC_6H4)(OPh)_2)(P(OPh)_3)_3$, X=Cl,Br	$800cm^{-1}$	208
$Ru(CO)_2(P(OC_6H_4)(OPh)_2)_2$, isomer a	$795cm^{-1}$	60
$Ru(CO)_2(P(OC_6H_4)(OPh)_2)_2$, isomer b	$820cm^{-1}$	60
$Ru_2H(CO)_3(P(OC_6H_4)(OPh)_2)_2$ $(OP(OPh)_2)$	$802cm^{-1}$	60

Table 6. Far IR Spectra of the (2-(arylazo)aryl) complexes.

Complex	(M-X) (cm^{-1})[a]	
	Trans to C	Trans to N
$(C_6H_5N_2C_6H_4)_2Pt_2Cl_2$	289	337
$(C_6H_5N_2C_6H_4)_2Pd_2Cl_2$	261	339
$(3,5'\text{-}Br_2C_6H_3N_2C_6H_3\text{-}4Cl)_2Pd_2Cl_2$	275	325
$(4'\text{-}MeC_6H_4N_2C_6H_3\text{-}4Cl)_2Pd_2Cl_2$	274	315
$(3'\text{-}MeC_6H_4N_2C_6H_3\text{-}4Cl)_2Pd_2Cl_2$	267	305
$(2'\text{-}MeC_6H_4N_2C_6H_3\text{-}4Cl)_2Pd_2Cl_2$	272	313
$(C_6H_5N_2C_6H_4)Pt(PEt_3)_2Cl$	265(276sh)	
$(C_6H_5N_2C_6H_4)Pt(PPh_2Me)_2Cl$	299br	
$(C_6H_5N_2C_6H_4)Pt(PPh_2Me)Cl$	286	
$(C_6H_5N_2C_6H_4)Pd(PEt_3)_2Cl$	298	
$(4'\text{-}MeC_6H_4N_2C_6H_3\text{-}4Cl)Pd(PEt_3)_2Cl$	295(285sh)	
$(3'\text{-}MeC_6H_4N_2C_6H_3\text{-}4Cl)Pd(PEt_3)_2Cl$	298(292sh)	
$(2'\text{-}MeC_6H_4N_2C_6H_3\text{-}4Cl)Pd(PEt_3)_2Cl$	299(294sh)	
$(C_6H_5N_2C_6H_4)HgI$	205[b]	
$(C_6H_5N_2C_6H_4)HgBr$	233[b]	
$(C_6H_5N_2C_6H_4)HgCl$	325	
$(4'\text{-}MeOC_6H_4N_2C_6H_4)HgCl$	330(322sh)	
$(4'\text{-}ClC_6H_4N_2C_6H_4)HgCl$	330	
$(4'\text{-}MeC_6H_4N_2C_6H_4)HgCl$	328(325sh)	
$(3'\text{-}MeC_6H_4N_2C_6H_4)HgCl$	328	
$(2'\text{-}MeC_6H_4N_2C_6H_4)HgCl$	326	
$(4'\text{-}MeC_6H_4N_2C_6H_3\text{-}4Cl)HgCl$	326(323sh)	
$(3'\text{-}MeC_6H_4N_2C_6H_3\text{-}4Cl)HgCl$	326(328,316sh)	
$(2'\text{-}MeC_6H_4N_2C_6H_3\text{-}4Cl)HgCl$	329(325sh,320sh)	
$(3',5'\text{-}Br_2C_6H_3N_2C_6H_4)HgCl$	326(321sh,314sh)	
$(3',5'\text{-}Br_2C_6H_3N_2C_6H_3\text{-}4Cl)HgCl$	334(330sh,325sh)	

br = broad, sh = shoulder [a] KBr disc [b] Rigidex disc

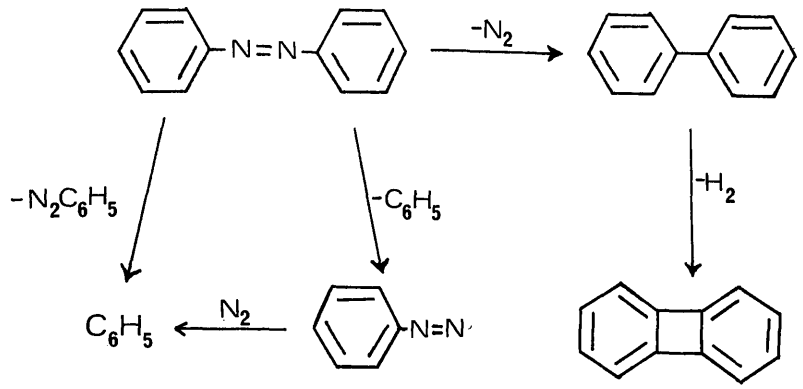
have been assigned to peaks at 337cm^{-1} and 262cm^{-1} respectively. A different assignment has been made by Fahey[117] for these vibrations, viz. 266cm^{-1} (trans to N) & 237cm^{-1} (trans to C). The former work seems more convincing since it is based on a comparison of spectra of chlorine and bromine analogues.

In the same way, comparison of $((C_6H_5N_2C_6H_4)PtCl)_2$ with $((C_6H_5N_2C_6H_4)PtBr)_2$ has allowed identification of the two ν(PtCl) modes at 337cm^{-1} and 289cm^{-1}. These values, along with the more tentative assignments for the (2-(arylazo)aryl) palladium dimers are presented in Table 6.

Mass Spectra.

Mass spectral investigations of azobenzene compounds and organomercury compounds are virtually limited to one investigation for each class of compound[211,212]. The results outlined below for several of the (2-(arylazo)aryl) mercuric halides generally confirm the combined findings of these studies. Five compounds have been examined qualitatively and the main peaks observed along with suggested assignments are found in Tables 7 and 8. The rough relative intensities are also included to give an indication of the favoured fragments.

The parent ion is observed in each case and its fragmentation shows that the most abundant peaks do not contain mercury. Mercury itself is observed and other fragments are in line with the expected stepwise cleavage of various groups from the molecular ion. Of interest, and in agreement with previous findings[212] are peaks corresponding to elimination of mercury with concomitant rearrangement of halogen to the organic substrate. The spectra also support the suggested breakdown pattern of simple organic azobenzene derivatives.[211]

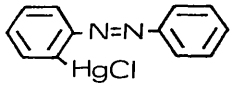


Peaks corresponding to these (or analogous substituted) fragments were observed in every case. The mass spectrum of 2-(phenylazo)phenyl iodide (Figure 7) is also in accord with this fragmentation pattern.

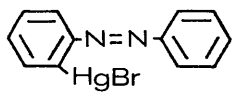
Mercury containing peaks were easily identified by the mercury isotope pattern illustrated in Figure 8a. In those cases where other polyisotopic elements are present (viz. Cl and Br) the mercury pattern is significantly changed. In several cases the resultant peak patterns for all possible combinations of these elements have been calculated using an available computer programme. These patterns are illustrated in Figures 8a and b, and in two cases the effect of the other atoms present has been included for comparison. The observed patterns match the calculated patterns exactly which gives support to the suggested assignments.

All spectra show very low intensity peaks at higher $\frac{m}{e}$ values than the molecular ion. The identification of a peak at 561 in the spectrum of $(C_6H_5N{:}NC_6H_4)HgI$ suggests that these peaks may arise from the symmetrised compound. It is not known whether the symmetrisation occurs by combination of fragment ions or prior to ionisation. If the latter is true then this may relate to the broad melting range observed for some of the (2-(aryazo)aryl) mercuric halides. Spontaneous symmetrisation has already been discussed as a possible explanation for this observation.

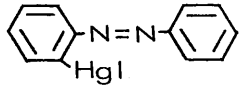
Table 7. Mass Spectral data for the (2-(phenylazo)phenyl) mercuric halides.



m/e(Intensity)	Probable Fragment
416(4.5)	$C_6H_5N_2C_6H_4HgCl$
353(0.7)	$C_6H_5C_6H_4Hg$
339(0.2)	$N_2C_6H_4HgCl$
310(2)	C_6H_5HgCl
276(0.5)	C_6H_4Hg
257(6)	$C_6H_5N_2C_6H_4C_6H_4$
235(0.2)	HgCl
216(0.4)	$C_6H_5N_2C_6H_4Cl$
200(7)	Hg
182(3)	$C_6H_5N_2C_6H_5$
181(2)	$C_6H_4N_2C_6H_5$
153(12)	$C_6H_4C_6H_5$
152(21)	$C_6H_4C_6H_4$
111(15)	C_6H_4Cl
105(110)	$N_2C_6H_5$
91(2)	NC_6H_5
90(2)	NC_6H_4
77(220)	C_6H_5
76(55)	C_6H_4

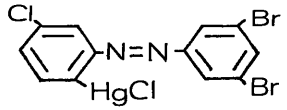


m/e(Intensity)	Probable Fragment
460(11)	$C_6H_5N_2C_6H_4HgBr$
385(0.4)	$N_2C_6H_4HgBr$
357(4)	C_6H_4HgBr
279(1)	HgBr
257(0.1)	$C_6H_5N_2C_6H_4C_6H_4$
232(0.5)	$C_6H_5C_6H_4Br$
200(2.5)	Hg
182(4)	$C_6H_5N_2C_6H_5$
181(1)	$C_6H_5N_2C_6H_4$
155(30)	C_6H_4Br
153(15)	$C_6H_4C_6H_5$
152(30)	$C_6H_4C_6H_4$
105(100)	$C_6H_5N_2$
91(2)	C_6H_5N
77(>60)	C_6H_5
76(50)	C_6H_4

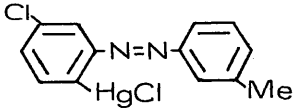


m/e(Intensity)	Probable Fragment
562(<0.1)	$(C_6H_5N_2C_6H_4)_2Hg$
508(14)	$C_6H_5N_2C_6H_4HgI$
431(0.2)	$N_2C_6H_4HgI$
403(3)	C_6H_4HgI
353(0.5)	$C_6H_5C_6H_4Hg$
327(3)	HgI
277(0.5)	C_6H_5Hg
276(0.5)	C_6H_4Hg
257(1)	$C_6H_5N_2C_6H_4C_6H_4$
203(30)	C_6H_4I
200(1)	Hg
181(1)	$C_6H_5N_2C_6H_4$
153(9)	$C_6H_5C_6H_4$
152(21)	$C_6H_4C_6H_4$
127(2)	I
105(42)	$C_6H_5N_2$
91(3)	C_6H_5N
90(2)	C_6H_4N
77(140)	C_6H_5
76(55)	C_6H_4

Table 8. Mass Spectral data for two (2-(arylazo)aryl) mercurials.

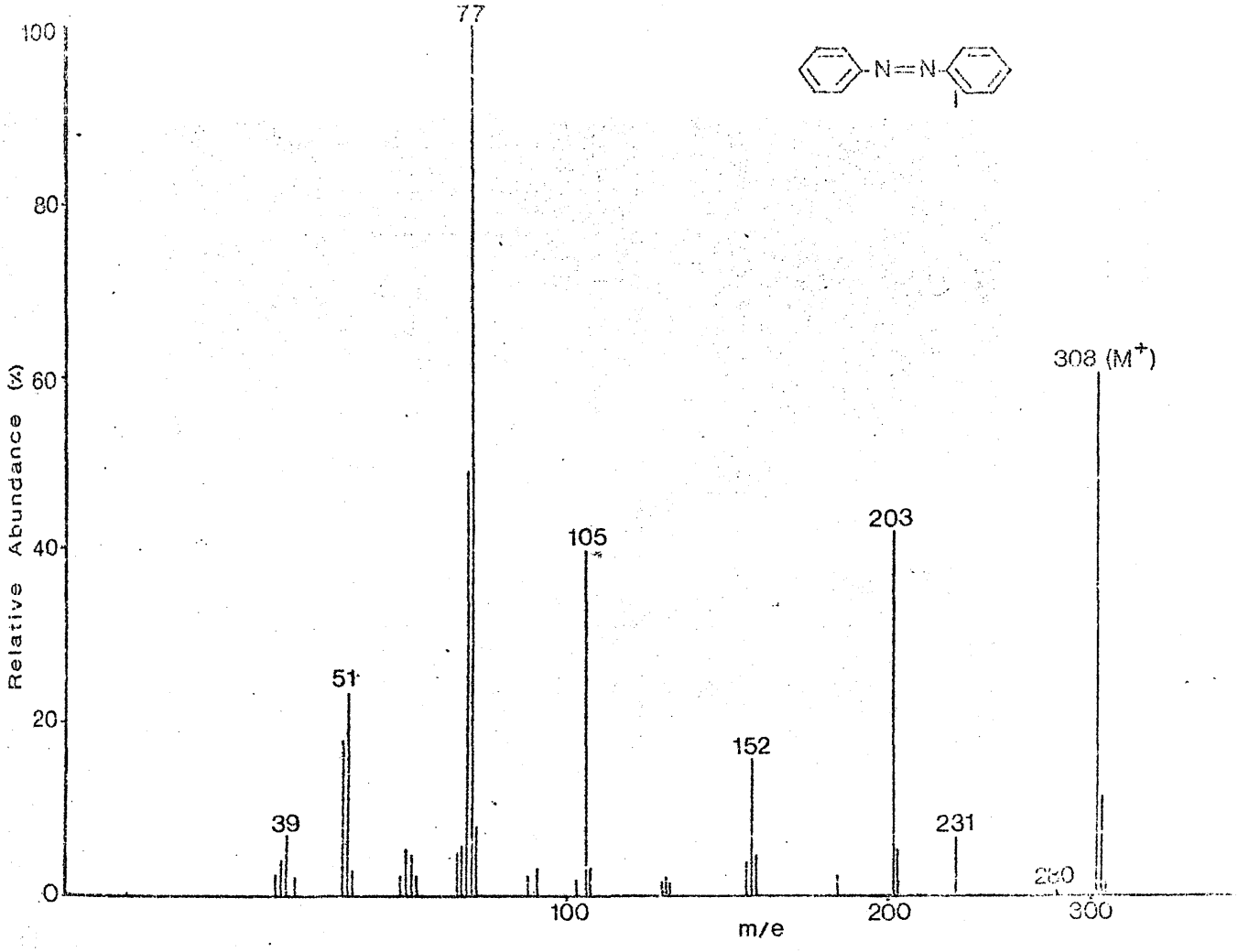


m/e(Intensity)	Probable Fragment
606(2)	$Br_2C_6H_3N_2C_6H_3ClHgCl$
389(0.5)	BrC_6H_3HgCl
373(0.5)	$N_2C_6H_3ClHgCl$
345(4)	ClC_6H_3HgCl
310(0.2)	C_6H_3HgCl
261(6)	$N_2C_6H_3Br_2$
233(13)	$C_6H_3Br_2$
220(1)	$Cl_2C_6H_3C_6H_3$
200(1)	Hg
185(2)	$ClC_6H_3C_6H_3$
178(0.2)	$C_6H_3N_2C_6H_3$
168(1)	NC_6H_3Br
154(11)	C_6H_3Br
150(3)	$C_6H_3C_6H_3$
145(10)	$C_6H_3Cl_2$
110(12)	C_6H_5Cl
75(150)	C_6H_3
74(40)	C_6H_2



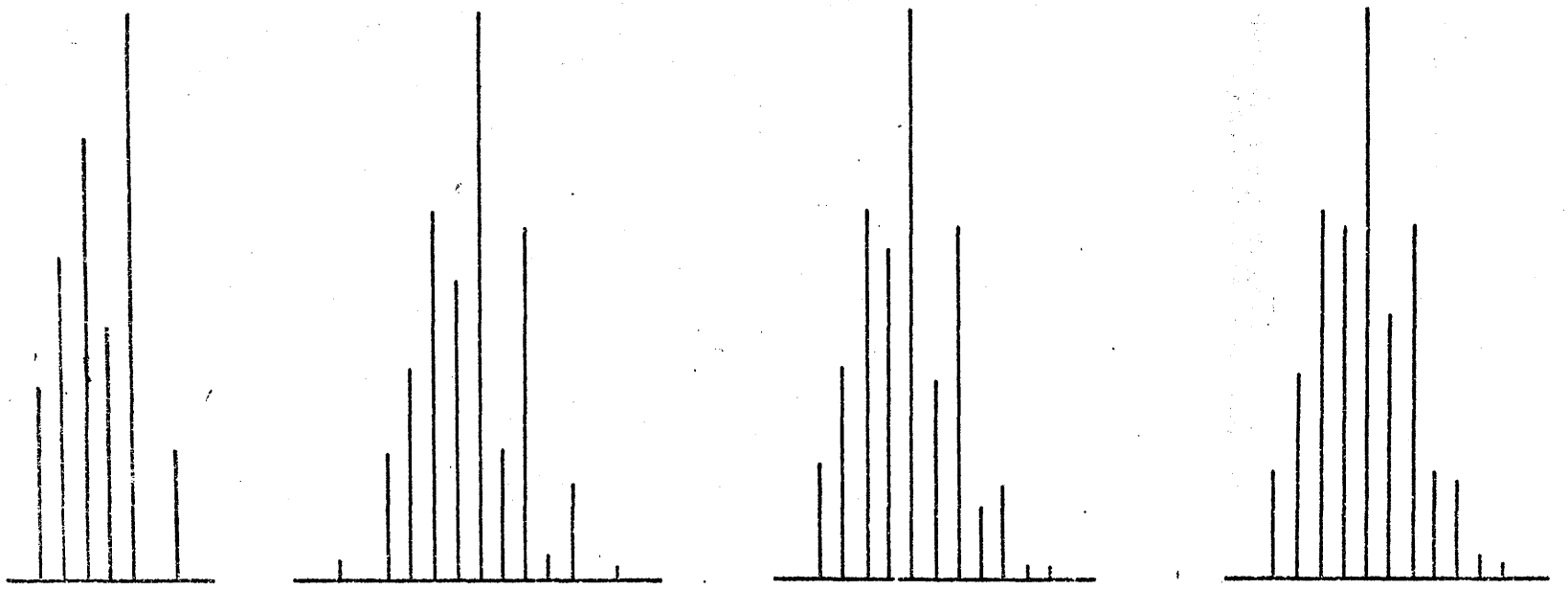
m/e(Intensity)	Probable Fragment
658(< 0.1)	$(ClC_6H_3N_2C_6H_4CH_3)_2Hg$
464(1)	$ClC_6H_3N_2C_6H_4CH_3HgCl$
345(0.4)	ClC_6H_3HgCl
201(0.3)	$ClC_6H_3C_6H_4CH_3$
200(0.5)	Hg
186(0.5)	$ClC_6H_3C_6H_4$
166(2)	$C_6H_3C_6H_4CH_3$
165(4)	$C_6H_3C_6H_3CH_3$
145(2)	ClC_6H_3Cl
119(16)	$N_2C_6H_4CH_3$
110(4)	ClC_6H_3
91(5)	$C_6H_4CH_3$
90(90)	NC_6H_4
75(30)	C_6H_3
74(5)	C_6H_2

Figure 7. Mass Spectral data 2-(phenylazo)phenyliodide.



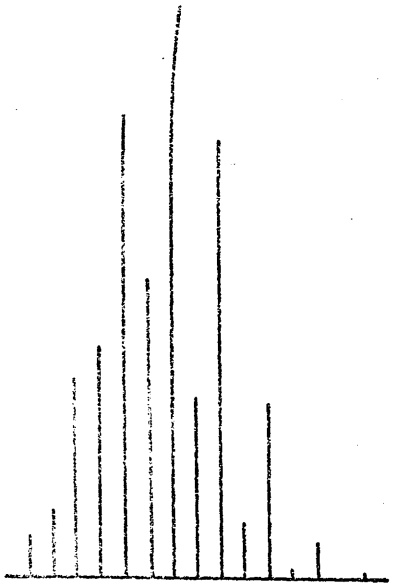
m/e	Probable Fragment
308	$C_6H_5N_2C_6H_4I$
280	$C_6H_5C_6H_4I$
231	$N_2C_6H_4I$
203	C_6H_4I
152	$C_6H_4C_6H_4$
105	$C_6H_5N_2$
77	C_6H_5
76	C_6H_4
51	C_4H_3

Figure 8a. Isotope patterns for combinations of mercury and other elements.



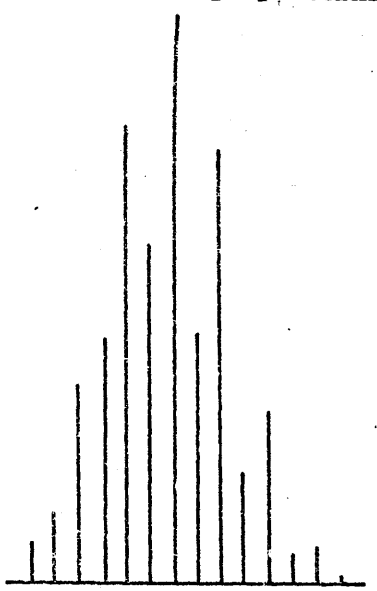
Hg		$HgCl_2$		$HgCl_2C_{13}H_{10}N_2$		$HgCl_2C_{26}H_{20}N_4$	
Mass	Abundance (%)	Mass	Abundance (%)	Mass	Abundance (%)	Mass	Abundance (%)
196	0.146	266	0.3185	460	0	654	0
197	0.000	267	0.0000	461	0	655	0
198	10.02	268	22.0655	462	20	656	19
199	16.84	269	36.7373	463	37	657	36
200	23.13	270	64.6565	464	65	658	65
201	13.22	271	52.6443	465	58	659	62
202	29.80	272	100.0000	466	100	660	100
203	0.00	273	22.5431	467	35	661	46
204	6.85	274	62.3636	468	62	662	62
		275	3.0271	469	12	663	19
		276	16.5063	470	16	664	17
		277	0.0000	471	2	665	4
		278	1.5685	472	2	666	2
				473	0	667	0
				474	0	668	0

Figure 8b. Isotope patterns for combinations of mercury and other elements.



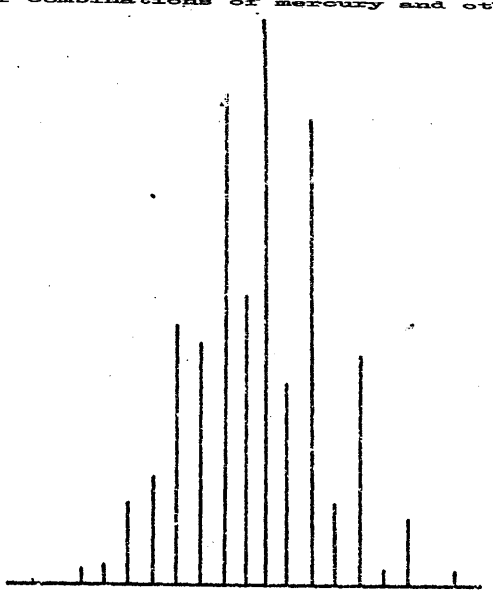
$HgCl_2Br_2$

Mass	Abundance (%)
424	0.0995
425	0.0000
426	7.0900
427	11.4800
428	33.7954
429	38.9200
430	77.3976
431	50.2373
432	100.0000
433	30.4888
434	73.2284
435	8.5980
436	29.2496
437	0.9059
438	5.8993
439	0.0000
440	0.4694



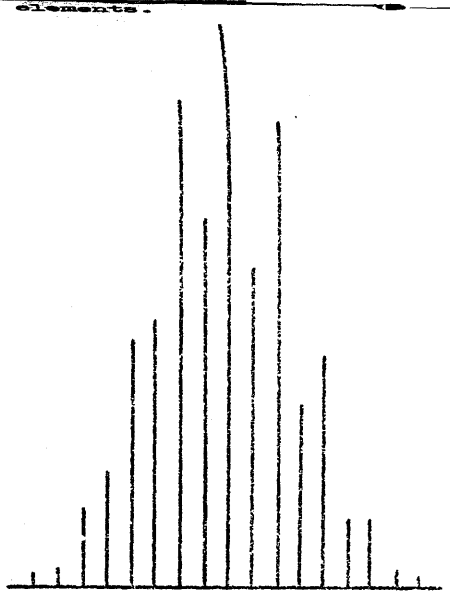
$HgCl_2Br_2C_{12}H_8N_2$

Mass	Abundance (%)
602	0
603	0
604	7
605	12
606	33
607	41
608	77
609	57
610	100
611	42
612	73
613	18
614	29
615	5
616	6
617	1
618	0
619	0
620	0



$HgCl_2Br_4$

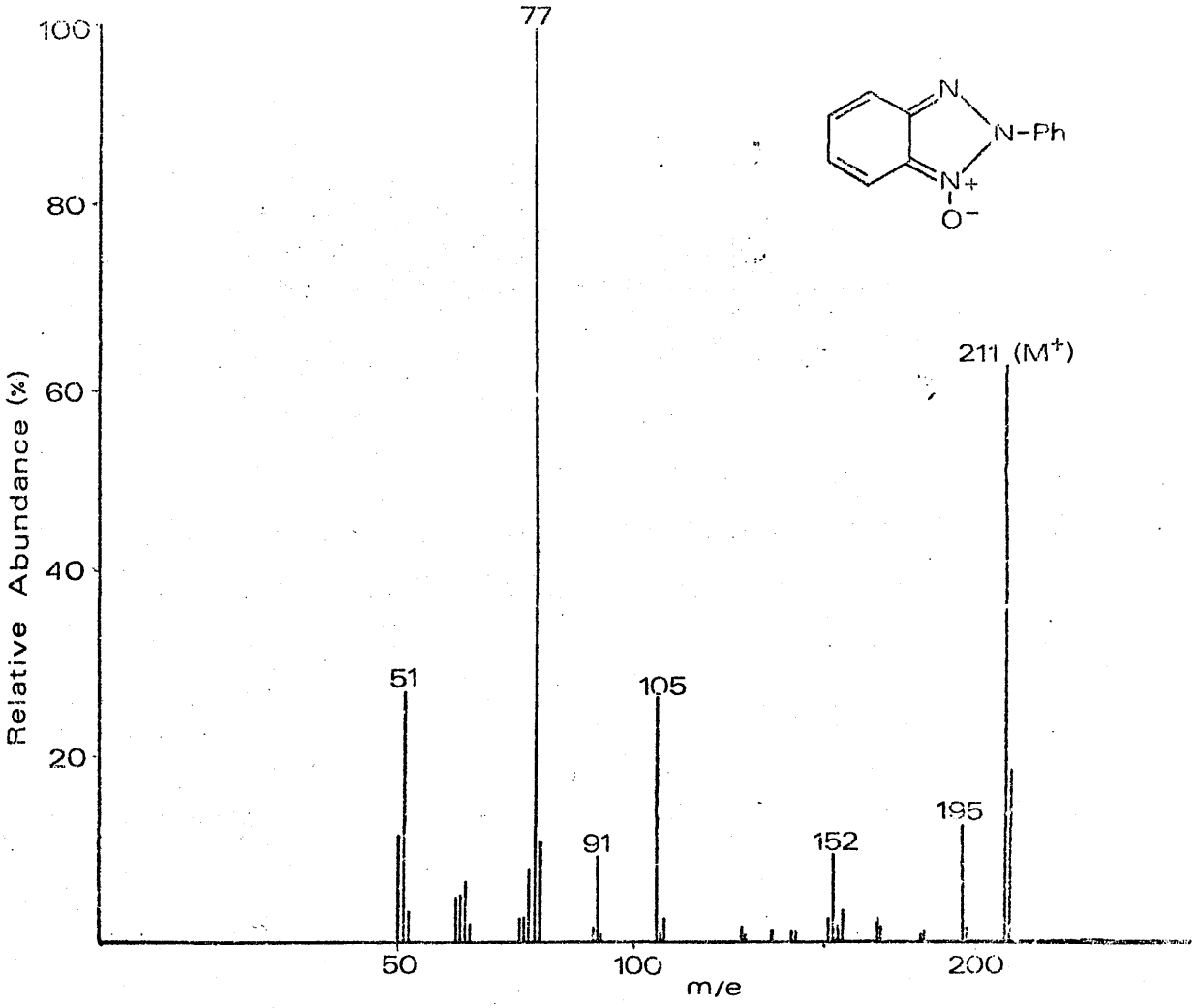
Mass	Abundance (%)
582	0.0290
583	0.0000
584	2.1234
585	3.3462
586	13.9232
587	17.8936
588	43.8190
589	40.0515
590	82.7370
591	48.4117
592	100.0000
593	33.9239
594	78.2176
595	13.6803
596	38.8483
597	2.9170
598	11.6675
599	0.2529
600	1.9146
601	0.0000
602	0.1310



$HgCl_2Br_4C_{24}H_{12}N_2$

Mass	Abundance (%)
938	0
939	0
940	2
941	3
942	13
943	19
944	42
945	45
946	82
947	62
948	100
949	54
950	78
951	31
952	39
953	12
954	12
955	3
956	2
957	0
958	0

Mass spectral data for 2-phenylbenzotriazole-1-oxide, Figure 9.



m/e	Probable Fragment
211	$(C_6H_5N_2C_6H_4NO)^+$
195	$(C_6H_5N_2C_6H_4N)^+$
182	$(C_6H_5N_2C_6H_5)^+$
181	$(C_6H_5N_2C_6H_4)^+$
167	$(C_6H_5C_6H_4N)^+$
166	$(C_6H_4C_6H_4N)^+$
154	$(C_6H_5C_6H_5)^+$
152	$(C_6H_4C_6H_4)^+$
134	$(C_6H_4N_3O)^+$
106	$(C_6H_4NO)^+$
105.5	$(C_6H_5N_2C_6H_4NO)^{2+}$
105	$(C_6H_5N_2)^+$
91	$(C_6H_5N)^+$
78	$(C_6H_5)^+$
51	$(C_4H_3)^+$

EXPERIMENTAL

Preparation of the sulphenyl halides

2,4-Nitrochlorobenzenesulphenyl chloride, $2\text{-}NO_2,4\text{-}ClC_6H_3SCl$.

Bis 2,4-nitrochlorophenyldisulphide (27.9346g, 75 m moles) and iodine (0.1108g) were added to dry carbon tetrachloride (150 ml). Chlorine was passed through this stirred suspension, maintained at 50°C. After 15 minutes a clear yellow solution had formed. The reaction was continued for $2\frac{3}{4}$ hours. Shaking the solution at room temperature in an open vessel to remove dissolved chlorine and cooling to 0°C produced a mass of yellow needles of the product which were removed by filtration. Removal of solvent from the filtrate gave more yellow 2,4-nitrochlorobenzenesulphenyl chloride (32.83g, 96%. M.p. 99-100°C, lit[214] 95-97°C)

2-Nitrobenzenesulphenyl chloride, $2\text{-}NO_2\text{-}C_6H_4SCl$

From a similar preparation but with longer reaction time ($4\frac{1}{2}$ hours) was obtained yellow needles of 2-nitrobenzenesulphenyl-chloride (76%. M.p. 73-75°C, lit[214] 73-74.5°C)

Preparation of the 2-nitro-arylsulphenanilide derivatives

2-Nitrobenzenesulphenanilide, $2\text{-}NO_2C_6H_4SNHC_6H_5$[153]

2-Nitrobenzenesulphenyl chloride (5.0218g, 26.5m moles) was dissolved in dry ether (60 ml) giving a straw coloured solution. Aniline (5.0777g, 54.5m moles) was added, with constant stirring, to the ice-cooled ether solution, A precipitate appeared on addition of the first drops of aniline and after complete addition the solution had a creamy yellow appearance.

Filtration and washing of the residue with ether gave white aniline hydrochloride. The ether was removed from the orange filtrate leaving a dark orange viscous liquid. To this was added petroleum ether (B.p. 60-80°C)(200 ml). The solution was stirred with heating and after a few minutes the viscous liquid solidified. Recrystallisation from petroleum ether (B.p. 60-80°C) gave orange microcrystalline clusters of 2-nitrobenzenesulphenanilide (5.4416g, 84% M.p. 90-92°C, lit[153] 94°)

2-Nitrobenzenesulphen p-anisidide, $2\text{-}NO_2C_6H_4SNHC_6H_4\text{-}OMe$

2-Nitrobenzenesulphenyl bromide[154] (2.3282g, 9.9m moles) was dissolved in ether (50 ml). p-Anisidine (2.5085g, 20.4m moles) was dissolved in ether (100 ml) and added in 5 ml portions, with stirring, to the ice-cooled solution of 2-nitrobenzenesulphenyl bromide. After 0.5 hr. stirring the creamy yellow solution was filtered to remove the white water-soluble precipitate. The ether was completely removed from the filtrate by rotary evaporation yielding an orange powder. Recrystallisation from benzene gave orange crystals of 2-nitrobenzensulphen-p-anisidide (2.3181g, 85% M.p. 140.5-141.5°, lit[151] 141.5-142.5°)

2-Nitrobenzenesulphen 4-chloroanilide, $2\text{-}NO_2C_6H_4SNHC_6H_4\text{-}4Cl$

2-Nitrobenzenesulphenyl bromide (3.8177g, 16.3m moles) was dissolved in dry ether (80 ml). To this ice-cooled straw-coloured solution was added, dropwise, 4-chloroaniline (4.0112, 39.4m moles) dissolved in ether (30 ml). A precipitate formed immediately and the creamy yellow suspension was stirred for 5 minutes after the complete addition of 4-chloroaniline. The white water-soluble residue was removed by filtration and washed with ether. The filtrate was reduced to zero volume producing a yellow powder. Recrystallisation from benzene produced yellow masses of 2-nitrobenzenesulphen 4-chloroanilide (3.7949g, 83% M.p, 142-144°C, lit[215] 143.5-144°C Found:M(mass spectrum ^{35}Cl) 280 $C_{12}H_9ClN_2O_2S$ requires M 280)

2-Nitrobenzenesulphen p-toluidide, $2\text{-}NO_2C_6H_4SNHC_6H_4\text{-}4Me$

2-Nitrobenzenesulphenyl bromide (3.6408g, 15.5m moles) was dissolved in dry ether (80 ml). To this ice-cooled, straw-coloured solution was added, dropwise, a solution of p-toluidine (3.3043g, 30.9m moles). The precipitate which formed immediately was filtered and washed with ether. removal of ether from the filtrate produced a yellow powder. Recrystallisation from benzene produced yellow and maroon crystalline clusters whose IR spectra were identical and correspond to 2-nitrobenzenesulphen p-toluidide (3.7140g, 91% M.p 137-139°C, lit[215] 136-136.5°C Found: M(mass spectrum) 260 $C_{13}H_{12}N_2O_2S$ requires 260)

2-Nitrobenzenesulphen m-toluidide, $2\text{-}NO_2C_6H_4SNHC_6H_4\text{-}3Me$

2-Nitrobenzenesulphenyl bromide (2.6328g, 11.2m moles) was dissolved in dry ether (75 ml) and a solution of m-toluidine (2.4788g, 23.1m moles) in ether (50 ml) added dropwise. The solution was stirred for 20 minutes after the immediate formation of a dense white precipitate. Filtration removed the white residue of m-toluidine hydrochloride and left a yellow filtrate. On removal of ether this produced a dark orange viscous liquid which solidified on addition of petroleum ether (200 ml). Recrystallisation from ethanol (100 ml) yielded brown shiny prisms of 2-nitrobenzenesulphen m-toluidide (2.8327g, 97% M.p. 108-110°, lit[215] 106.5-107°)

2-Nitrobenzenesulphen o-toluidide, $2\text{-}NO_2C_6H_4SNHC_6H_4\text{-}2Me$.

2-Nitrobenzenesulphenyl bromide (2.3480g, 11.2m moles) was dissolved in dry ether (75 ml) and a solution of o-toluidine (2.4882g, 23.2m moles) in ether (50 ml) added dropwise. An immediate precipitate formed and the solution was stirred for a further 30 minutes. The white precipitate of o-toluidinehydrochloride was filtered from the

yellow solution. The solvent was removed from the filtrate and the golden powder produced was recrystallised from ethanol (100 ml). This afforded golden crystals of 2-nitrobenzenesulphen o-toluidide (2.3005g, 80% M.p. 121.5-123.5°C, lit 115.5-116°C[215] 119.5-120°C[216])

2-Nitrobenzenesulphen 3,5-dibromoanilide, $2\text{-}NO_2C_6H_4SNHC_6H_3\text{-}3,5\text{-}Br_2$

To an ice-cooled solution of 2-nitrobenzenesulphenyl bromide (3.0211g, 12.9m moles) in ether was added, dropwise, a solution of 3,5-dibromoaniline (6.5025g, 26.3m moles) in ether. The dense precipitate which formed immediately was filtered. The solvent was removed from the filtrate and the yellow powder produced was recrystallised from ethanol giving pale yellow clusters of 2-nitrobenzenesulphen 3,5-dibromoanilide (2.9240g, 61% M.p 198-202°C. Found: M(mass spectrum ^{79}Br) 402 $C_{12}H_8Br_2N_2O_2S$ requires 402)

2,4-Nitrochlorobenzenesulphen p-toluidide, $2\text{-}NO_2 4\text{-}ClC_6H_3SNHC_6H_4\text{-}4Me$.

To an ice-cooled solution of 2,4-nitrochlorobenzenesulphenyl chloride (3.1906g, 14.2m moles) in ether (100 ml) was added dropwise a solution of p-toluidine (2.7328g, 25.2m moles) in ether (100 ml). A dense white precipitate formed immediately and after complete addition the suspension was stirred for a further 30 minutes. Filtration removed the white residue of p-toluidinehydrochloride. The ether was removed from the yellow filtrate. Recrystallisation of the residual dark red material from ethanol yielded maroon crystals of 2,4-nitrochlorobenzenesulphen-p-toluidide (4.0063g, 96% M.p.140-142°C lit.[156] 137°C Found: M(mass spectrum ^{35}Cl) 294 $C_{13}H_{11}ClN_2O_2S$ requires 294).

2,4-Nitrochlorobenzenesulphen m-toluidide, $2\text{-}NO_2,4\text{-}ClC_6H_3SNHC_6H_4\text{-}3Me$.

To an ice-cooled solution of 2,4-nitrochlorosulphenyl chloride (2.9613g, 13.1m moles) in anhydrous ether (200 ml) was added a solution

of m-toluidine (2.9304g, 27.4m moles) in ether (50 ml). During the dropwise addition the solution was cooled by an ice bath and was stirred vigorously. A dense precipitate formed immediately and after 30 minutes was removed by filtration. The solvent was removed from the yellow filtrate leaving a red oil which solidified on standing for 96 hours. This solid was dissolved in hot ethanol and the volume reduced to 20 ml. Addition of petroleum ether (B.p.40-60°) (10 ml) yielded dark orange crystals of 2, 4-nitrochlorobenzenesulphen m-toluidide (3.4489g, 89% M.p 109-111°C)

2,4-Nitrochlorobenzenesulphen o-toluidide, $2\text{-}NO_2 4\text{-}ClC_6H_3SNHC_6H_4\text{-}2Me$.

To an ice-cooled solution of 2,4-nitrochlorobenzenesulphenyl chloride (2.9241g, 13.0m moles) in ether (200 ml) was added, dropwise, a solution of o-toluidine (2.8714g, 26.8m moles) in ether (50 ml). A dense precipitate formed immediately and after 30 minutes stirring the suspension was filtered. The solvent was removed from this filtrate leaving an orange powder. Recrystallisation of this material from hot ethanol yielded orange crystals of 2,4-nitrochlorobenzenesulphen-o-toluidide (3.2949g 85% M.p. 126-128°C, lit 127°C[217] 123°C[156]
Found: M(mass spectrum ^{35}Cl) 294 $C_{13}H_{11}ClN_2O_2S$ requires 294)

2,4-Nitrochlorobenzenesulphen 3',5'-dibromoanilide, $2\text{-}NO_2,4\text{-}ClC_6H_5SNHC_6H_3\text{-}3',5'Br_2$.

2,4-Nitrochlorobenzenesulphenyl chloride (3.3329g, 14.8m moles) was dissolved in dry ether. Dropwise addition of a solution of 3,5-dibromoaniline (7.4395g, 30.0m moles) in ether produced an immediate precipitate. Filtration removed the white precipitate and removal of the solvent from the filtrate gave a yellow material. Recrystallisation from ethanol produced a brown solution which on addition of petroleum ether gave yellow needles of 2,4-nitrochlorobenzenesulphen-3',5'-dibromoanilide (5.3480g, 90% M.p 144-147°C)

Preparation of the 2-(arylazo)arylsulphinate derivatives

Sodium 2-(phenylazo)phenylsulphinate, $(C_6H_5N_2C_6H_4)SO_2Na$.[151]

Sodium hydroxide (0.8888g, 22.2m moles) was dissolved in water (5.5ml) and added to a solution of 2-nitrobenzensulphenanilide (5.4416g 22.1m moles) in ethanol (25ml). The solution was refluxed for 6¼ hours, the colour darkening markedly. The solution was then cooled to room temperature and water (25ml) added. After 2 hours at 0°C, 3.2927g of orange crystalline material was obtained. Reduction in volume of the mother liquors produced a further batch of glistening orange crystals of sodium 2-(phenylazo)phenylsulphinate which were washed with ether and dried under vacuo (4.6411g 78% M.p > 300°C)

Sodium 2-(4'-methoxyphenylazo)phenylsulphinate, $(4'\text{-}MeOC_6H_4N_2C_6H_4)SO_2Na$[151]

A solution of 2-nitrobenzenesulphen p-anisidide (1.6404g, 5.9m moles) in ethanol (25ml) was added to a solution of sodium hydroxide (0.8462g, 21.1m moles) in water (5ml). The solution was refluxed for 7 hours, the solution developing a dark brown colour almost immediately. The solution was cooled to room temperature and diluted to twice its volume with water. Cooling to 0°C for 16 hours produced a mass of shiny, orange crystals. Reduction in volume of the mother liquors and cooling produced more light orange crystals of sodium 2-(4'-methodyphenylazo) phenylsulphinate (1.3883g, 79%)

Sodium 2-(4'-chlorophenylazo)phenylsulphinate, $(4'\text{-}ClC_6H_4N_2C_6H_4)SO_2Na$

A solution of 2-nitrobenzensulphen p-chloroanidide (2.5267g, 9.0 m moles) in ethanol (40ml) was added to a solution of sodium hydroxide (1.2050g, 30.1m moles) in water (7.5ml). The solution was brought to reflux and immediately darkened in colour. After 6 hours reflux the solution was cooled to room temperature, diluted to twice its volume with

water and cooled to 0°C. After 2 days a mass of orange crystals had formed. Reduction in volume of the mother liquors and cooling to 0°C produced more fine orange crystals of 2-(4'-chlorophenylazo)phenylsulphinate (2.6961g, 99%)

Sodium 2-(4'-methylphenylazo)phenylsulphinate, (4'-$MeC_6H_4N_2C_6H_4$)SO_2Na

2-Nitrobenzenesulphen p-toluidide (1.5001g, 5.8m moles) was added to a solution of sodium hydroxide in ethanol (25 ml) and water (5ml). The solution was refluxed for $5\frac{1}{2}$ hours with almost immediate darkening of colour. The solution was cooled to room temperature, diluted to twice its volume with water, and kept at 0°C for 2 days. Orange crystals had formed as well as some unidentified white, water soluble material (0.0937g, no melting < 300°C). Concentration and cooling of the mother liquors produced more orange crystals of sodium 2-(4'-methylphenylazo)-phenylsulphinate (1.5054g, 91%)

Sodium 2-(3'-methylphenylazo)phenylsulphinate, (3'-$MeC_6H_4N_2C_6H_4$)SO_2Na.

A solution of sodium hydroxide (1.1591g, 28.9m moles) in water (7.5ml) was added to a solution of 2-nitrobenzenesulphen m-toluidide (2.3298g, 8.9m moles) in ethanol (25ml). The solution was refluxed for 6 hours. To the resultant dark brown solution at room temperature was added an equal volume of water. Cooling to 0°C yielded shiny orange crystals. Concentration and cooling of the mother liquors produced more light orange 2-(3'-methylphenylazo)phenylsulphinate (2.1752g, 87%)

Sodium 2-(2'-methylphenylazo)phenylsulphinate, (2'-$MeC_6H_4N_2C_6H_4$)SO_2Na

A solution of sodium hydroxide (1.1591g, 28.9m moles) in water (7.5ml) was added to a solution of 2-nitrobenzenesulphen o-toluidide (2.2451g, 8.6m moles) in ethanol (25ml). This solution was refluxed for $5\frac{3}{4}$ hours. The resultant dark brown solution was cooled to room

temperature, an equal volume of water added, and set aside at 0°C. Glistening orange crystals were produced. Concentration and cooling of the mother liquors produced more orange crystals of 2-(2'-methylphenylazo)-phenylsulphinate (1.9110g, 79%)

Sodium 2-(3',5'-dibromophenylazo)phenylsulphinate, (3',5'-$Br_2C_6H_3N_2C_6H_4$)-SO_2Na

A solution of sodium hydroxide (1.1591g, 28.9m moles) in water (7.5ml) was added to a suspension of 2-nitrobenzenesulphen 3',5'-dibromo-anilide (2.9240g, 7.2m moles) in ethanol (80ml). The solution was refluxed producing a colour change to dark brown. After 6 hours the solution was cooled and an equal volume of water added. There was an immediate precipitate. The solution was set aside at 0°C for 7 days and filtered giving a dark yellow material, probably starting material and unidentified white feathery crystals.

The filtrate was reduced in volume and cooled to 0°C for 12 hours producing orange powdery 2-(3',5'-dibromophenylazo)phenylsulphinate (2.0373g, 66%)

Sodium 2-(4'-methylphenylazo) 4-chlorophenylsulphinate,

(4'-$MeC_6H_4N_2C_6H_3$-4Cl)SO_2Na

A solution of 2,4-nitrochlorobenzenesulphen p-toluidide (2.8239g 9.6m moles) in ethanol (25 ml) was added to a solution of sodium hydroxide (1.0687g, 26.7m moles) in water (7.5ml). The solution was refluxed for 6 hours. Initially the colour changed to violet but after a few minutes became dark orange. The solution was cooled to room temperature, an equal volume of water added and set aside at 0°C. Orange flakey crystals were produced. Concentration of the mother liquors gave more sodium 2-(4'-methylphenylazo)4-chlorophenylsulphinate,

(2.9133g, 96%)

Sodium 2-(3'-methylphenylazo)4-chlorophenylsulphinate,

(3'-$MeC_6H_4N_2C_6H_3$-4Cl)SO_2Na

A solution of sodium hydroxide (1.1591g, 28.9m moles) in water (7.5ml) was added to a solution of 2,4-nitrochlorobenzenesulphen-m-toluidide (2.6423g, 9.0m moles) in ethanol (25ml). The solution was refluxed for 4-5 hours. The colour of the solution changed initially to deep violet but after 10 minutes became dark orange. The solution was cooled, an equal volume of water added, and set aside at 0°C. After 16 hours orange flakey crystals had formed. Concentration of the mother liquors produced more sodium 2-(3'-methylphenylazo)4-chlorophenylsulphinate (2.5600g, 90%)

Sodium 2-(2'-methylphenylazo)4-chlorophenylsulphinate,

(2'$MeC_6H_4N_2C_6H_3$-4Cl)SO_2Na

A solution of 2,4-nitrochlorobenzenesulphen o-toluidide (2.7920g, 9.5m moles) in ethanol (25ml) was added to a solution of sodium hydroxide (1.0687g, 26.7m moles) in water (7.5ml). The solution was refluxed for $5\frac{1}{2}$ hours. Initially the colour became deep violet but after a few minutes developed a dark orange colour. Cooling to room temperature, addition of an equal volume of water, and cooling to 0°C produced, after 16 hours, glistening orange crystals. Concentration of the mother liquors produced more sodium 2-(2'-methylphenylazo)4-chlorophenylsulphinate (2.9673g, 99%)

Sodium 2-(3',5'-dibromophenylazo)4-chlorophenylsulphinate,

(3',5'-$Br_2C_6H_3N_2C_6H_3$-4Cl)SO_2Na

2,4-nitrochlorobenzenesulphen 3',5'-dibromoanilide (3.76g, 9.3

m moles) was added to a solution of sodium hydroxide (1.4258g, 37.4 m moles) in water (10ml) and ethanol (30ml). The brown solution was refluxed for 6 hours, cooled and an equal volume of water added. Cooling at $0^{o}C$ produced after 16 hours a mass of flesh-coloured crystals. Concentration of the mother liquors gave more crystals of sodium 2-(3',5'-dibromophenylazo)4-chlorophenylsulphinate (3.0681g,77%)

Preparation of (2-(arylazo)aryl)mercury derivatives.

(2-(phenylazo)phenyl)mercuric chloride, $(C_6H_5N{:}NC_6H_4)HgCl$

A solution of sodium 2-(phenylazo)phenylsulphinate (2.3926g, 8.9m moles) in ethanol (25ml) was added to a solution of mercuric chloride (2.6496g, 9.8m moles) in hot ethanol (100ml). An immediate fluffy precipitate was produced and the solution was refluxed for 30 minutes. The evolution of sulphur dioxide was indicated by a pungent smell at the neck of the flask. Cooling, concentration and filtration of the solution yielded feathery orange crystals. Addition of mercuric chloride (0.4466g, 1.6m moles) to the ethanol filtrate gave no further precipitate. Recrystallisation of the product from hot benzene produced orange needles of (2-(phenylazo)phenyl)mercuric chloride (2.5g 70% M.p. 200-202^{o}C, lit 151-154^{o}C,[138] 202-204^{o}C[167] Found:C,34.62; H,2.42; N,6.75% $C_{12}H_9N_2HgCl$ requires C,34.54; H,2.17; N,6.71%)

(2-(phenylazo)phenyl)mercuric bromide, $(C_6H_6N{:}NC_6H_4)HgBr$

A solution of sodium 2-(phenylazo)phenylsulphinate (3.3755g, 12.6m moles) in ethanol (50ml) was added to a solution of mercuric bromide (4.5735, 12.7m moles) in hot ethanol (200ml). A feathery precipitate formed immediately and remained while the solution was refluxed for $2\frac{1}{2}$ hours. Concentration to 25ml and cooling produced orange

feathery crystals. Recrystallisation from hot benzene afforded orange-red needles of (2-(phenylazo)phenyl)mercuric bromide (4.2434g, 72% M.p. 178-180°C Found: C,31.54; H,2.07, N5.97% $C_{12}H_9N_2HgBr$ requires C,31.22; H,1.96; N,6.07%)

(2-(phenylazo)phenyl)mercuric iodide, $(C_6H_5N{:}NC_6H_4)HgI$

A solution of sodium 2-(phenylazo)phenylsulphinate (4.0300g, 15.0m moles) in ethanol (50ml) was added to a solution of mercuric iodide (6.8118g, 15.0m moles) in hot ethanol (250ml). The clear orange solution was refluxed for 3 hours. Cooling the solution to room temperature produced a mass of feathery orange crystals. Concentration and cooling to 0°C produced more of the same material. Recrystallisation from benzene yielded red-orange needles of (2-(phenylazo)phenyl)mercuric iodide (6.7019g, 87%. M.p.148.5-150.5°C. Found: C,28.26; H,1.58; N,5.37% $C_{12}H_9N_2HgI$ requires C,28.33; H,1.78; N,5.50%)

(2-(4'-methoxyphenylazo)phenyl)mercuric chloride, $(4'\text{-}MeOC_6H_4N{:}NC_6H_4)HgCl$

A solution of sodium 2-(4'methoxyphenylazo)phenylsulphinate (1.1497g, 3.9m moles) was added to a refluxing solution of mercuric chloride (1.1372g 4.2m moles). A precipitate formed immediately and reflux was continued for 2 hours. Cooling and concentration of the solution produced feathery orange crystals. Recrystallisation from benzene yielded orange needles of (2-(4'-methoxyphenylazo)phenyl)mercuric chloride (1.2815g, 74% M.p. 205-207°C Found: C,35.21; H,2.45; H,6.48% $C_{13}H_{11}N_2OHgCl$ requires C,34.91; H,2.48; N,6.26%)

(2-(4'-chlorophenylazo)phenyl)mercuric chloride, $(4'\text{-}ClC_6H_4N{:}NC_6H_4)HgCl$.

Sodium 2-(4'-chlorophenylazo)phenylsulphinate (2.3085g, 7.6m moles) was added to a solution of mercuric chloride (2.0613g, 7.6m moles) in hot

ethanol (200ml). An immediate, dense, flocculent precipitate formed. The solution was refluxed for 1½ hours. Cooling to 0°C and filtration afforded orange feathery crystals which were recrystallised from hot benzene giving beautiful orange needles of (2-(4'-chlorophenylazo)phenyl)-mercuric chloride (3.0005g, 89% M.p. 194-196°C Found: C,31.81; H,1.92; N,6.41% $C_{12}H_8N_2HgCl_2$ requires C,31.91; H,1.79; N,6.20%)

(2-(4'-methylphenylazo)phenyl)mercuric chloride, $(4'\text{-}MeC_6H_4N{:}NC_6H_4)HgCl$

Sodium 2-(4'-methylphenylazo)phenylsulphinate (1.3481g, 4.78m moles) was added to a refluxing solution of mercuric chloride (1.3693g, 5.16m moles) in ethanol (300ml). A fluffy precipitate appeared immediately and remained throughout the 1½ hour reflux. Concentration of the solution and filtration produced orange material which on recrystallisation from benzene gave orange needles of (2-(4'-methylphenylazo)phenyl)mercuric chloride (1.7897gm 87% M.p. 200-202°C Found: C,36.42; H,2.50; N,6.44% $C_{13}H_{11}N_2HgCl$ requires C,36.21; H,2.57; N,6.50%)

(2-(3'-methylphenylazo)phenyl)mercuric chloride, $(3'\text{-}MeC_6H_4N{:}NC_6H_4)HgCl$

A solution of sodium 2-(3'-methylphenylazo)phenylsulphinate (1.7074g, 6.1m moles) in ethanol (50ml) was added to a refluxing solution of mercuric chloride (1.7492g, 6.5m moles) in ethanol (200ml). After 1½ hours reflux a small amount of grey solid material was present. Concentration and cooling of the solution produced orange crystals which were recrystallised from T.H.F., in which mercurous chloride is insoluble. This gave orange crystalline clusters of (2-(3'-methylphenylazo)phenyl)-mercuric chloride (1.9348g, 67% M.p. 188-190°C Found: C,36.22; H,2.66; N,6.31% $C_{13}H_{11}N_2HgCl$ requires C,36.21; H,2.57; N,6.50%)

(2-(2'-methylphenylazo)phenyl)mercuric chloride, $(2'\text{-}MeC_6H_4N{:}NC_6H_4)HgCl$

A solution of sodium 2-(2'-methylphenylazo)phenylsulphinate

(1.6594g, 5.9m moles) in ethanol (75ml) was added to a refluxing solution of mercuric chloride (1.6480g, 6.1m moles) in ethanol (200ml). After 2 hours reflux the orange solution contained a small amount of grey material. Concentration and cooling of the solution produced a feathery orange product which was isolated by filtration. Recrystallisation from T.H.F. yielded orange crystals of (2-(2'-methylphenylazo)phenyl)-mercuric chloride (2.0116g, 79% M.p 189-191°C Found: C,36.45; H,2.64; N,6.41% $C_{13}H_{11}N_2HgCl$ requires C,36.21; H,2.57; N,6.50%)

(2-(3',5'-dibromophenylazo)phenyl)mercuric chloride, $(3',5'\text{-}Br_2C_6H_3N{:}NC_6H_4)HgCl$.

A solution of sodium 2-(3',5'-dibromophenylazo)phenylsulphinate (2.0372g, 4.7m moles) and mercuric chloride (1.3100g, 4.7m moles) in ethanol (250ml) was refluxed for 1½ hours. A flocculent precipitate formed almost immediately. Concentration and cooling of the solution produced orange feathery material which was recrystallised from T.H.F. giving orange crystals of (2-(3',5'-dibromophenylazo)phenyl)mercuric chloride (1.65g, 61% M.p. 252-257°C Found: C,25.21; H,1.33; N,5.14% $C_{12}H_9N_2HgBr_2Cl$ requires C,25.06; H,1.23; N,4.87%)

(2-(4'-methylphenylazo)-4-chlorophenyl)mercuric chloride

A solution of sodium 2-(4'-methylphenylazo)-4-chlorophenylsulphinate (2.4353g, 7.8m moles) in hot ethanol (100ml) was added to a refluxing solution of mercuric chloride in ethanol (200ml). After 1½ hours reflux the solution contained a dense feathery precipitate. Concentration and filtration of this solution produced a mass of orange feathery material. Recrystallisation from T.H.F. removed insoluble grey mercurous chloride (0.2730g, 1.0m moles , characterised by spot tests) and produced deep orange needles of (2-(4'-methylphenylazo)-4-chlorophenyl)mercuric chloride.

An analytically pure sample was obtained by recrystallisation from carbon tetrachloride (2.8092g, 77% M.p 215-217°C Found: C,33.44; H,2.26; N,5.97% $C_{13}H_{10}N_2HgCl_2$ requires C,33.53; H,2.16; N,6.01%)

(2-(3'-methylphenylazo)-4-chlorophenyl)mercuric chloride,

(3'-$MeC_6H_4N{:}NC_6H_3$4Cl)HgCl

A solution of sodium 2-(3'-methylphenylazo)-4-chlorophenylsulphinate (2.3663g, 7.6m moles) in hot ethanol (100ml) was added to a refluxing solution of mercuric chloride (2.1080g, 7.8m moles) in ethanol (200ml). After 1½ hours reflux a dense flocculent precipitate was present. Concentration and filtration of the solution produced orange feathery crystals. Recrystallisation from T.H.F. removed grey mercurous chloride (0.429g, 019m moles), identified by spot tests, which was insoluble, and produced deep orange crystals of (2-(3'-methylphenylazo)-4-chlorophenyl)-mercuric chloride (2.9743g, 83% M.p. 224-246°C Found: C,33.54; H,2.28; N,6.03% $C_{13}H_{10}N_2HgCl_2$ requires C,33.53; H,2.16; N,6.01%)

(2-(2'-methylphenylazo)-4-chlorophenyl)mercuric chloride,

(2'-$MeC_6H_4N{:}NC_6H_3$-4Cl)HgCl

A solution of sodium 2-(2'-methylphenylazo)-4-chlorophenylsulphinate (2.5228g, 8.1m moles) in hot ethanol (100ml) was added to a refluxing solution of mercuric chloride (2.2489g, 8.3m moles) in ethanol (200ml). After 1½ hours reflux, the deep orange solution contained a flocculent precipitate. Concentration and filtration of the solution produced an orange feathery material. Recrystallisation from T.H.F. allowed separation of grey powdery mercurous chloride (0.4120g, 0.9m moles, identified by spot tests) and produced orange needles of (2-(2'-methyl-phenylazo)-4-chlorophenyl)mercuric chloride (2.2582g, 61% M.p. 209-214°C Found: C,33.44; H,2.26; N,5.97% $C_{13}H_{11}N_2HgCl_2$ requires C,33.53; H,2.16; N,6.01%)

(2-(3',5'-dibromophenylazo)-4-chlorophenyl)mercuric chloride, $(3',5'\text{-}Br_2C_6H_3N{:}NC_6H_3\text{-}4Cl)HgCl$.

To a solution of mercuric chloride (1.7237g, 6.3m moles) in hot ethanol (100ml) was added a solution of sodium 2-(3',5'-dibromophenylazo)--4-chlorophenylsulphinate (2.8157g, 6.1m moles) in hot ethanol (200ml). The orange solution was refluxed for 2 hours. Removal of solvent and extraction with T.H.F. gave insoluble mercurous chloride (0.0675g, 0.45m moles, identified by spot tests). Removal of solvent from the T.H.F. extract and recrystallisation from carbon tetrachloride gave fine orange needles of (2-(3'5'-dibromophenylazo)-4-chlorophenyl)mercuric chloride (2.1955g, 59% M.p. 273-280°C. Found: C,23.59; H,1.05, N,4.39% $C_{12}H_6N_2HgBr_2Cl_2$ requires C,23.65; H,0.99; N,4.59%)

Bis(2-(phenylazo)phenyl)mercury, $(C_6H_5N{:}NC_6H_4)_2Hg$.

(a) To a suspension of (2-(phenylazo)phenyl)mercuric chloride (4.3391g, 10.4m moles) in hot acetone (150ml) was added a solution of triphenylphosphine (2.73g, 10.4m moles) in acetone (20ml). A clear orange solution resulted. Removal of solvent and ether extraction of the residue left white crystals of bis(triphenylphosphine)mercury(II) chloride (3.9887g, 96%) whose IR spectrum and M.p. (267-270°C) were identical with an authentic sample[170]. Concentration of the ether extracts and cooling to 0°C produced orange crystals which were recrystallised from ethanol giving orange prisms of bis(2-(phenylazo)phenyl)-mercury (2.6460g, 90% M.p. 144-146°C Found: C,51.35; H,3.37; N,10.22% $C_{24}H_{18}N_4Hg$ requires C,51.20; H,3.22, N,9.95%)

(b) A 15cm x 2cm chromatography column was packed with Amberlyst A26 resin in water, then converted to its iodide form by eluting with a solution of potassium iodide (6.5600g, 39.5m moles) in water (100ml) Excess potassium halide was removed by water washing (800ml). At this

stage 4 drops from the column gave no precipitate with silver nitrate solution. The column solvent was replaced by methanol (200ml) followed by benzene (200ml). A solution of (2-(phenylazo)phenyl)mercuric chloride (0.7906g, 1.9m moles) in benzene (7.5ml) was applied to the column and eluted with benzene (200ml) followed by ethanol (100ml) until the eluant was colourless. Evaporation of the combined eluants produced bis(2-(phenylazo)phenyl)mercury (0.52g, 96%)

Preparation of (2-(arylazo)aryl) complexes of palladium.

Di- μ -chloro-di(2-(phenylazo)phenyl)dipalladium (II), $(C_6H_5N_2C_6H_4PdCl)_2$

(a) From azobenzene and $PdCl_2$. A suspension of palladous chloride (1.6374g, 9.3m moles) in a methanol solution (75ml) of azobenzene (2.6085g, 14.4m moles) was stirred for 48 hours. The orange precipitate produced was filtered and washed with benzene. Recrystallisation from hot benzene produced, on concentration of the solution, bright yellow crystals identified, by comparison with an authentic sample, as trans dichlorobis(azobenzene)palladium(II) (0.0721g, 0.1m moles, 1%). On standing, maroon crystals of di- μ - chloro-di(2-(phenylazo)phenyl)di-palladium(II) were produced (2.5162g, 85% M.p.272-275°C(dec), lit [99] 279-281°C (dec) Found: C,44.97; H,2.91; N,8.42% $C_{24}H_{18}N_4Pd_2Cl_4$ requires C,44.61; H,2.81; N,8.67%)

(b) From azobenzene and K_2PdCl_4. Potassium chloropalladite (1.8693g, 5.9m moles) was dissolved in warm water (50ml). Azobenzene (1.0306g, 5.7m moles) dissolved in methanol (120ml) was added. The solution was set aside for 18 days. Filtration of the orange product, washing with ethanol and recrystallisation from hot benzene gave maroon

crystals of di-μ-chloro-di(2-(phenylazo)phenyl)dipalladium(II) (1.63g, 85%)

(c) From (2-(phenylazophenyl)mercuric chloride and $PdCl_2$.

A suspension of palladous chloride (0.1868g, 1.1m moles) and (2-(phenylazo)phenyl) mercuric chloride (0.5093g, 1.2m moles) in methanol (100ml) was stirred at room temperature for 14 hours. The resultant orange precipitate was removed by filtration and washed with methanol. Evaporation of the methanol filtrate and extraction with water gave mercuric chloride (0.0402g, 0.2m moles). Recrystallisation of the orange residue from benzene gave maroon crystals of di-μ-chloro-di(2-(phenylazo)phenyl)dipalladium(II) (0.2821g 83%).

Di-μ- chloro-di(2-(4'-methylphenylazo)-4-chlorophenyl)dipalladium (II), $((4'\text{-}MeC_6H_4N_2C_6H_3\text{-}4Cl)PdCl)_2$.

Palladium chloride (0.3753g, 2.1m moles) and (2-(4'-methylphenylazo)-4-chlorophenyl) mercuric chloride were added to methanol (75ml). This suspension was stirred for 63 hours at room temperature. The dense maroon precipitate which had formed was filtered and washed with methanol (250ml). The solvent was removed from the filtrate. Extraction with water (75ml) and evaporation to dryness yielded mercuric chloride (M.p 278-282°C, lit[313] 276-280°C) identified by spot tests. The maroon residue was recrystallised from benzene producing deep red crystalline clusters of di-μ-chloro-di(2-(4'-methylphenylazo)-4-chlorophenyl)-dipalladium(II) (0.7535g, 96% M.p 285-295°C(dec) Found: C,42.01; H,2.99; N,7.77% $C_{26}H_{20}N_4Pd_2Cl_4$ requires C,42.03; H,2.71; N,7.54%)

Di-μ-chloro-di(2-(3'-methylphenylazo)-4-chlorophenyl)dipalladium(II), $((3'\text{-}MeC_6H_4N_2C_6H_4\text{-}4Cl)PdCl)_2$.

A suspension of palladium chloride (0.3530g, 2.0m moles) and

(2-(3'-methylphenylazo)-4-chlorophenyl) mercuric chloride (0.9548g, 2.0m moles) in methanol (75ml) was stirred at room temperature for 63 hours. The dense maroon precipitate which had formed was filtered and washed with methanol (200ml). The solvent was removed from the filtrate and the residue extracted with hot water (50ml). Removal of solvent from this extract yielded mercuric chloride (0.4405g, 1.6m moles, 80% M.p. 276-278°C lit[313] 276-286°C) identified by spot tests. Recrystallisation of the maroon residue from benzene produced deep maroon crystals of di-μ-chloro-di(2-(3'-methylphenylazo)-4-chlorophenyl)-dipalladium(II) (0.7246g, 97% M.p. 285-300°C(dec). Found: C,41.93; H,2.79; N,7.63% $C_{26}H_{20}N_4Pd_2Cl_4$ requires C,42.03; H,2.71; N,7.54%)

Di-μ-chloro-di(2-(2'-methylphenylazo)-4-chlorophenyl)dipalladium(II), $((2'\text{-}MeC_6H_4N_2C_6H_4\text{-}4Cl)PdCl)_2$.

A suspension of palladium chloride (0.3338g, 1.9m moles) and (2-(2'-methylphenylazo)-4-chlorophenyl) mercuric chloride (0.9457g, 2.0m moles) was stirred for 109 hours. The light orange coloured precipitate was filtered. The brown filtrate, on standing, afforded more light orange precipitate. Recrystallisation of both batches of this material from hot benzene produced orange microcrystalline clusters of di-μ-chloro-di(2-(2'-methylphenylazo)-4-chlorophenyl)dipalladium(II) (0.5494g, 81% M.p 262-267°C(dec) Found: C,42.03; H,2.80; N,7.29% $C_{26}H_{20}N_4Pd_2Cl_4$ requires C,42.03; H,2.71; N,7.54%)

Di-μ-chloro-di(2-(3',5'-dibromophenylazo)-4-chlorophenyl)dipalladium(II), $((3',5'\text{-}Br_2C_6H_3N_2C_6H_4\text{-}4\text{-}Cl)PdCl)_2$.

A suspension of palladium chloride (0.2230g, 1.3m moles) and (2-(3',5'-dibromophenylazo)-4-chlorophenyl) mercuric chloride in methanol (75ml) was stirred for 61 hours at room temperature. The deep maroon

precipitate produced was filtered and washed with methanol (200ml). The solvent was removed from this filtrate and the residue extracted with water (50ml). Removal of the water from this extract gave mercuric chloride (0.2620g, 9.7m moles, 77% M.p. 276-278°C, lit[313] 276-280°C) identified by spot tests. Washing of the very insoluble maroon product with hot benzene gave analytically pure samples of di-μ-chloro-di-(2-(3',5'-dibromophenylazo)-4-chlorophenyl)dipalladium(II) (0.6034g, 93% M.p. 310-320°C(dec). Found: C,27.86; H,1.34; N,5.10% $C_{24}H_{12}N_4Pd_2Br_4Cl_4$ requires C,27.97; H,1.17; N,5.44%).

Preparation trans-chloro(2-(arylazo)aryl)bis(triethylphosphine)-palladium(II) complexes.

trans-Chloro(2-(phenylazo)phenyl)bis(triethylphosphine)palladium(II).

(a) Bis(2-(phenylazo)phenyl) mercury (0.1509g, 0.27m moles) was added to a solution of dichlorobis(triethylphosphine)palladium(II) (0.1160g, 0.27m moles) in ethanol (30ml). Stirring this suspension for 18 hours produced no reaction. Refluxing for 24 hours, reduction of the volume of ethanol to 5ml, and cooling to 0°C produced (2-(phenylazo)-phenyl) mercuric chloride (0.0710g, 0.17m moles) identified by comparison with an authentic sample. Removal of ethanol from the filtrate and recrystallisation from hexane gave orange plates of trans-chloro-(2-(phenylazo)phenyl)bis(triethylphosphine)palladium(II) (0.1287g, 85% M.p. 116-118°C)

(b) Triethylphosphine (0.5ml) was added by syringe to a suspension of di-μ-chloro(2-(phenylazo)phenyl)dipalladium(II) (0.5423g, 0.87m moles) in benzene (50ml) under a flow of nitrogen. Heating to 60°C gave a clear orange solution. Removal of solvent and recrystallisation

of the product from hexane gave on complete, slow evaporation of solvent, orange prisms of trans-chloro(2-(phenylazo)phenyl)bis(triethylphosphine)-palladium(II) (0.7515g, 78% M.p 116-118°C Found: C,52.07; H,6.92; N,5.44; Cl,5.79% $C_{24}H_{39}N_2P_2PdCl$ requires C,51.54; H,7.03; N,5.01; Cl,5.92%).

Similarly prepared were,

trans-Chloro(2-(4'-methylphenylazo)-4-chlorophenyl)bis(triethylphosphine)-palladium(II) (56% M.p. 154-156°C Found: C,49.53; H,6.90; N,4.89% $C_{25}H_{40}N_2P_2PdCl_2$ requires C,49.40; H,6.63; N,4.61%)

trans-Chloro(2-(3'-methylphenylazo)-4-chlorophenyl)bis(triethylphosphine)-palladium(II) (74% M.p. 165-167°C Found: C,49.30; H,6.76; N,4.49% $C_{25}H_{40}N_2P_2PdCl_2$ requires C,49.40; H,6.63; N,4.61%)

trans-Chloro(2-(2'-methylphenylazo)-4-chlorophenyl)bis(triethylphosphine)-palladium(II) (85% M.p. 130-132°C Found: C,49.49; H,6.87; N,4.53% $C_{25}H_{40}N_2P_2PdCl_2$ requires C,49.40; H,6.63; N,4.61%)

Preparation of (2-(arylazo(aryl) complexes of platinum

Di-μ-chloro-di(2-(phenylazo)phenyl)diplatinum(II), $(C_6H_5N_2C_6H_4PdCl)_2$

(a) From azobenzene and K_2PtCl_4. To a solution of potassium chloroplatinite (3,0036g, 7.2m moles) in water (50ml) was added a solution of azobenzene (1.3956g, 7.7m moles) in methanol (200ml). The solution was set aside and after 2 days was deep cherry coloured. After 6 days a dark precipitate was present. Removal of solvent and extraction with hot benzene produced some insoluble maroon material and a dark red solution which gave, on cooling, shiny purple crystals of di-μ-chloro-di-

(2-(phenylazo)phenyl)diplatinum(II) (0.5167g, 17% M.p. 258-265°C(dec), lit[99] ~ 270°C(dec) Found: C,35.62; H,2.33, N,7.10% $C_{24}H_{18}N_4Pt_2Cl_2$ requires C,35.00; H,2.20; N,6.80%)

(b) From azobenzene and $PtCl_2$. A suspension of platinous chloride (0.8075g, 3.0m moles) in a methanol solution (100ml) of azobenzene (0.8879g, 4.9m moles) was stirred for 6 weeks. The colour gradually darkened to dark maroon and filtration removed unreacted $PtCl_2$ (0.7063g, 2.6m moles). The solvent was removed from the filtrate leaving a viscous black liquid. (The presence of hydrogen chloride was deduced from its pungent smell and white fumes produced with ammonia). Extraction of the viscous liquid with hot benzene (75ml) gave a solution which yielded glistening purple crystals of di-μ-chloro-di(2-(phenylazo)-phenyl)diplatinum(II) (0.0372g, 3% M.p. and IR spectrum identical with an authentic sample).

Di-μ-bromo-di(2-(phenylazo)phenyl)diplatinum(II), $(C_6H_5N_2C_6H_4PtBr)_2$

Metathesis of di-μ- chloro-di(2-(phenylazo)phenyl)diplatinum(II) (0.2010g, 0.24m moles) with lithium bromide (0.1908g, 1.1m moles) in boiling acetone gave, on recrystallisation from benzene, purple crystals of di-μ- bromo-di(2-(phenylazo)phenyl)diplatinum(II) (0.2085g, 95% M.p. 272-282°C(dec) Found: C,31.69; H,2.12; N,6.29% $C_{24}H_{18}N_4Pt_2Cl_2$ requires C,31.59; H,1.98; N,6.14%)

Interaction of bis(2-(phenylazo)phenyl) mercury and platinous chloride.

A suspension of bis(2-(phenylazo)phenyl) mercury (0.2099g, 0.37m moles) and platinous chloride (0.0991g, 0.37m moles) was stirred at room temperature for 24 hours. No visible reaction occurred. Refluxing for 1½ hours produced a dark red solution, a black precipitate thought to be platinum metal (0.0651g, 90%) and a little metallic mercury

(0.0058g). Cooling of the solution produced (2-phenylazo)phenyl) mercuric chloride (0.019g) as feathery crystals. Column chromatography of the remaining solution gave azobenzene (0.0010g) and bis(2-(phenylazo)phenyl)-mercury (0.0569g) as the only identified products. A subsequent orange-brown fraction was not characterised.

Interaction of azobenzene and dichlorobis(benzonitrile)platinum(II) in the presence of triethylamine.

A solution of dichlorobis(benzonitrile)platinum(II) (0.5476g, 1.2m moles) azobenzene (0.8559g, 4.7m moles) and triethylamine (5ml, ~ 36m moles) was stirred at room temperature. After 47 hours the bright orange solution had developed a dark maroon colour, and a white precipitate was present. The solution was stirred for a further 16 hours by which time the precipitate was no longer present. Removal of solvent produced a dark maroon unidentified material and a small amount of azobenzene. No di-μ-chloro(2-(phenylazo)phenyl)diplatinum(II) was isolated.

Preparation of chloro(2-(phenylazo)phenyl)platinum(II) phosphine and related complexes.

Chloro(2-(phenylazo)phenyl)(diphenylmethylphosphine)platinum(II)

Diphenylmethylphosphine (0.1334g, 0.67m moles) in benzene (5ml) was added to a suspension of di-μ-chloro-di(2-(phenylazo)phenyl)-diplatinum (0.2137g, 0.26m moles) in benzene (25ml). Stirring for 5 minutes produced a cherry coloured solution. Removal of solvent by rotary evaporation and recrystallisation from ethanol produced dark purple prisms of chloro(2-(phenylazo)phenyl)(diphenylmethylphosphine)-platinum(II) (0.293g, 92% M.p. 196-198°C Found: C,49.14; H,3.77;N,4.55%

$C_{25}H_{22}N_2PPtCl$ requires C,49.06; H,3.62; N,4.57%)

Similarly prepared were,

Chloro(2-(phenylazo)phenyl)(isobutylamine)platinum(II) (80% M.p. 152-159°C (melts with decomposition) lit [99] 162-164°C)

Chloro(2-(phenylazo)phenyl)carbonyl)platinum(II) - Chapter III

trans-Chloro(2-phenylazo)phenyl)bis(triethylphosphine)platinum(II)

(a) Bis(2-(phenylazo)phenyl) mercury (0.2962g, 0.53m moles) was added to a solution of cis-dichlorobis(triethylphosphine)platinum(II) (0.2631g, 0.53m moles) in ethanol (35ml). Refluxing for 19 hours produced a small amount of metallic mercury (0.0018g 0.009m moles). Concentration and cooling of the solution produced feathery orange crystals of (2-(phenylazo)phenyl) mercuric chloride (0.1628g, 0.39m moles) and colourless crystals identified, by M.p. and IR, as cis-dichlorobis-(triethylphosphine)platinum(II) (0.0260g, 0.05m moles) both of which were removed by filtration.

Removal of ethanol from the filtrate produced a brown oil. Addition of hot petroleum ether (B.p. 40-60°C) followed by filtration, produced more cis-dichlorobis(triethylphosphine)platinum(II) and a filtrate which, on removal of solvent and subsequent sublimation, produced azobenzene (0.0015g, 0.0085m moles). The residue from the sublimation was dissolved in hexane and yielded orange plates of trans-chloro-(2-(phenylazo)phenyl)bis(triethylphosphine)platinum(II) (0.0972g, 29% M.p. 129-131°C).

(b) To a suspension of di-μ-chloro-di(2-(phenylazo)phenyl)-diplatinum(II) (0.2208g, 0.2m moles) in benzene (40ml), under nitrogen, was added triethylphosphine (0.12g, 0.4m moles) by syringe. The solution

was stirred for 10 minutes at 60°C. Removal of solvent and recrystallisation from hexane produced orange plates of trans-chloro(2-(phenylazo)phenyl)bis-(triethylphosphine)platinum(II) (0.2771g, 86% M.p. 129-131°C Found: C,44.71; H,5.88; N,4.70% $C_{24}H_{39}N_2P_2PtCl$ requires C,44.48; H,6.07; N,4.32%)

Similarly prepared were,

trans-Chloro(2-(phenylazo)phenyl)bis(diphenylmethylphosphine)platinum(II) (90% M.p. 154-156°C, ex ethanol Found: C,56.45; H,4.53; N,3.27% $C_{38}H_{35}N_2P_2PtCl$ requires C,56.20; H,4.34; N,3.45%)

trans-Chloro(2-(phenylazo)phenyl) - (dimethylphenylphosphine)platinum(II) (88% M.p. 176-178°C ex ethanol Found: C,43.95; H,3.71% $C_{20}H_{20}N_2PPtCl$ requires C,43.69; H,3.67%)

Preparation of other metal (2-(arylazo)aryl) complexes.

(h^5-cyclopentadienyl)(2-(phenylazo)phenyl)nickel(II)

To a solution of freshly sublimed nickelocene (0.1412g, 0.7m moles) in benzene (50ml) was added bis(2-(phenylazo)phenyl)mercury (0.3898g, 0.7m moles). The solution was stirred under nitrogen at room temperature for 48 hours. Removal of solvent and sublimation of the residue (0.1mm Hg, 70°C) gave recovery of nickelocene (0.1334g, 95%)

The same reagents in benzene (50ml) were refluxed under nitrogen for 18 hours. Chromatography of the resultant blue solution on neutral Alumina, eluting with benzene/hexane mixture (1/1), produced bis(2-(phenylazo)-phenyl)mercury (0.0188g, 0.02m moles) followed by a deep blue band. Recrystallisation of this material from petroleum ether (B.p. 40-60°C) gave deep blue crystals of h^5-cyclopentadienyl(2-(phenylazo)phenyl)nickel (0.2006g, 91% M.p. 118-120°C, lit[118] 118-119°C Found: M(mass spectrum ^{58}Ni) 304 $C_{17}H_{14}N_2Ni$ requires M 304)

Tetracarbonyl(2-(phenylazo)phenyl)manganese(I)

A solution of manganese pentacarbonyl chloride[218] (0.0550g, 0.24m moles) and (2-(phenylazo)phenyl)mercuric iodide (0.1249g 0.24m moles)

in benzene (50ml) was refluxed under nitrogen for 20 hours. Removal of solvent and extraction with petroleum ether (B.p. 40-60°C) produced a maroon solution. Sublimation of the product from this solution produced maroon crystals of tetracarbonyl(2-(phenylazo)phenyl)manganese(I) (0.0598g, 70% Found: M(mass spectrum) 348 $C_{16}H_9N_2O_4Mn$ requires 348)

Cleavage reactions of the (2-(arylazo)aryl) metal complexes.

Halogen Cleavage.

Preparation of 2-(phenylazo)phenyliodide

To a solution of iodine (0.5163g, 2.0m moles) in ethanol (30ml) was added (2-(phenylazo)phenyl) mercuric iodide (1.0508g, 2.1m moles) in ethanol (20ml). After 10 minutes reflux the iodine colour disappeared. Removal of solvent and extraction of the residue with benzene followed by filtration, removal of the benzene and crystallisation from ethanol, produced red crystals of 2-(phenylazo)phenyliodide (0.5332g, 87% M.p. 61.5 - 62.5°C, lit[219] 62°C Found: C,46.78; H,3.12; N,9.07%; M(mass spectrum) 308 $C_{12}H_9N_2I$ requires C,46.78; H,2.94; N,9.09%; M308)

Similarly prepared were,

2-(4'-methoxyphenylazo)phenyliodide (86% M.p. 81.5 - 83.5°C Found: C,46.24; H,3.36; N,8.35; M(mass spectrum) 338 $C_{13}H_{11}N_2OI$ requires C,46.18; H,3.28; N,8.23; M338)

2-(4'-methylphenylazo)phenyliodide (89% M.p. 78 - 80°C Found: C,48.27; H,3.52; N,8.91%; M(mass spectrum) 322 $C_{13}H_{11}N_2I$ requires C,48.45; H,3.44; N,8.70%; M322)

2-(4'-chlorophenylazo)phenyliodide (98% M.p. 100.5 - 102.5°C Found: C,41.92;

H,2.36; N,8.33%; M(mass spectrum,^{35}Cl) 342 $C_{12}H_8N_2ClI$ requires C,41.96; H,2.35; N,8.16%; M342)

2-(4'-methylphenylazo)phenylbromide (90% M.p. 58-60°C, lit [220] 60.5-61.5°C Found: C,56.86; H,4.08; N,10.34%; M(mass spectrum,^{79}Br)274 $C_{13}H_{11}N_2Br$ requires C,56.75; H,4.03; N,10.18%; M274), by bromine cleavage.

2-(4'-methylphenylazo)phenylchloride (76% M.p. 28-40°C, ex water/ethanol Found: C,67.56; H,4.76; N,12.14%; M(mass spectrum,^{35}Cl)230 $C_{13}H_{11}N_2Cl$ requires c,67.68; H,4.81; N,12.14%; M230), by chlorine cleavage.

Nitrosyl Chloride Cleavage.

Preparation of 2-phenylbenzotriazole 1-oxide.

Nitrosyl chloride gas was bubbled through a stirred suspension of (2-(phenylazo)phenyl) mercuric chloride (2.2970g, 5.5m moles) in chloroform (100ml). After ½ hour the mixture had turned to a deep orange-red liquid containing a pale precipitate of mercuric chloride. The reaction was continued for a further hour when the solution was filtered and the filtrate extracted with water (2x50ml). The water extract was pale green coloured and gave off brown, pungent fumes on shaking. The pale yellow chloroform solution was dried ($MgSO_4$) and concentrated to an orange viscous liquid. This was dissolved in the minimum amount of ether and cooled to 0°C. This procedure produced pale yellow prisms of 2-phenylbenzotriazole 1-oxide (0.89g 77% M.p. 85.5-87.5°C, lit 85°C [175], 88.5°C [221] Found: C,68.03; H,4.46; N,20.15% M(mass spectrum)211 $C_{12}H_9N_2O$ requires C,68.28; H,4.30; N,19.90%; M211)

Interaction of (2-(phenylazo)phenyl) complexes with styrene.

(a) A suspension of (2-(phenylazo)phenyl) mercuric chloride (0.7789g, 1.9m moles) and potassium chloropalladite (0.6077g, 1.9m moles) in a solution of styrene (4ml ~ 36m moles) in ethanol (75ml) was stirred for 48 hours. The fine orange precipitate present was filtered, recrystallised from hot methanol and identified as di-μ-chloro-(2-(phenylazo)phenyl)dipalladium (0.56g, 93%)

(b) Di-μ-chloro(2-(phenylazo)phenyl)dipalladium (0.4994g, 0.8m moles) in a solution of styrene (0.1695g, 1.7m moles) in methanol (50ml) was stirred for 48 hours at room temperature. Subsequent reflux for 24 hours in the dark, resulted in recovery of starting material.

(c)Di-μ-chloro(2-(phenylazo)phenyl)diplatinum (0.1317g, 0.16m moles) was added to a solution of styrene (0.0322g, 0.31m moles) in methanol (50ml). Stirring for 42 hours at room temperature followed by 5 hours reflux gave recovery only of starting material.

CHAPTER II.

PHOSPHINE EXCHANGE IN CHLORO(2-(PHENYLAZO)PHENYL)BIS(DIPHENYLMETHYLPHOSPHINE)PLATINUM(II).

CHAPTER II.

INTRODUCTION.

Numerous phosphine complexes have been reported in the literature to undergo rapid phosphine exchange in solution at room temperature. Exchange is usually detected by broadening and decoupling of ^1H NMR signals, most often of alkyl groups attached to phosphorus (e.g. ref.243), but occasionally of similar groups or hydrogen atoms bonded directly to the metal (e.g. ref.222). Whilst many complexes exhibit this behavour spontaneously (e.g. $Pt(PMePh_2)_4$[229]) some others undergo fast exchange only in the presence in solution of an excess of phosphine (e.g. $(PhMe_2P)_2PtCl_2+PhMe_2P$[255]). Information on phosphine exchange, both with and without additional free ligand is summerised in Table 9.

Fackler et.al.[252] have considered theoretically the effects of phosphine exchange on the NMR spectra of virtually coupled systems. He summarised their conclusions[249] in relation to the exchange observed by Deeming and Shaw[248] between excess dimethylphenylphosphine and trans-$RhCl(CO)(PMe_2Ph)_2$. It is found that the form of the ^1H NMR spectrum depends on three factors: the size of the coupling constants involved, the concentration of free ligand present, and the rate of exchange. The relationship between these factors and the ^1H NMR spectrum is summarised below for the equilibrium,

$$ML_2B_2 + L^* \rightleftharpoons MLL^*B_2 + L$$

where L is a methylphosphine and M is a metal to which L and ligand B are coordinated.

Methyl Pattern	Exchange Rate	Size of Coupling Constants	Concentration of Free Phosphine
(a)(i) DOUBLET	Slow	J(P-H)≈10-14Hz, J(P-P')≈0Hz (i.e. typical of a cis planar complex)	$[L] \ll [ML_2B_2]$
(ii) TRIPLET	Slow	J(P-P')≫(J(H-P)-J(H-P')) (i.e. typical of a trans planar complex)	
(b)(i) TRIPLET	Slow	J(P-P')/J(P-H)>5Hz, J(P-H)/J(P'-H)≈1 Hz. (i.e. typical of a trans planar complex)	$[L] \ll [ML_2B_2]$
(ii) SINGLET	Intermediate		
(iii) DOUBLET	Fast		
(c) DOUBLET	Fast	J(P-P')/J(P-H)>5Hz, J(P-H)/J(P'-H)≈1 Hz	$[L] \approx [ML_2B_2]$
(d) DOUBLET + NARROW DOUBLET (free phosphine)	Fast	(i.e. typical of a trans planar complex)	$[L] \gg [ML_2B_2]$

This complete sequence of changes in the phosphine-methyl pattern was observed by Deeming and Shaw for the $PhMe_2P$/trans-$RhCl(CO)(PMe_2Ph)_2$ system.

Fackler's study extends to the ^{31}P spectrum. For rapid exchange and situations in which the proton spectrum collapses from a triplet to a doublet (i.e. (biii) and (c)) the ^{31}P spectrum changes from a doublet to a triplet. For situations where the proton spectrum collapses to a singlet (i.e. (bii)) the ^{31}P spectrum also appears as a singlet.

Two other mechanisms have been observed and theoretically characterised which produce broadening and collapse of coupling in the

^{1}H NMR spectrum of phosphine complexes. Spin-Lattice (T_1) relaxation, associated with the presence of paramagnetic metal ions, results in collapse of the coupling, shifting of peak positions, and broadening. These effects are observed, for example, with $(Ph_2MeP)_2NiCl_2$ in solution in the presence of excess phosphine[252]. Horrocks has used this effect to study the ligand exchange of some tetrahedral bisphosphine nickel and cobalt dihalide complexes for which he established the lability trends I<Br<Cl and Co<Ni[258].

Broadening with loss of coupling can also arise in systems with no virtual coupling from chemical exchange which produces averaging of the coupling constants of free and coordinated phosphine. One example is the exchange of free and coordinated phosphine (PMe_3, $PPhMe_2$ or PPh_2Me) in triethyl aluminium/phosphine systems[259]. Rapid exchange gives rise to averaged values of chemical shifts and coupling constants. In fact, for one specific ratio of phosphine to Et_3Al, the coupling constant, J(P-Me), is zero. This indicates that the coupling constants of free and coordinated phosphine have opposite sign.

Although broadening of NMR signals as a result of phosphine exchange is clearly a fairly common phenomenon, no proposals have been made which attempt to unify the governing factors. In this Chapter further examples of rapid room temperature phosphine exchange are presented and some of the important factors leading to exchange are discussed.

Table 9. Compounds exhibiting rapid phosphine exchange at room temperature (observed from ^{1}H NMR spectrum unless specified)

Compound	Solvent	Remarks	Reference
$RhHL_4$	THF	$L=Ph_3P>Ph_2MeP$ [a]	222
$RhH(CO)(PPh_3)_3$	-	No rapid exchange in Ir analogue.	224
		No rapid exchange with $RhH(PF_3)(PPh_3)_3$	223
			227
$RhMe(COD)(PMe_2Ph)_2$	CH_2Cl_2	No rapid exchange in Ir analogue.	225
$(Ir(CO)(PMe_2Ph)_4)^+ClO_4^-$	$CDCl_3$	Ph_2MeP analogue could not be isolated.	226
NiL4	C_6D_6	$L=Ph_3P, Ph_2MeP, Et_3P>Me_3P, (MeO)PPh_2$	228
$Pd(PMePh_2)_4$	toluene-d_8		229
PtL4	toluene-d_8	$L=Ph_2MeP>C_6F_5Me_2P>PhMe_2P$	229
$(AuMe_2L_2)^+X^-$	$CDCl_3$	$L=Ph_2MeP>PhMe_2P>Me_3P$; $X=I>Cl$	230
CdI_2L_2	CH_2Cl_2	Exchange observed from ^{31}P spectrum.	
		$L=PhMe_2P, Ph_2MeP, Et_3P, PhEt_2P, Ph_2EtP$	231
		$L=Ph_2EtP>Et_3P$	
$HgI_2(PBu^nPh_2)_2$	CH_2Cl_2	Exchange observed from ^{31}P spectrum.	
		No rapid exchange for Cl or Br analogues.	232
		No rapid exchange for $Bu^n{}_3P$ or $Bu^n{}_2PhP$ analogues.	
$HgI_2(P(NMe_2)_3)_2$	$CDCl_3$		233

Table 9 continued.

$RhCl(CO)(PPh_3)(PMePh_2)$	$CDCl_3$		234
$RhCl(CO)(PMePh_2)_2$	CS_2	No rapid exchange in $CDCl_3$.	234
$(Rh(PMePh_2)_4)^+$		No rapid exchange for $Ph(MeO)_2P$ or $Ph_2(MeO)P$ analogues.	235
$(Ir((PMePh_2)_4)^+ClO_4^-$		Signal at high field, 9.6τ	236
$Pd(CH_2Ph)Cl(PPh_3)_2$	$CDCl_3$	Ready loss of Ph_3P observed.	30
$(PdClL_2(CNC_6H_4Me))^+PF_6^-$	CH_2Cl_2	$L=Ph_2MeP > PhMe_2P$	238
$(MCl(PMe_2Ph)_2CNC_6H_4R)^+PF_6^-$	CH_2Cl_2	M=Pd or Pt > Ni	238,239
$(PtMeL_2(CNMe))^+SbF_6^-$	CH_2Cl_2	$L=Ph_2MeP > PhMe_2P$	239
$(Pt(PMe_2Ph)_4)^{2+}(PF_6^-)_2$	acetone-d_6		240
<u>cis</u> & <u>trans</u> $PtH(SeR)L_2$	CH_2Cl_2	$L=Ph_2MeP > Ph_3P$ cis > trans R=<u>p</u>tolyl > Ph No exchange in <u>trans</u> $Pt(SeR)_2L_2$ analogues.	241
<u>trans</u> $PtH(ER)(PPh_3)_2$	CH_2Cl_2	R=H > Ph R=H, E=Se > S R=Ph, E=S > Se	242
<u>trans</u> $PtH(CN)(PMePh_2)_2$	CH_2Cl_2	No exchange in PEt_3 analogue.	243
<u>trans</u> $Pt(CN)_2(PMePh_2)_2$	$CHCl_2$		243
$(Pt(S_2CNEt_2)(PMePh_2)_2)^+S_2CNEt_2^-$	$CDCl_3$		244
<u>trans</u> $Pt(X)Me(AsMe_2Ph)_2$		$X=Cl^-,Br^-,I^-$ No exchange in $PhMe_2P$ analogue.	245

Table 9 continued

Compounds exhibiting phosphine exchange in the presence of free ligand.

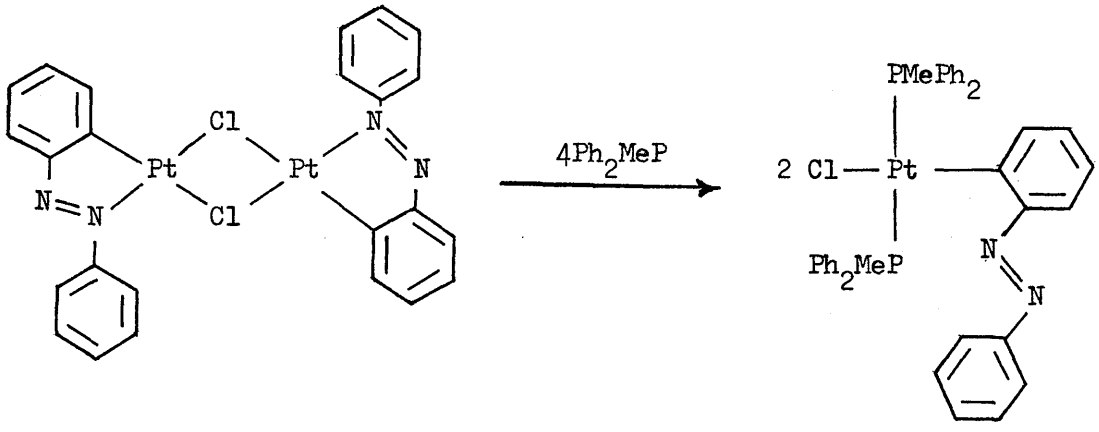
$(RhCl(PF_3)_2)_2$	C_6H_6	PF_3, CO, or C_2H_4 produce exchange.	246,247
$RhCl(PF_3)(PPh_3)_2$	C_6H_6	PF_3 or PPh_3 produce exchange, but PPh_3 only exchanges with coordinated PPh_3	247
$RhCl(CO)(PMe_2Ph)_2$	C_6H_6		248,249
$NiX_2(PMe_2Ph)_3$	$CHCl_2$	$X=Cl^- > Br^- > CN^-$ Spectrum in absence of added phosphine not described.	250
$(Et_3P)_2NiN_2Ni(PEt_3)_2$ [b.]	toluene	Exchange observed from ^{31}P spectrum.	251
$PdCl_2(PMePh_2)_2$	$CDCl_3$		252
$PdCl_2(PMe_2Ph)_2$	CH_2Cl_2	Exchange observed from ^{31}p spectrum.	253
$PdCl_2(PMe(\underline{o}\text{-tolyl}))_2$	$CDCl_3$		254
$PdCl_2(PMe_2(\underline{\alpha}\text{-napthyl}))_2$	$CDCl_3$		254
$PtX_2(PMe_2Ph)_2$	$CDCl_3$	$X=I > Cl$	255
$Pt(I)Me(P(\underline{p}\text{-tolyl})_2)_2$	CH_2Cl_2		256
$(MH(PEt_3)_3)^+BPh_4^-$	acetone d^6	M=Pt, exchange produces no scrambling of <u>cis</u> & <u>trans</u> PEt_3. M=Pd, exchange produces scrambling of <u>cis</u> & <u>trans</u> PEt_3. M=Ni, intramolecular exchange of phosphine occurs initially.	257

[a] Inequalities refer to rate of exchange

[b] This species not conclusively characterised

RESULTS AND DISCUSSION.

Chloro(2-(phenylazo)phenyl)bis(diphenylmethylphosphine)platinum (II) is easily prepared by bridge cleavage of di-μ-chloro di(2-(phenylazo)phenyl)-diplatinum(II), as described in Chapter I



The temperature variations in the methyl region of the ^1H NMR spectra of this complex are shown in Figure 10. Only at -30°C are the three triplets expected for the methyl signals of virtually coupled trans-phosphines at platinum resolved. The parameters extracted from this spectrum are displayed in Table 10 and are quite normal for trans diphenylmethylphosphine complexes[243]. On raising the temperature to -20°C the phosphorus-hydrogen coupling is no longer resolved and at +10°C a singlet is formed which persists to 60°C, the highest temperature reached with $CDCl_3$ as solvent. This broadening of the methyl region accompanied by broadening of the aromatic signals. In nitrobenzene a singlet is observed for the methyl resonances up to ~ 120°C. Above this temperature the spectrum appears as a doublet. These changes are reversible.

These observations are consistent with the predictions made by Fackler for the appearance of the exchange spectra in virtually coupled systems at different rates of exchange when the concentration of free

Variable temperature ^1H NMR spectra of the methyl signals of

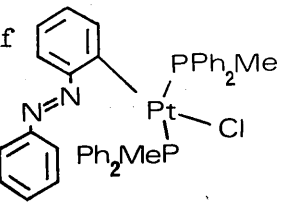


Figure 10.

(A) $CDCl_3$ solution at 100 MHz, = 1.74, (Varian HA100).

(B) $C_6H_5NO_2$ solution at 60 MHz, = 1.84, (Jeol C-60H).

phosphine is low relative to the concentration of the complex itself (conditions of (b) above). Paramagnetism is excluded as the cause on the grounds that paramagnetic planar platinum(II) complexes are unknown nor are other paramagnetic species likely to be involved.

Simple exchange averaging of free and coordinated phosphine is also ruled out as the mechanism for the broadening of the spectrum since chemical shift variations of the methyl signals are associated with this mechanism. No chemical shift changes were in fact observed. Nor was the signal due to free phosphine, which would be expected from this mechanism, detected at low temperature.

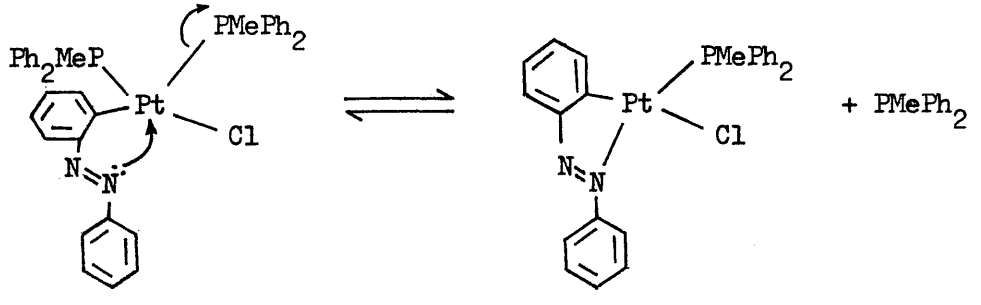
Naively, one can imagine that the room temperature singlet results because rapid ligand exchange eliminates coupling with ^{195}Pt ($I=\frac{1}{2}$, 33.8%) and coupling with the other phosphorus atom, i.e. time averaging eliminates the anticipated splitting due to spin-coupling. Deeming and Shaw explained the singlet produced with $RhCl(CO)(PMe_2Ph)_2/PMe_2Ph$ on this basis, but Fackler disallows this conception. He makes the point that strong P-P coupling is required to obtain these observations. This coupling decouples the phosphorus-hydrogen atom coupling.

The changes in the spectrum of $(C_6H_5N{:}NC_6H_4)Pt(PMePh_2)_2Cl$ are reversible though above 140°C decomposition occurs producing a spectrum consistent with the irreversible formation of a mixture of diphenylmethylphosphine oxide and chloro(2-(phenylazo)phenyl)(diphenylmethylphosphine)platinum(II),

$$(C_6H_5N{:}NC_6H_4)Pt(PMePh_2)_2Cl \xrightarrow[140^{\circ}C]{PhNO_2} \text{[chloro(2-(phenylazo)phenyl)(diphenylmethylphosphine)platinum(II)]} + Ph_2MeP(O)$$

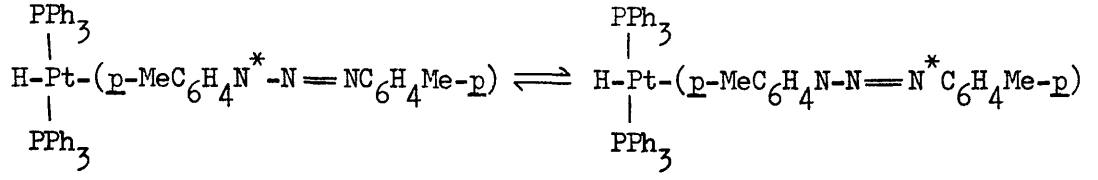
This is unusual for bis(phosphine) complexes of platinum(II) even when the phosphine itself is more prone to oxidation than diphenylmethylphosphine. In particular, no change in the ^1H NMR spectrum or in the appearance of the solution was observed on heating $(Et_3P)_2PtCl_2$ in nitrobenzene to 140°C. A separate experiment confirmed that free Ph_2MeP in nitrobenzene is oxidised to $Ph_2MeP(O)$ under these conditions. The red colour of the resultant solution may be due to the presence of nitrosobenzene, the likely by-product. This reaction is in accord with the reduction of aromatic nitro-groups by phosphines and phosphites, a procedure well established in organic syntheses[189].

In contrast to the behaviour of $(C_6H_5N{:}NC_6H_4)Pt(PMePh_2)_2Cl$, no exchange of ligands was apparent from the ^1H NMR spectra of $(Ph_2MeP)_2PtX_2$ (X = Cl, Br, or I) in $CDCl_3$. A mechanism for exchange whereby internal nucleophilic attack of a nitrogen atom promotes loss of phosphine is, therefore, proposed. The released phosphine may then undertake intermolecular nucleophilic substitutions.

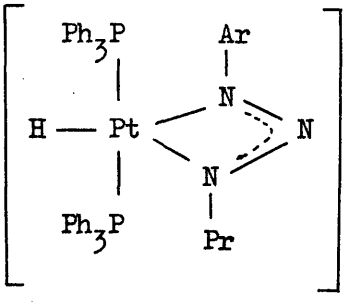


Associative (S_N2) mechanisms are well established for square-planar platinum(II) complexes, and are undoubtedly involved in at least some of the systems prone to rapid phosphine exchange listed in Table 9. This is the only example where the complex itself has a free ligating group available to participate in an intramolecular (S_{Ni}) displacement mechanism.

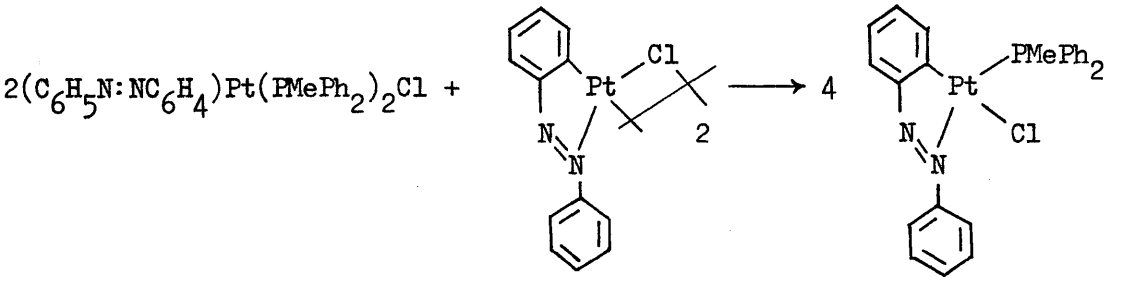
Interestingly, the equilibrium [260],



is thought to proceed by an associative mechanism involving a five coordinate intermediate which results from intramolecular attack of a nitrogen atom.



The facile loss of Ph_2MeP from chloro(2-(phenylazo)phenyl)bis-(diphenylmethylphosphine)platinum(II) is confirmed by the reaction.



Rapid transfer of phosphine takes place in $CDCl_3$ at room temperature yielding chloro(2-(phenylazo)phenyl)diphenylmethylphosphine platinum(II), identified by its N.M.R. spectrum. In contrast, no transfer of phosphine occurs when $(C_6H_5N{:}NC_6H_4)Pd(PEt_3)_2Cl$ and $(C_6H_5N{:}NC_6H_4)_2Pd_2Cl_2$ are mixed under the same conditions. This is in keeping with the well-resolved ^1H NMR spectrum of the former which shows no evidence of phosphine exchange.

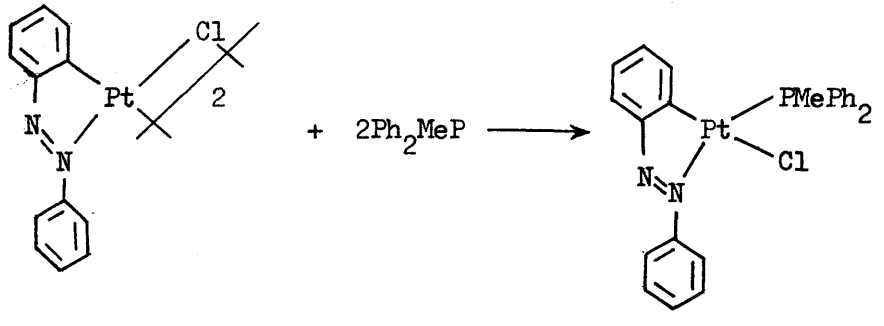
The halides, $(Ph_2MeP)_2PtX_2$, do not exhibit exchange phenomena themselves in $CDCl_3$, and Table 10 includes NMR data for these complexes which conforms with that of the $PhMe_2P$ analogues[200]. Addition of Ph_3P, Ph_2MeP of $PhMe_2P$ to their solutions causes immediate broadening and decoupling of the methyl ^1H NMR resonances, typical of fast exchange. These observations are consistent with an S_N2 exchange process of the type which may operate for $(C_6H_5N{:}NC_6H_4)Pt(MePhP)_2Cl$ in conjunction with the S_{Ni} mechanism. The addition of triethylamine to cis $(Ph_2MeP)_2PtCl_2$ also produces exchange broadening but, interestingly free azobenzene does not, perhaps due to steric hindrance or low basicity. Addition of free Ph_2MeP to $CDCl_3$ solutions of cis or trans $(Et_3P)_2PtCl_2$ does not produce broadening of the ^1H NMR spectrum. In both cases the spectrum is consistent with the formation of an ionic species, $((Et_3P)_2(Ph_2MeP)PtCl)^+Cl^-$, with a trans arrangement of the triethylphosphine groups.

Exchange broadening of this type can be a distinct hindrance in compound identification by ^1H NMR. This problem was encountered in the course of this work in an unsuccessful series of reactions between $(Ph_2MeP)_4Pt$ and mercuric halides. These reactions failed to substantiate the reported formation of a complex, $(R_3P)_2Pt(X)HgX$, containing a platinum-mercury bond[261]. The products are thought, from C and H analysis and their IR spectra, to include $(Ph_2MeP)_2PtX_2$ but the ^1H NMR spectra of these compounds show only a broad singlet for the methyl resonances. It appears, therefore, that trace amounts of free phosphine in the reaction product are producing the exchange process described above.

Phosphine exchange involving ionic intermediates analogous to those mentioned above has been reported by Powell[254/5] for complexes of platinum and palladium. Broadening of the methyl resonances is observed with cis $(Ph_2MeP)_2PdCl_2$ and free Ph_2MeP[252], with cis(o-tolyl-$Me_2P)_2PdCl_2$

and free o-tolyl-Me_2P, $PhMe_2P$, Bu^n_3P, or $PhMe_2As$[254], and with $(PhMe_2P)_2PtI_2$ and free $PhMe_2P$, Ph_3P, Bu^n_3P, $(o\text{-tolyl})Me_2P$, $(o\text{-tolyl})_2MeP$ or $PhMe_2As$[255]. Addition of Ph_3As or py does not collapse the methyl resonances in this latter case. Low temperature spectra were characteristic of ionic species $(MXL_2L')^+X^-$. At room temperature attack by both phosphine and halide promotes rapid exchange leading to a broad singlet in the ^1H NMR.

A contrast to the behaviour of chloro(2-(phenylazo)phenyl)-bis(diphenylmethylphosphine)platinum(II) is provided by the ^1H NMR spectrum of the chelating azobenzene derivative, $(azb)Pt(PMePh_2)Cl$. This can also be prepared by adding two equivalents of Ph_2MeP to di-μ-chloro-(2-(phenylazo)-phenyl) diplatinum(II).



This compound shows no evidence of phosphine exchange and displays a typical doublet pattern with platinum satellites. The magnitude of $^1J(Pt\text{-}P)$ confirms the configuration shown (vide infra).

The foregoing results are now considered in the light of the reported examples of phosphine exchange broadening and an attempt is made to unify the controlling factors which lead to rapid exchange of phosphines.

Factors influencing phosphine exchange.

Table 9 collates the available information on complexes exhibiting phosphine exchange detected by broadening of the NMR resonances

(either ^{1}H or ^{31}P). The tabulation is not limited to broadening by the mechanism of phosphine exchange which operates in virtually coupled systems. It is clear from comparison of the compounds listed in Table 9 that two factors are important; the nature of the metals, and the nature of the phosphine and other ligands.

The effect of the metals. It can be seen that the vast majority of systems which show rapid phosphine exchange involve group VIII metals. This region of the periodic table sees the transition from stable 18-electron molecules to stable 16-electron species[37a]. Consequently, conversions between the two systems are common, and many 18-electron compounds undergo reactions via loss of a 2-electron donor, where 16-electron complexes react via ligand capture.

Accordingly, 18-electron molecules appear to undergo exchange reactions by an S_N1 mechanism, spontaneously losing a phosphine. Examples include $RhH(PPh_3)_4$[222], $Pd(PMePh_2)_4$[229] and $Pt(PMe_2Ph)_4$[229]. $RuH_2(PMePh_2)_4$ does not exhibit exchange at room temperature but heating to 80°C in T.H.F. produces broadening of both the H and Me resonances. The reluctance of this 18-electron ruthenium complex to undergo spontaneous phosphine loss is presumably a reflection of the greater stability of 18-electron compounds in that area of the periodic table, compared to complexes of other group VIII elements. Because of irregularities in the nd $\longrightarrow$ (n+1)p promotion energies as the groups are descended, the elements of group VIII least likely to be found in 18-electron configurations are those of the second row[37a]. This can account for the faster exchange at Rh than at Ir in the complexes $MH(CO)(PPh_3)_3$[223/4], and the failure to observe exchange in $IrMe(COD)(PMe_2Ph)_2$[225] while rapid exchange is noted for the rhodium analogue.

Of the Group VIII 16-electron molecules which undergo rapid

exchange, most can be assigned to one of two categories, both involving S_N2 mechanisms. In the first category, free ligand is added to provide the nucleophile. This is the case with, for example, $RhCl(CO)(PMe_2Ph)_2$,[248/9] $PtX_2(PMe_2Ph)_2$[255] and $PdCl_2(PMePh_2)_2$[252] as well as the complexes $PtX_2(PMePh_2)_2$ described earlier as part of this work. As a variation, S_N2 attack by certain solvents may promote exchange and this can account for the exchange broadening observed for $RhCl(CO)(PMePh_2)_2$ in CS_2, but not in $CDCl_3$[234]. (The strong interaction between CS_2 and Rh(I) compounds of this type is well known)[262]

In the second category, part of the molecules themselves provide the attacking nucleophile. This can be a potential chelating ligand (as with chloro(2-(phenylazo)phenyl)bis(diphenylmethylphosphine)platinum(II)) a bridging ligand or a coordinating anion.

Probable cases where the attacking group is a bridging ligand are those compounds involving CN^- (e.g. $Pt(CN)_2(PMePh_2)_2$), SeR^- and SR^- (e.g. $Pt(ER)Cl(PMePh)$). The bridging abilities of CN^-, SeR^- and SR^- are well recognised in platinum and palladium chemistry.

Attack by a coordinating anion is illustrated by $(Pt(S_2CNEt_2)(PMePh_2)_2)S_2CNEt_2$[244] and $(AuMe_2L_2)^+X^-$[230]. The addition of free ligand to bis(phosphine)platinum and palladium dihalide may also be considered under this category since ionic species (e.g. $((PhMe_2P)_3PtCl)^+Cl^-$) have been shown to form[255]. At room temperature attack of Cl^- promotes exchange. When the halide anion is replaced by an anion with no potential for coordination (e.g. PF_6^- or BPh_4^-) no exchange broadening is observed. Thus $((Ph_2MeP)_3PtCl)^+Cl^-$ shows exchange broadening at room temperature in $CDCl_3$ while $((Ph_2MeP)_3PtCl)^+PF_6^-$ does not. Addition of $(AsPh_4)^+Cl^-$ broadens the spectrum in this last case.

Despite the classification of most examples into these two categories, some 16-electron molecules do not obviously fit into either

category. The complexes $(MCl(PMe_2Ph)_2CNR)PF_6$ (M=Ni, Pd, or Pt) are exceptions and a dissociative mechanism enhanced by bond-weakening has been proposed for them[238,239]. Evidence now exists which indicates that spontaneous formation of 14-electron species from 16-electron complexes of the Group VIII elements can occur. Whitesides has shown that dissociation of one molecule of triphenylphosphine is the rate determining step for the thermal decomposition of $(Ph_3P)_2PtBu_2^n$,[263] and Mawby has observed that the carbonyl insertion found with $Pt(CO)ClEt(AsPh_3)$ is not assisted by solvent or added nucleophile[264]. A dissociative mechanism might also operate with the complex $Pd(PPh_3)_2Cl(CH_2Ph)$[30] although intermolecular attack of coordinated Cl may also produce the suggested equilibrium.

$$2(Ph_3P)_2PdCl(CH_2Ph) \rightleftharpoons 2Ph_3P + \text{[Ph}_3\text{P, Cl, CH}_2\text{Ph; Pd; Pd; PhCH}_2\text{, Cl, PPh}_3\text{]}$$

XVIII

Interestingly, a strong interaction between $PdCl(CH_2Ph)(PPh_3)_2$ and halocarbon solvents is reported, producing XVIII as the isolated product. Interaction between $(Pt(PMe_2Ph)_4)(PF_6)_2$ and the solvent (acetone-d_6) may also explain this apparent exception. Although acetone does not form a pure isolable complex with platinum(II), the isolation of $((Ph_3P)_2Pt(CF_3)_2CO)$[265] indicates that solvent promoted exchange may well be possible with acetone. (In this respect the intermediacy of an ionic complex <u>trans</u> $(PtH(PMePh_2)_2(acetone))^+ PF_6^-$ has been proposed for the reaction of ethylene with <u>trans</u> $PtHCl(PEt_3)_2$).[266] The exchange observed for $RhCl(CO)(PPh_3)(PMePh_2)$, $(M(PMePh_2)_4)^+ClO_4^-$ (M=Rh or Ir) and <u>trans</u> $PtX(Me)(AsMe_2Ph)_2$ still lack an explanation at present.

The effect of the phosphines and other ligands. The nature of the phosphine is obviously important. Most frequently encountered in exchanging systems is methyldiphenylphosphine with dimethylphenylphosphine and triphenylphosphine next in importance. (It is possible that exchange of Ph_3P may be much more common but lack of convenient alkyl NMR signals presents difficulties in examining these systems). It is difficult to differentiate between electronic and steric effects since in the systems reported substituents on phosphorus which decrease the bulkiness of the phosphine commonly also increase its basicity. As the aryl groups of Ph_3P are progressively replaced by alkyls the rate of exchange is seen to decrease.

To establish the effect of the nature of the phosphines it is again convenient to consider 18 and 16-electron molecules separately. For 18-electron molecules an S_N1, dissociative mechanism is likely to operate. Bulky phosphines should accelerate phosphine exchange by this mechanism while strongly bonded phosphines should slow the exchange. Those 18-electron molecules in Table 9 conform to these predictions although it is difficult to specify whether bulk or strength of bonding is the more important factor. Both may be important but comparison of $RhH(CO)(PPh_3)_3$[223] (which does undergo exchange) with $RhH(PF_3)(PPh_3)_3$[227] (which does not undergo exchange) indicates that the greater bond strength in the latter case outweighs the greater steric crowding and prevents exchange.

With the 16-electron molecules the situation is not so straightforward. These molecules can be further subdivided into those which undergo exchange by an S_N1 process producing 14-electron intermediates and those which undergo exchange by an S_N2 associative mechanism. Unfortunately it is difficult to assign some molecules specifically to a particular mechanism.

The implications of the S_N1 mechanism mentioned above also hold

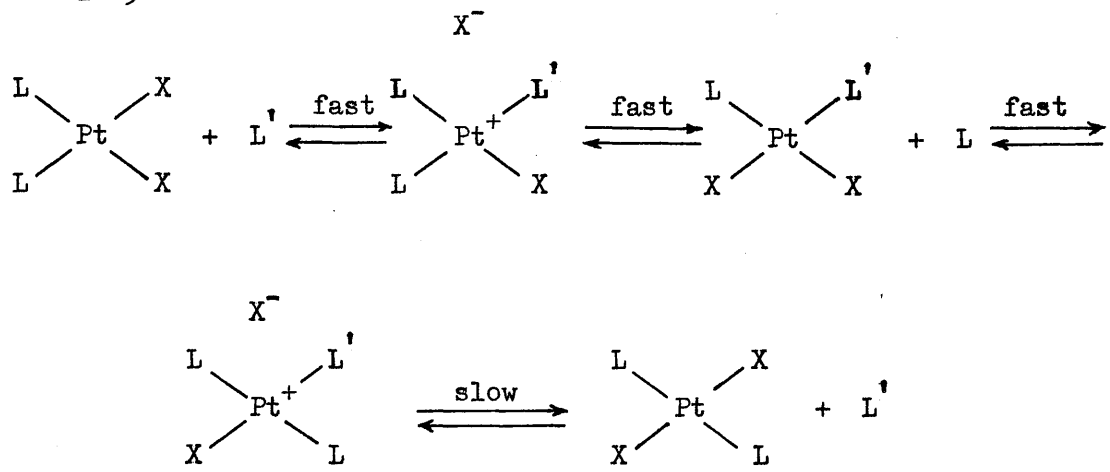
for the dissociation of 16-electron molecules. It is possible that for the compounds $(M(PMePh_2)_4)^+ClO_4^-$ (M = Ir[236] or Rh[235]) the severe steric crowding indicated by the X-Ray structure of the Ir complex[236] may promote exchange by a dissociative mechanism. No fast exchange in CH_2Cl_2 was found, however, for the molecules $RhCl(CO)(PBu^t_2Ph)_2$[267] or $(Bu^t_2PhP)_2MCl_2$ (M = Pd[268] or Pt[91]) despite the bulky phosphines. It seems, therefore, that even a high degree of steric crowding fails to initiate a rapid S_N1 exchange process in these complexes.

For 16-electron molecules where an associative S_N2 mechanism operates, bulky phosphines should slow the exchange process while ligands with strong bonding ability* should accelerate the exchange. The compound $(AuMe_2L_2)^+X^-$, where the order of exchange rate, $X^- = I^- > Cl^-$ is observed, is probably an example of this effect. On the other hand the rate-determining step for the S_N2 mechanism may in some cases be dissociation of the trigonal bipyramidal transition state[106]. This is more likely to be the case when the initial molecule contains ligands which are strongly bonded. The nature of both the incoming nucleophile and the ligand being displaced is then important and a balance of effects may be necessary to achieve rapid phosphine exchange. This can be illustrated by the ionic complexes $((R_3P)_3PtX)^+X^-$. If the phosphine and halogen have similar bonding abilities then both displacement of phosphine by halogen and displacement of bonded halogen by phosphine should occur easily and the system undergo rapid phosphine exchange (as with $((PhMe_2P)_3PtX)^+X^-$[255]). If, however, the phosphine is too strongly bound no exchange takes place (as with $((Et_3P)_2(Ph_2MeP)PtCl)^+Cl^-$).

These observations may have some bearing on the mechanism of the phosphine catalysed cis-trans isomerisation of bis(phosphine)platinum-dihalide complexes. A consecutive displacement mechanism has been proposed

* This term is used to include both basicity and polarisability of the ligand.

for cis $(PhMe_2P)PtI_2/PhMe_2P$ from the onset of exchange broadening of the various methyl signals in a solution of cis and trans $(PhMe_2P)PtI_2$ and $((PhMe_2P)_3PtI)^+I^-$.



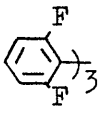
The consecutive displacement of mechanism has subsequently been disputed for cis $(Et_3P)_2PtCl_2$ because of the failure of $((Et_3P)_3PtCl)^+$ to react with Cl^- to produce cis or trans $(Et_3P)_2PtCl_2$.[269] This failure is in line with the observation in the present work that cis $(Et_3P)_2PtCl_2/Ph_2MeP$ does not show exchange broadening (the spectrum being consistent with non-exchanging $((Et_3P)_2(Ph_2MeP)PtCl)^+Cl^-$) while cis $(Ph_2MeP)_2PtCl_2/Ph_2MeP$ does. It is tempting, therefore, to speculate that the mechanism of cis-trans isomerisation may depend on the nature of the phosphine.

The similarity of rapid phosphine exchange reactions and phosphine displacement reactions makes the effect of the nature of the phosphine on displacement reactions relevant here. The size of the phosphine is reported to be the controlling factor in determining the stability towards ligand displacement. This has been claimed for NiL_4[228], $Co(CN)_2L_3$[270], $(L_2RhCl)_2$[271], L_2PdX_2[272] and L_2PtX_2[272], by competitive displacement reactions. For example, in the system,

$$L_2PtCl_2 + 2L' \longrightarrow L'_2PtCl_2 + 2L$$

Kemmitt established an order of stability of complexes L_2PtCl_2 to ligand

displacement. He showed that ligands at the L.H.S. of the series

$$(C_6F_5)_3P < (C_6F_5)Ph_2As < (C_6F_5)_2PhP < \left(\text{  }\right)_3P < Ph_3As < (C_6F_5)Ph_2P < Ph_3P < (PhO)_3P$$

are preferentially displaced by ligands at the R.H.S. of this series. These reactions can have synthetic use and have been extended to platinum-fluoro-olefin complexes where the order of stability $Ph_3P, Ph_3As < Ph_2MeP$ obtains.[330] It is also found that initial arsine exchange is favoured over CO elimination or insertion in the reaction,[273]

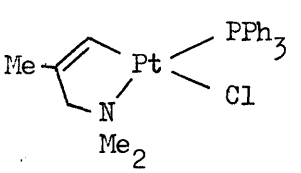
$$Ir(CO)_2Cl_2Et(AsPh_3) \xrightarrow{AsMe_2Ph} Ir(CO)_2Cl_2Et(AsMe_2Ph) \xrightarrow{AsMe_2Ph} Ir(COEt)(CO)(AsMe_2Ph)_2$$

In conclusion the effect of the nature of the phosphine in fast exchange reactions is difficult to assess. Lack of detailed knowledge of the mechanism of exchange limits interpretation of some results. Comparitive information which unambiguously differentiates between steric and electronic influences is also lacking. It does appear, however, that both these factors are probably important though which predominates will depend on the system.

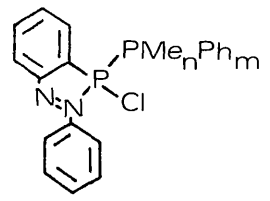
NMR EXAMINATION OF (azb)Pt($PMePh_2$)Cl AND (azb)Pt(PMe_2Ph)Cl.

These compounds show no evidence of phosphine exchange and display the expected doublet pattern, with platinum satellites. Heteronuclear double resonance experiments allow the determination of ^{195}Pt and ^{31}P chemical shifts and the platinum-phosphorus coupling constant, $^{1}J(Pt-P)$. In addition, the relative signs of the various coupling constants can be assigned by observing the pattern of collapse of peaks in the ^{1}H NMR spectrum while irradiating at low power the individual peaks in the platinum and phosphorus spectrum. This is expressed pictorially in Figure 11 . $^{1}J(Pt-P)$ and $^{2}J(P-H)$ are found to have opposite signs while $^{1}J(Pt-P)$ and $^{3}J(Pt-H)$ have the same sign. On the assumption of a -ve value for $^{2}J(P-H)$[274] the absolute signs of the couplings $^{3}J(Pt-H)$ and $^{1}J(Pt-P)$ can, therefore, be assigned. This information along with the chemical shift data is shown in Table 10.

Of particular interest is $^{1}J(Pt-P)$. Variations in the values of this coupling constant have been related to trans influence[104] . The very high value of ~4100Hz lies well outside the range of values (1577-1704Hz) found for phosphines trans to aromatic groups.[275] This implies that the phosphine is trans to the nitrogen atom and this conclusion is supported by the low value of ν(Pt-Cl) typical of a chlorine atom trans to carbon. The reported values of $^{1}J(Pt-P)$ trans to amines[102] are mostly lower than 4000Hz although for one closely related complex, XIX, a value of 4260Hz has been determined[276] . The similarity of this value with that for the azobenzene complex adds weight to the suggested configuration.



XIX

Figure 11. ^{1}H NMR Spectrum of  (n=2 m=1, n=1 m=2)

Position of irradiation(diagramatic)

^{1}H Spectrum, Me signals

^{31}P Spectrum

^{195}Pt Spectrum

20 Hz

H ⟶

H ⟶

Table 10. ^{1}H, ^{31}P and ^{195}Pt NMR parameters[a].

Compound	Chemical Shift					Coupling Constants (Hz)		
	$^{1}H(Me)$ τ	^{31}P $\Xi(^{31}P)$/Hz[c]	p.p.m.[d]	^{195}Pt $\Xi(^{195}Pt)$/Hz[c]	p.p.m.[e]	$^{2}J(P-H)$	$^{3}J(Pt-H)$	$^{1}J(Pt-P)$
Ph_2MeP[b]	8.56		+ 37.3			3.9		
Ph_2MeP	8.44					4.0		
cis$(Ph_2MeP)_2PtCl_2$	8.04		+ 1.0			10.8	35.2	
cis$(Ph_2MeP)_2PtBr_2$	7.96		+ 0.7			10.8	36.0	
cis$(Ph_2MeP)_2PtI_2$	7.85		+ 6.8			9.7	36.4	
trans$(Ph_2MeP)_2PtI_2$	7.43		+ 3.8			3.4	26.0	
$(PhN_2C_6H_4)Pt(PMePh_2)Cl$	7.39	24,288,580	-4.0,-5.6[f]	12,843,691	+ 739	11.0	35.5	4,100
$(PhN_2C_6H_4)Pt(PMePh_2)_2Cl$	8.19		- 7.3br			3.5	32.0	
$(PhN_2C_6H_4)Pt(PMe_2Ph)Cl$	7.85	24,288,251	+8.6,+7.9[f]	12,843,865	+ 725	11.0	40.0	4,050

[a] $CDCl_3$ solution unless otherwise specified [b] Neat liquid [c] Resonance frequency at a polarising field strength such that the T.M.S. resonance is exactly 60 MHz [d] Positive shift indicates a resonance to high field of H_3PO_4 reference (Ξ (^{31}P)= 24,288,444 Hz) [e] Positive shift indicates a resonance to high field of cis $(Me_2S)_2PtCl_2$ reference (ref.277) (Ξ (^{105}Pt) = 12,853,188 Hz) [f] From $^{1}H-\{^{31}P\}$ heteronuclear double resonance.

EXPERIMENTAL.

The (2-(phenylazo)phenyl) platinum complexes were prepared as described in Chapter I.

Preparation of the dihalo-bis(diphenylmethylphosphine)platinum(II) complexes.

Dichloro-bis(diphenylmethylphosphine)platinum(II).

Diphenylmethylphosphine (2.7ml) was added by syringe to a suspension of platinum dichloride (1.9422g, 7.3m moles) in ethanol (100ml) under nitrogen. The solution was refluxed for 30 minutes. The ivory coloured precipitate was filtered and recrystallised from ethanol to give colourless prisms of dichloro-bis(diphenylmethylphosphine)platinum(II) (4.01g, 82% M.p. 251-253°C Found: C,46.23; H, 3.86% $C_{26}H_{26}P_2PtCl_2$ requires C,46.86; H,3.93%)

Metathetical replacement reactions in ethanol using excess lithium bromide and lithium iodide produced,

A. dibromo-bis(diphenylmethylphosphine)platinum(II) (M.p. 241-243°C Found C,40.51; H,3.55% $C_{26}H_{26}P_2PtBr_2$ requires C,41.34, H,3.46%)

B. di-iodo-bis(diphenylmethylphosphine)platinum(II) (Two crystal forms M.p.(a) 223-230°C(dec), (b) 263-265°C Found C,37.19; H,3.30% $C_{26}H_{26}P_2PtI_2$ requires C,36.77; H,3.09%)

Interaction of tetrakis(diphenylmethylphosphine)platinum(o) with mercuric iodide.

Tetrakis(diphenylmethylphosphine)platinum (1.1891g, 1.2m moles) was dissolved in degassed benzene (120ml) under nitrogen. Mercuric iodide (0.542g, 1.2m moles) was added and produced an immediate colour change from yellow to olive green. After 5 minutes stirring, some mercuric iodide remained but a grey material had been produced. After 1 hour the supernatant liquid was decanted from the solid product which had the

appearance of a mixture of green and white material.

The orange benzene solution, maintained under a nitrogen atmosphere, deposited a cream precipitate after 16 hours. Benzene was removed from this suspension at low temperature producing an orange oily material with a smell of diphenylmethylphosphine.

Recrystallisation of both this orange oily material and the above solid product from ethanol produced cream coloured powders. The ^1H NMR spectra of these products showed broadening of the methyl regions. Their IR spectra were very similar (though not identical) to that of a cis/trans mixture of $(Ph_2MeP)_2PtI_2$ (Found: C,36.09; H,2.95% $C_{26}H_{26}P_2I_2Pt$ requires C,36.77; H,3.08%)

NMR experiments. 2ml of $CDCl_3$ was added to the samples listed below and the NMR spectra of the resultant solutions recorded.

(a) cis $(Ph_2MeP)_2PtCl_2$ (0.0234g, 0.035m moles) and Ph_3P (0.0091g, 0.036m moles).

(b) cis $(Ph_2MeP)_2PtCl_2$ (0.0220g, 0.033m moles) and $PhMe_2P$(0.0064g,0.046m moles).

(c) $(Ph_3P)_2PtCl_2$(0.0175g, 0.022m moles) and Ph_2MeP (0.0075g, 0.055m moles).

(d) cis $(Et_3P)_2PtCl_2$(0.0333g, 0.066m moles) and Ph_2MeP(0.0136g, 0.10m moles).

(e) trans$(Et_3P)_2PtCl_2$(0.0335g, 0.066m moles) and Ph_2MeP(0.0169g, 0.124m moles)

(f) cis$(Ph_2MeP)_2PtCl_2$(0.0183g, 0.027m moles) and PhN:NPh(0.0038g, 0.021m moles)

(g) cis$(Ph_2MeP)_2PtCl_2$(0.0189g, 0.027m moles) and Et_3N (0.0031g, 0.031m moles)

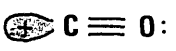
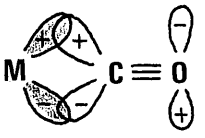
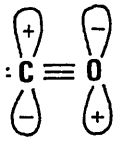
CHAPTER III.

PLATINUM(II) CARBONYL COMPLEXES.

CHAPTER III.

INTRODUCTION.

Very many transition metal complexes have been isolated which contain one or more carbon monoxide molecule bonded to the metal. Carbon monoxide has lone pairs on both carbon and oxygen but in the majority of complexes the molecule is bonded through the carbon atom. The conventional description of the metal-carbon bonding in metal carbonyls considers the bonding in two parts; a "forward" metal←C σ bond and a "backward" metal→C π bond.

Metal Orbital	Bond Formed	CO Orbital
		
Empty hybrid σ orbital	Metal-carbon σ bond	Filled non-bonding orbital localised on carbon
		
Filled non-bonding metal d-orbital	Metal-carbon π bond	Empty antibonding π^* orbital of CO multiple bond

This bonding description involving π back-bonds is typical of unsaturated ligands (e.g. olefins) or other ligands with low-lying empty orbitals of the correct symmetry (e.g. phosphines). The existence of the carbon-metal σ -bond alone could not explain the formation of metal carbonyls since CO is a very poor base. The presence of back-bonding from the metal to the vacant CO π^* orbitals explains the lowering of the C-O stretching frequency produced by coordination.

Carbonyl complexes of platinum.

Since metal carbonyls are formed mainly with metals in low oxidation states and with several full d-orbitals, it is not surprising that many platinum(II) carbonyl complexes have been prepared. Platinum(0) carbonyl complexes have been reported less frequently and are less easily handled. Phosphine carbonyl complexes such as $Pt(CO)_2(PR_3)_2$[278] have been described but apart from spectroscopic data their chemistry is not well established. Their decomposition to form polynuclear species is a common process.

Mononuclear carbonyl platinum(II) complexes are generally prepared by one of three main routes: displacement of halide, olefin displacement, or halogen bridge cleavage.

Ionic complexes are prepared by displacement of halide by carbon monoxide and may be isolated as the perchlorate or tetraphenylborate salt.[237]

$$\underline{cis} \text{ or } \underline{trans}\ (Et_3P)_2PtCl_2 + CO + NaClO_4 \longrightarrow \underline{trans}\ ((Et_3P)_2Pt(CO)Cl)^+ClO_4^-$$

With palladium a two stage reaction has been shown to occur[279].

$$2((Et_3P)_2PdCl_2) + 4BF_3 \longrightarrow ((Et_3P)_4Pd_2Cl_2)(BF_4)_2 + 2BF_2Cl$$

$$((Et_3P)_4Pd_2Cl_2)(BF_4)_2 \xrightarrow{2CO} 2\ \underline{trans}\ ((Et_3P)_2Pd(CO)Cl)BF_4$$

Both olefins and acetylenes bonded to platinum(II) are easily displaced by carbon monoxide[280].

$$(Pt(C_2H_4)Cl_3)K + CO \longrightarrow (Pt(CO)Cl_3)K + C_2H_4$$

$$(Pt(CO)Cl_3)K \xrightarrow{PR_3} \underline{cis}\ (R_3P)Pt(CO)Cl_2$$

Cleavage of halogen bridged complexes by carbon monoxide is a widely used route to neutral mononuclear platinum carbonyl complexes.[280] This route has been employed extensively in the course of the work described in this chapter.

$$((R_3P)PtCl_2)_2 + CO \longrightarrow \underline{cis}\ (R_3P)Pt(CO)Cl_2$$

Carbonyl Insertion Reactions.

Although carbonyl insertion into metal-hydrogen bonds has been observed[281], insertion of carbon monoxide into transition metal-carbon bonds is the most common process and has recently been reviewed[282].

$$L_nM\text{-}R + CO \longrightarrow L_nM\text{-}\overset{\overset{O}{\|}}{C}\text{-}R$$

Throughout this chapter the term "carbonyl insertion" will be used without any mechanistic implications. In most cases it is not known whether the reaction proceeds by insertion of carbon monoxide into the metal-carbon bond or by migration of the organic group on to the carbonyl. In all cases the product is an acyl complex.

Carbonyl insertion is an important industrial process. It constitutes one of the key steps in, for example, the so-called "OXO" process for hydroformylation of olefins in the presence of catalytic amounts of dicobaltoctacarbonyl[283]. The important steps of this reaction are shown in Figure 12. The olefin is thought to undergo insertion into the cobalt-hydrogen bond of hydridocobalt tricarbonyl. Subsequent insertion of carbon monoxide into the cobalt-carbon bond forms the acyl derivative and cleavage by hydrogen produces the aldehyde and regenerates $HCo(CO)_3$ to continue the catalytic process.

The carbonylation of olefins catalysed by palladium[183] (Figure 13) is also thought to involve insertion of CO into a metal-alkyl bond forming

Figure 12. "OXO" process for hydroformylation of olefins.

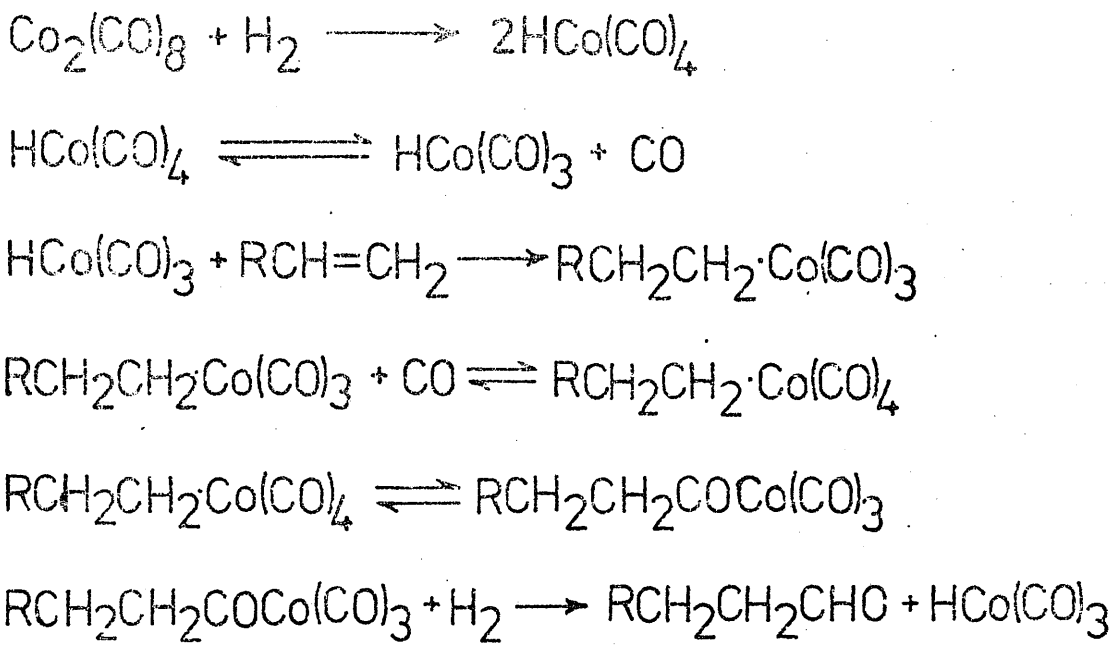
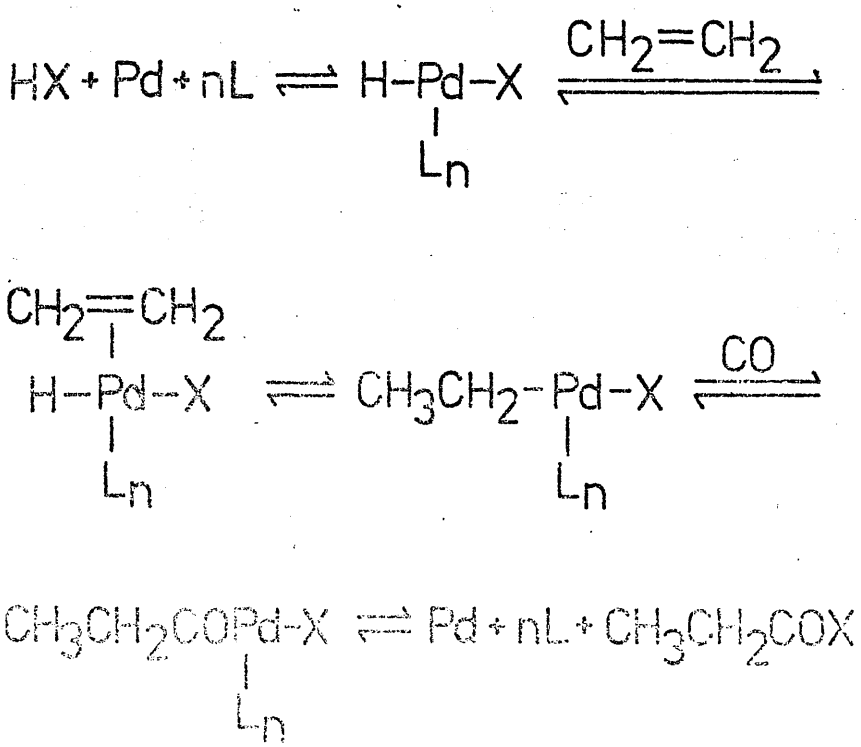


Figure 13. Palladium catalysed carbonylation of olefins.



an intermediate acyl complex. This affords the acyl halide by reductive elimination at palladium. If the reaction is performed in alcohol then the ester is produced.

Factors influencing carbonyl insertion.

Several factors have been shown to influence the carbonyl insertion process. Those considered particularly relevant to the work described in this Chapter are; the nature of added ligand, the nature of the organic group and the nature of ancillary ligands. These will be considered briefly in turn.

In many cases the insertion is promoted by addition of a Lewis Base to the carbonyl complex. Different systems have been found to display different dependence on the nature of the incoming ligand. Some M(CO)R systems, for example $MeMn(CO)_5$[282], react with a wide range of ligands (such as phosphines, phosphites, arsines, stibines, amines, iodide and carbon monoxide) whereas others do not. $CpMo(CO)_3Me$ and $CpFe(CO)_2Me$,[284] for example, do not react with I^-, or N, S and As donor ligands.

The effect of resident organic group on the ease of insertion is not clear and again results differ for different systems. Ease of insertion in a series of alkyl manganese pentacarbonyl complexes has been shown to follow the order[285]

$$\underset{\text{fast}}{Pr^n > Et > Ph > Me} \gg \underbrace{CH_2Ph \text{ and } CF_3}_{\text{immeasurably slow}}$$

A different order for methyl and phenyl groups obtains with platinum complexes. Insertion into the Pt-Me bond appears to be the easier process.[288] The ease of decarbonylation reactions have, however, been shown to follow the opposite order, Me < Ar.[38]

The effect of ancillary ligands is illustrated by two examples

It appears that higher basicity of the ligand already coordinated to the metal promotes the insertion reaction,

$$EtIr(CO)_2LCl_2 + L' \longrightarrow (EtCO)Ir(CO)L_2Cl_2$$ Ref. 264

The entering group, L', was shown not to affect the reactivity of this system but the dependence of the rate on the coordinated ligand, L, followed the order, P donor $\gg AsMe_2Ph > AsPh_3$.

The opposite trend holds for insertion with $MeRh(CO)L_2ClI$[286] promoted by methyl iodide. The effect of the more electron-withdrawing ligands may be either in weakening the Rh-Me bond or in rendering the metal more susceptible to nucleophilic attack by MeI or solvent.

Carbonyl Insertions in platinum(II) complexes.

Platinum carbonyl complexes most commonly form acyl complexes by CO insertion into a metal carbon bond already present in the molecule[287-290]. In one series of reactions the original platinum complex does not contain a platinum-carbon bond and the organic group is provided by a diorganomercurial[150].

$$(R_3P)Pt(CO)Cl_2 + HgR'_2 \longrightarrow ((R_3P)Pt(COR')Cl)_2 + R'HgCl$$

Platinum (II) has been shown to increase its coordination number to 5 before undergoing fluoro-olefin insertion[291].

$$\underline{trans}\ (PhMe_2As)_2Pt(Me)Cl + C_4F_6 \longrightarrow (PhMe_2As)_2Pt(C_4F_6)Me(Cl) \longrightarrow$$

$$\underline{trans}\ (PhMe_2As)_2Pt\ (CF_3C = C(Me)CF_3)Cl$$

A 6-coordinate complex is the probable intermediate in the reaction of $(R_3P)Pt(CO)Cl_2$ with diorganomercurials and a 5-coordinate species,

$RM(CO)(PR_3)_2X$ is the likely precursor of the acyl complex in the reactions,

$$(R_3P)_2M(R)X \xrightarrow{CO} (R_3P)_2M(COR)X \qquad \text{Ref. 288}$$

M = Pt,Pd R = Me,Ph

$$\underline{\text{trans}}\ (PhMe_2P)_2Pt(Me)Cl \xrightarrow{CO} (PhMe_2P)_2Pt(COMe)Cl. \qquad \text{Ref. 292}$$

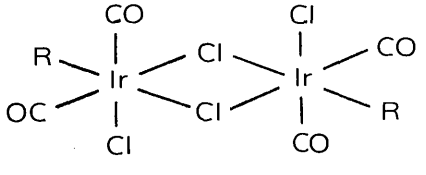
Glyde and Mawby have reported contrasting results from a kinetic investigation of the carbonyl insertion reaction,

$$(Ph_3As)Pt(CO)Cl(Et) + AsPh_3 \longrightarrow (Ph_3As)_2Pt(COEt)Cl. \qquad \text{Ref. 264}$$

Their proposed mechanism differs from that which normally operates for substitution reactions of platinum (II) complexes. The rate determining step involves the combination of ethyl and carbonyl ligands and is not assisted by either solvent or incoming nucleophile. This result is in accord with their findings for $Ir(CO)_2Cl_2RL$ [273] and can be expressed by the two step mechanism,

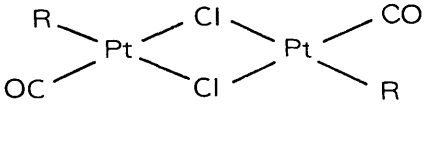
$$(Ph_3As)Pt(CO)Cl(Et) \xrightarrow{\text{slow}} (Ph_3As)Pt(COEt)Cl \xrightarrow[AsPh_3]{\text{fast}} (Ph_3As)_2Pt(COEt)Cl$$

It is found that with both the platinum and iridium complexes XX [287] and XXI [293] addition of phosphine causes carbonyl insertion in preference to bridge cleavage. Excess phosphine was employed in the platinum case (the addition was stoicheiometric in the iridium case) and fast addition favoured loss of carbon monoxide.



R = Me, Et

XXI



R = $Me(CH_2)_n$ n = 4-7

XX

Bridge cleavage without insertion occurred, however, with py (for Ir case) and acac (for Pt case).

Decarbonylation Reactions.

Most types of insertion reaction are reversible though, for example, there is no insertion counterpart to the elimination of N_2 from arylazoplatinum complexes[294]. Carbonyl insertion reactions are often but not always reversible. $(Ph_3P)_2Pt(COPh)Cl$[262] (prepared by oxidative addition of RCOCl to $(Ph_3P)_4Pt$) was shown to eliminate CO on heating whereas carbonylation of triphenylphosphine platinum(II) complexes could not be achieved[288]. The important factor may be the size of the phosphine. The bulkiness of Ph_3P is likely to inhibit the formation of 5-coordinate intermediates, $(R_3P)_2Pt(CO)RX$ compared to Et_3P. In accord with this suggestion, carbonyl insertion occurs less easily with triphenylphosphine complexes.[288]

In addition to many reports of conventional thermal decarbonylations of platinum acyl complexes[262], an interesting conversion of a platinum acyl complex to a mononuclear cationic platinum species has been reported[295].

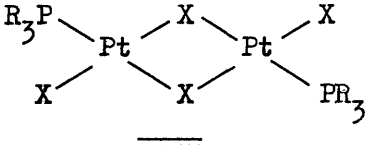
$$(Ph_3P)_2Pt(COR)Cl \xrightarrow[\text{acetone}]{AgPF_6} ((Ph_3P)_2Pt(CO)R)^+PF_6^-$$

RESULTS AND DISCUSSION.

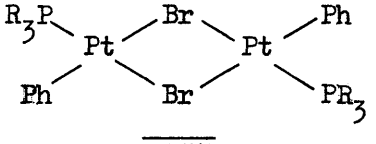
Coordination of Lewis Bases and oxidative addition to transition metal complexes are two processes which increase the electron count at the metal by two. In particular such reactions will convert square planar 16-electron platinum(II) complexes to 18-electron species. Since 16-electron platinum complexes are known to be favoured it was expected that carbonyl insertion, which reduces the electron count at the metal by two, would be a likely reaction path for 18-electron intermediates. The investigation of platinum(II) carbonyl complexes described in this Chapter was, therefore, undertaken with a view to examining the validity of this postulate.

Preparation of the mononuclear platinum carbonyl complexes.

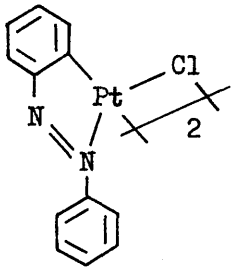
The mononuclear platinum carbonyl complexes used in this study were prepared by bridge cleavage of dinuclear halogen-bridged complexes,



XXII



XXIII

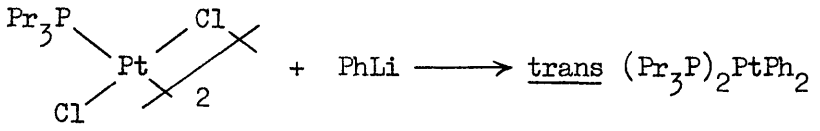


R_3P = Ph_2MeP; X = Cl,Br,I

R_3P = Et_3P, X = Cl

R_3P = Ph_2MeP, Et_3P

These bridged complexes were prepared by standard methods although many of them are new compounds. The preparation of $((azb)PtCl)_2$ has been described in Chapter I. Yields of the phosphine complexes XXII are quantitative but the conversion of the bromine bridged complexes to the phenyl derivatives XXIII is a low yield process. For complexes with chlorine bridges it is known that reaction with phenyl lithium gives the diphenyl-bis(phosphine)platinum(II) complex as the only product isolated



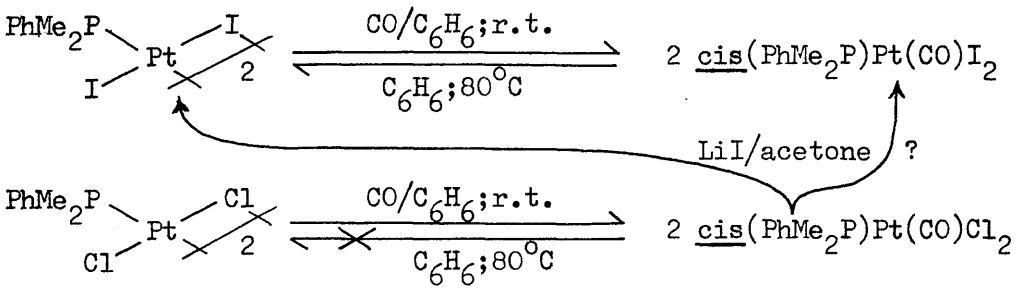
The reason for the failure of this reaction is not understood. The isolation of $((Ph_3P)PtCl(Ph))_2$ by another route[150] demonstrates its thermal stability and implies that the arylation reaction may pass through an unstable intermediate which decomposes to trans $(R_3P)_2PtAr_2$.

Preparation of the mononuclear complexes, cis $(R_3P)Pt(CO)X_2$, was easily achieved by passing carbon monoxide through a suspension of the bridged complexes XXII in benzene.

$$((R_3P)PtX_2)_2 \xrightarrow{CO} \underline{cis}\ (R_3P)Pt(CO)X_2$$

The yellow colour of the bridged complexes was replaced by colourless crystalline precipitates of the products. Only the thermodynamically more stable cis isomers were isolated, presumably reflecting the greater trans effect of R_3P than Cl^-.

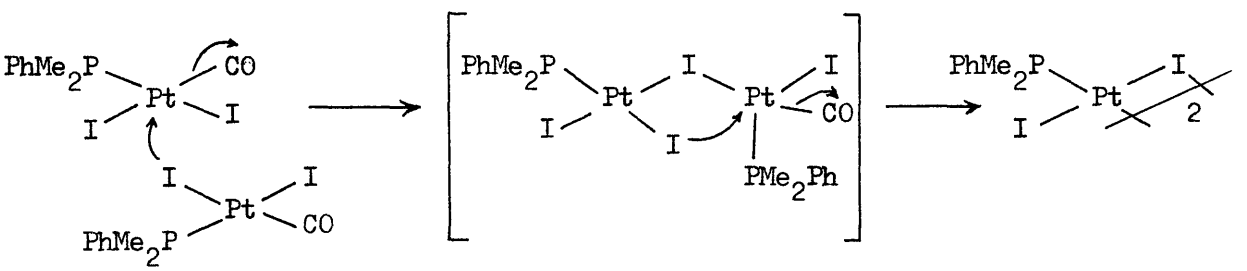
In the series of diphenylmethylphosphine complexes, the iodide is markedly less stable than the chloride or bromide. Heating in benzene or in the absence of solvent, or standing at room temperature in chloroform or sym tetrachloroethane results in loss of carbon monoxide and regeneration of $((Ph_2MeP)PtI_2)_2$. This compound also resulted from an attempted metathetical replacement reaction with cis $(Ph_2MeP)Pt(CO)Cl_2$ and lithium iodide.



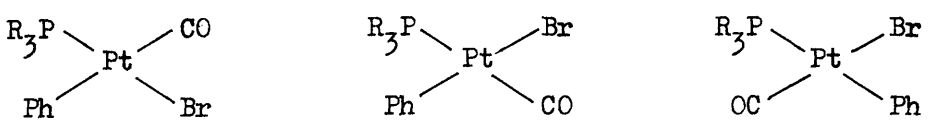
It is not established whether the lithium iodide reaction involves intermediate formation of cis $(Ph_2MeP)Pt(CO)I_2$ which then eliminates CO.

The thermal instability of similar iodide complexes compared to their chloride and bromide analogues has been reported previously[296] Heating cis $(Et_3P)Pt(CO)I_2$ causes loss of carbon monoxide, and the reaction of cis $(Et_3P)Pt(C_2H_4)Cl_2$ with lithium iodide results in loss of ethylene. In both cases $((Et_3P)PtI_2)_2$ was reformed.

The explanation of this behaviour may be a combination of the greater trans effect and the greater nucleophilicity of coordinated iodide compared to the other halides. The greater trans influence (though not necessarily related to the trans effect) of I^- is evidenced by the order of decrease of $\nu(CO)$: $Cl^- > Br^- > I^-$. (Table 12). The relevance of the nucleophilicity of the halogen is indicated by one possible mechanism for CO loss.



Passing carbon monoxide through benzene solutions of di-μ- bromo-diphenyl-bis(phosphine)diplatinum complexes XXIII resulted in two terminal carbonyl stretching modes in the IR spectrum. These bands are of equal intensity and it is concluded that they arise from equal amounts of two isomers of $(R_3P)PtPh(CO)Br$. The ^1H NMR of the dimethylphenylphosphine derivative is very complex, consistent with the presence of more than one isomer. There are three possibilities for these isomers.

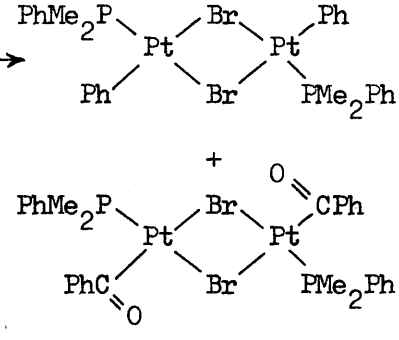


Examples of mononuclear platinum complexes are known with CO trans to

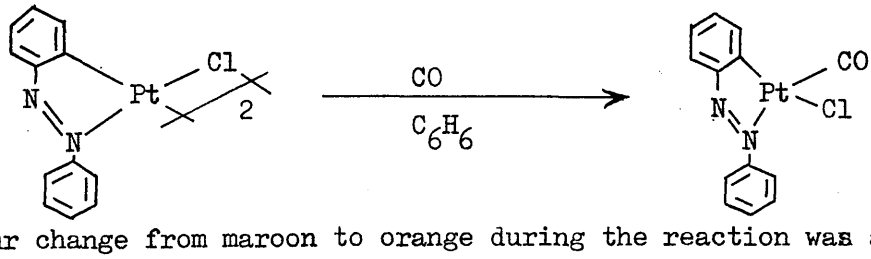
halogens[296] and trans to phosphine[57,297] despite its high trans effect. The high trans effect of phosphine, however, and the knowledge that only <u>cis</u> $(R_3P)Pt(CO)Cl_2$ complexes are produced indicate that the isomer of $(R_3P)PtPh(CO)Br$ which is absent is that with CO trans to the phosphine. It should be pointed out that all three isomers may be present with accidental overlap of peaks occurring.

The carbonyl bands persist in solution for 12 hours with little decrease in intensity but the compounds were not sufficiently stable to be isolated as pure solids. Addition of hexane, presaturated with carbon monoxide, to cooled solutions of the diphenylmethylphosphine species resulted in precipitation of an oil which showed both terminal and acyl carbonyl IR bands. The only products isolated on work-up of this material were $((PhMe_2P)Pt(Br)Ph)_2$ and small amounts of the binuclear bromine-bridged acyl complex $((PhMe_2P)PtBr(COPh))_2$. Clearly the mononuclear carbonyl complex is unstable and decomposes predominantly by loss of carbon monoxide and to a minor extent by insertion of carbon monoxide.

$$((PhMe_2P)Pt(Ph)Br)_2 \xrightarrow[C_6H_6]{CO} (PhMe_2P)Pt(CO)PhBr \xrightarrow{\text{hexane}}$$



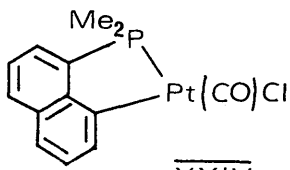
$((Azb)PtCl)_2$ reacted readily with carbon monoxide at room temperature.



A colour change from maroon to orange during the reaction was accompanied by the appearance of a single band at 2118cm^{-1} in the IR spectrum. The orange

complex chloro-(2-(phenylazo)phenyl)(carbonyl)platinum(II) was isolated either by removal of benzene under vacuum at low temperature or by addition of hexane, presaturated with carbon monoxide, to the benzene solution. Although the isolation of the pure crystalline solid was possible by this means, it was found that heating the compound in absence of solvent or in benzene solution regenerated $((azb)PtCl)_2$ by loss of carbon monoxide.

The single carbonyl peak indicates that (azb)Pt(CO)Cl is a single isomer. The configuration is likely to be that shown since ν(Pt-Cl), 298 cm^{-1}, matches that found for phosphine derivatives where the configuration is better established. The formation of a single isomer probably reflects the much greater trans effect of the aromatic group compared to the azo link of the phenylazophenyl ligand. The production of one isomer is in line with the preparation of complexes $(R_3P)Pt(CO)X_2$ described above but contrasts with $(R_3P)PtPh(CO)Br$ and with complex XXIV which contains the internally metallated dimethyl(1-naphthyl)phosphine ligand[57].



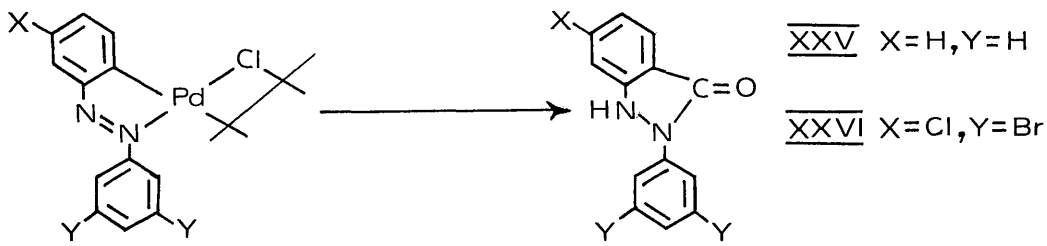
XXIV

In both these cases the mixture of isomers produced may be ascribed to the similarity in trans effect of phosphine and aryl[106].

Several mononuclear platinum complexes have been reported to contain carbon monoxide trans to a nitrogen donor ligand[298-300]. (Azb)Pt(CO)Cl has in fact been briefly reported in a U.S. Patent[139] which also describes the palladium analogue. The reaction of carbon monoxide with $((azb)PdCl)_2$ has been investigated in the course of this work but no extensive reaction took place on passing carbon monoxide through a benzene suspension of this compound. After 68 hours the majority of starting material remained though small amounts of 1 H-2 phenyl-3 indazolone, XXV, were isolated from the pale

yellow solution.

Use of DMSO, the only solvent in which $((azb)PdCl)_2$ dissolves readily, did lead to a rapid reaction at room temperature. Again no palladium carbonyl species was isolated. Instead decomposition to 1 H-2phenyl-3indazolone and palladium metal took place. The reaction of the substituted azobenzene complex di-μ-chloro-di(2-(3',5'-dibromo-phenylazo)4-chlorophenyl)dipalladium proceeds in the same way to give XXVI.



XXV X=H,Y=H

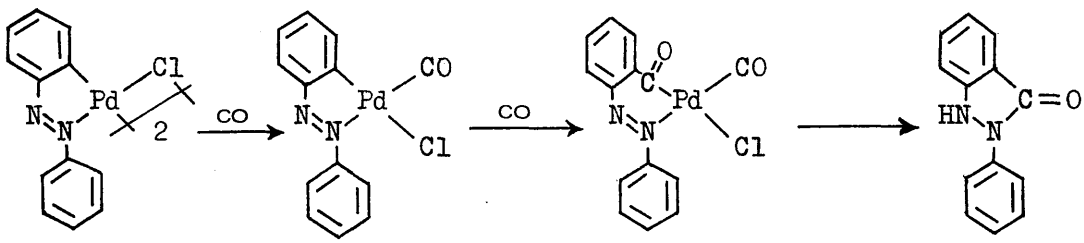
XXVI X=Cl,Y=Br

The mild conditions and probable generality of this reaction make it a good route to substituted 1H-2 aryl -3indazolones; compounds which are difficult to prepare by other means. The preparation of this heterocyclic product complements the isolation of 2-phenylbenzotriazole-1-oxide from the reaction of $(PhN{:}NC_6H_4)HgCl$ and nitrosyl chloride. As with that reaction, the use of specifically substituted 2-(arylazo)aryl complexes (made possible by the synthetic route described in Chapter I) can lead to specifically substituted organic derivatives. Although the pure indazolone compounds were isolated only in ~ 50% yield it is thought that the reaction is a high yield process. The work-up involves an extraction from which complete recovery of product is difficult for small amounts of starting material.

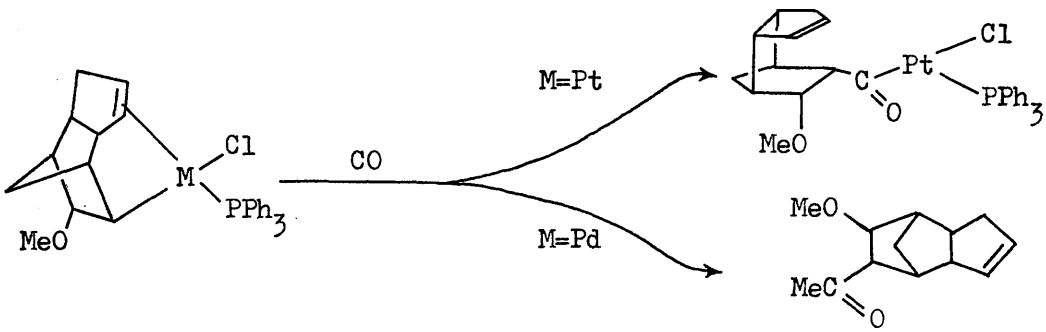
The N-H bond in the indazolones is clearly indicated by ν(N-H) at $\sim 3100 cm^{-1}$. The source of this proton is probably the solvent or small amounts of water present in the solvent. In the DMSO reaction of $((azb)PdCl)_2$ a very small amount of dimethyl sulphone was detected from the reaction. This was identified by mass measurement using mass spectrometry and from its IR spectrum. The significance of the presence of this compound is

not clear and indeed it may be a solvent impurity (despite distillation of DMSO prior to use).

A series of 1H-2aryl-3indazolones has in fact been obtained previously by Takashi and Tsuji[97] from high pressure, high temperature reactions with substituted azobenzene palladium complexes in protonic solvents. The present reaction obviates the need for these drastic conditions which were probably necessitated by the insolubility of $((azb)PdCl)_2$ in the solvents employed in that work. The mechanism proposed for the reaction involves formation of a mononuclear palladium complex followed by carbonyl insertion.

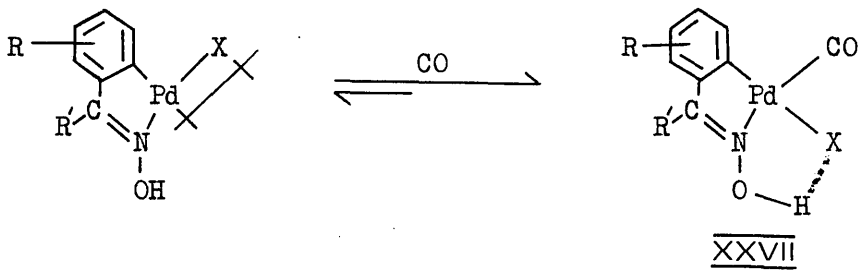


The intermediacy of the mononuclear carbonyl complex is supported by the isolation of its platinum analogue in the present work. The decomposition in the palladium case is not surprising on the basis of the lower stability shown by organo-palladium complexes compared to their platinum analogues. This is illustrated by the carbonylation reaction,



Ref. 297

In fact although IR evidence indicates that chlorine bridges of palladium complexes are cleaved by carbon monoxide[301], only one stable series of compounds, XXVII, has been obtained by this method.



XXVII

Ref. 53

In addition to the expected greater instability of the 2-(phenylazo)-phenyl palladium complex, the greater ease of insertion into the Pd-C bond implied by the palladium reaction is also expected. Chatt and Booth have shown that palladium alkyl and aryl complexes require lower temperature and pressure than platinum complexes to effect carbonyl insertion.[288]

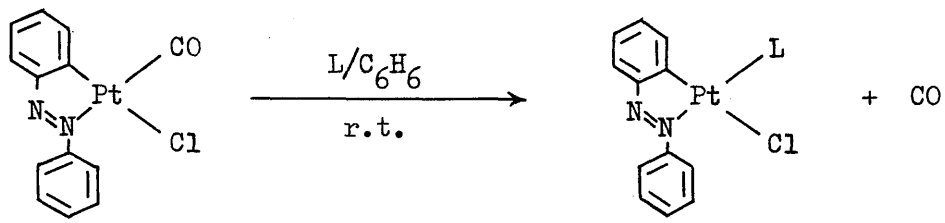
The production of 1H-2phenyl-3indazolone from ((azb)PdCl) has been related to the cobalt carbonyl catalysed carbonylation of azobenzene[142] This reaction also produces 1H-2phenyl-3indazolone. It is therefore a reasonable supposition that an ortho-metallated intermediate is produced which undergoes insertion of carbon monoxide and cleavage of the organic product with regeneration of the catalytic cobalt carbonyl species. Carbonylation of $(azb)Co(CO)_3$ in ethanol, however, has been found to give 2-carbomethoxyhydrazobenzene[137] but it is thought that this derivative would be converted to the indazolone under the conditions employed for the catalytic reaction.

The various mononuclear platinum(II) carbonyl complexes described above were employed in a series of reactions whose aim was to clarify some of the factors which lead to carbonyl insertion at platinum(II).

Carbonyl Insertion and Displacement Reactions.

Reaction of (azb)Pt(CO)Cl with Lewis Bases. (Azb)Pt(CO)Cl was treated

with a series of Lewis Bases of varying basicity and bulkiness, some of which are known to produce insertion with other platinum[287,289,290] or iridium[293,264,273] carbonyl complexes. In each case addition of benzene solutions of the ligand to a benzene solution of (azb)Pt(CO)Cl resulted in a rapid colour change from orange to maroon. The compounds isolated showed that CO displacement had occurred.

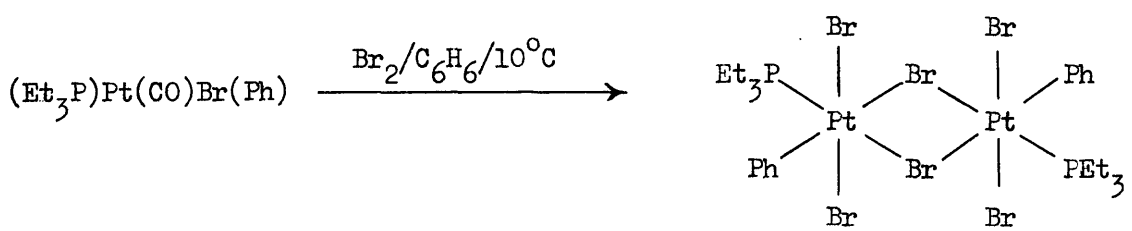


L = $PMePh_2$, PEt_3, $AsPh_3$, $NH_2CH_2CHMe_2$

Several of these products were identical to those produced by bridge cleavage of the chloro-(2-(phenylazo)phenyl)platinum dimer. The addition of $AsPh_3$ was made dropwise and at low temperature, conditions known to favour insertion[287,290]. IR spectroscopy indicated that the addition was accompanied by a gradual decrease in intensity of the ν(CO) band. No evidence for an intermediate acyl complex was obtained, so a fast insertion/decarbonylation reaction can be ruled out.

Reactions of $(R_3P)Pt(CO)Br(Ph)$.

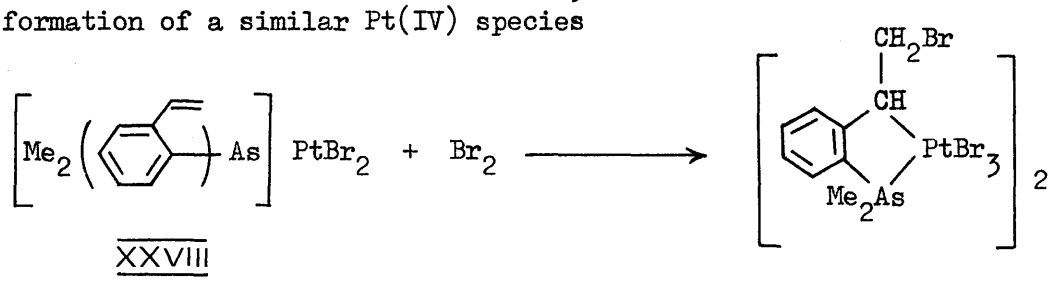
With Br_2. Dropwise addition of a benzene solution of bromine to $(Ph_3P)Pt(CO)Br(Ph)$, prepared in situ, led to loss of CO and precipitation of a light orange material. This product, a novel bromine-bridged organoplatinum(IV) complex, di-μ-bromo-tetrabromodiphenyl-bis(triethylphosphine)diplatinium(IV), is produced quantitatively.



The stereochemistry is not yet established but is depicted as shown because of the report that oxidative addition of bromine leads to trans configuration of entering bromine atoms[26]. The identity of the product is based on elemental analysis and the presence of peaks in the IR spectrum characteristic of aromatic groups. Furthermore, the same product is isolated for addition of bromine to $((Et_3P)PtBr(Ph))_2$.

Heating $((Et_3P)Pt(Ph)Br_3)_2$ in dichloromethane or dichloroethane solution results in reductive elimination of bromobenzene (identified by G.L.C.) and formation of $((Et_3P)PtBr_2)_2$.

Platinum (IV) bridged compounds containing a metal carbon bond are uncommon. Bennett has shown that bromination of XXVIII leads to formation of a similar Pt(IV) species[302]



XXVIII

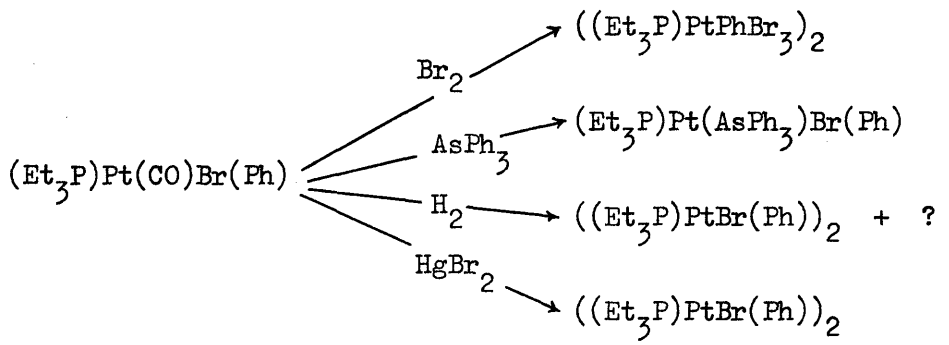
The exact position of bromination of the olefin is not known but this structure is favoured by comparison with the X-Ray Structure of a similar gold complex[303]. Interestingly, on standing in organic solvents the Pt-C bond is not cleaved in the same way as in the present work. Instead the starting material is re-formed.

With $AsPh_3$. The dropwise addition of benzene or methylene chloride solutions of $AsPh_3$ to $(Et_3P)Pt(CO)Br(Ph)$ prepared in situ in these solvents, was monitored by IR spectroscopy. The intensity of the two ν(CO)bands decreased as the addition proceeded but no bands appeared in the acyl carbonyl region. Complete loss of carbon monoxide resulted and the IR spectrum of the product is consistent with the formation of (Et_3P)-$Pt(AsPh_3)Br(Ph)$.

With H_2. IR spectroscopy indicated the gradual decrease in intensity of the ν(CO) bands associated with $(Et_3P)Pt(CO)Br(Ph)$ and the simultaneous growth of a broad band at 1740 cm^{-1}. This reaction mixture produced almost quantitative recovery of $((Et_3P)PtBr(Ph))_2$ and a very small amount of a viscous liquid whose IR showed the presence of the same broad band at 1740 cm^{-1}. This band is higher than that normally associated with ν(CO) in organic compounds. The material has not yet been identified but its presence may indicate that some insertion occurred.

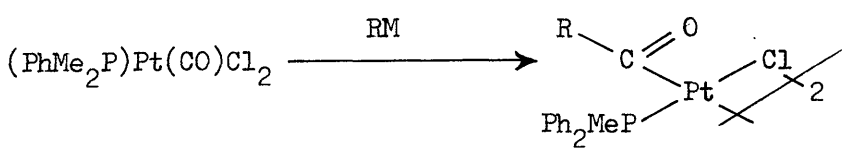
With $HgBr_2$. Addition of mercuric bromide to a benzene solution of $(Et_3P)Pt(CO)BrPh$ prepared in situ resulted again in loss of carbon monoxide. IR showed that the products isolated from the reaction were a mixture of $((Et_3P)PtBrPh)_2$ and mercuric bromide.

These reactions of $(Et_3P)Pt(CO)Br(Ph)$ are summarised in the scheme below.



Reactions of $(PhMe_2P)Pt(CO)Cl_2$ with $Hg(o\text{-tolyl})_2$ and Ph_4Sn.

The room temperature reaction between chloro(carbonyl)bis-(diphenylmethylphosphine)platinum and either di(ortho-tolyl)mercury or tetraphenyltin resulted in insertion.



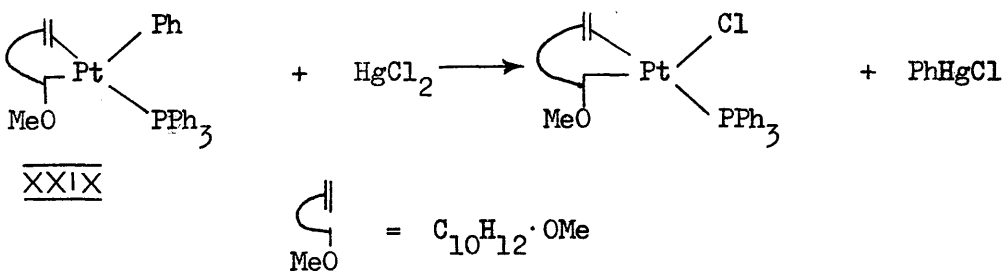
R = Ph M + Ph_3Sn

R = (o-tolyl) M = (o-tolyl)Hg

The production of these chloride bridged platinum acyl complexes by this method has been observed by Cross and Wardle for the diorganomercurials[150] but the tin route had not previously been investigated. This route has the distinct practical advantage that the by-product, triphenyltin chloride, can be easily separated because it is much more soluble than the bridged acyl complex. The solubilities of organomercuric chlorides and the platinum acyl complex are very similar.

Insertion of isocyanide promoted by a variety of metal arylating agents (e.g. Ph_2Hg, Ph_4Sn and Ph_4Pb) has been shown to lead to analogous palladium dimers[304].

The mechanism of these carbonyl insertions is not certain and although both the mercury and the tin routes produce the same type of acyl complex, there is no evidence that the mechanisms are the same. Oxidative addition is favoured[150] for the mercurial reaction and has also been postulated for the mode of cleavage of the phenyl group from XXIX by mercuric chloride[305].



XXIX

= $C_{10}H_{12}\cdot OMe$

This mechanism is supported by the observation that mercuric chloride reacts with Vaska's complex by oxidative addition. In this case a stable Ir^{III} complex is isolated[45] reflecting the greater stability of octahedral Ir^{III} species over Pt^{IV} species. The evidence for isolable compounds containing Pt-Hg bonds is less well established. The literature contains two reports of a stable platinum complex $(Ph_3P)_2Pt(X)HgX$[261,306] Repetition of one of these preparations (as described in Chapter II) in the course of the present work, failed to substantiate the formation of

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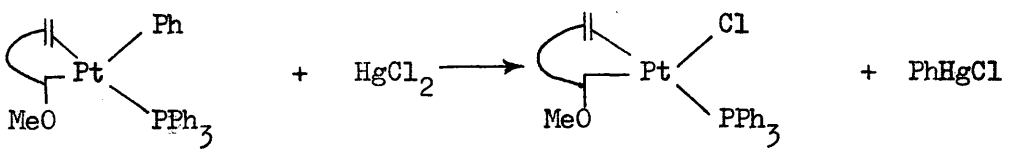
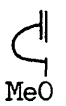


XXIX



= $C_{10}H_{12}\cdot OMe$

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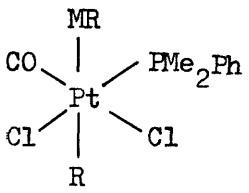
this complex. Nyholm's reported preparation of Pt-Pt bonds has also been disputed[261,307].

The absence of any well documented examples of stable compounds containing platinum-mercury bonds does not, however, preclude the possibility of carbonyl insertion <u>via</u> an unstable Pt(IV) intermediate.



The information on the reaction course of organotin complexes with platinum complexes is equally sparse. Trimethyltin hydride is known to produce a stable Pt(IV) complex most probably by oxidative addition.

$$(diphos)Pt(MMe_3)Cl + Me_3SnH \longrightarrow (diphos)PtH(SnMe_3)_3 + H_2 + Me_3MH + Me_3MCl$$

Ref. 308

M = Si,Ge

In addition, many complexes containing platinum-tin bonds are known and Pt(IV) intermediates arising from oxidative addition at platinum are thought to be involved[309].

Nevertheless, although oxidative addition mechanisms are likely, reactions involving bimolecular electrophilic substitution cannot yet be ruled out. Such reactions are well established for both organomercury[166] and organotin derivatives.[310]

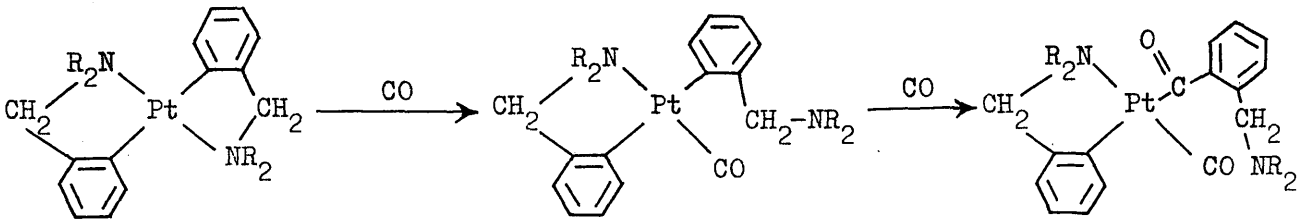
<u>Rationalisation of the reactions of the platinum carbonyl complexes.</u>

The stereochemistry of the starting carbonyl is likely to be important in determining whether carbonyl insertion takes place. It is probable that a cis arrangement of carbon monoxide and the metal-carbon bond will favour insertion and may be a prerequisite for it. The presence

of this configuration for (azb)Pt(CO)Cl is indicated by comparison with the phosphine complexes (azb)Pt(PR_3)Cl where the configuration can be more certainly determined.

No insertion, however, took place when (azb)Pt(CO)Cl was reacted with a variety of Lewis Bases of varying bulk and basicity. Formation 5-membered rings by internal metallation is known to be favoured over 6-membered ring formation(eg ref 89) The occurrence of carbonyl elimination may in this case, therefore, be controlled by the chelate ring strain which would result from production of a 6-membered ring by CO insertion. This argument has been used to explain the failure to observe any insertion with several of the internally metallated platinum complexes shown in Table 11. The effect of ring size may also explain the occurrence of insertion with $(Ph_3P)_2Rh(C_6H_4PPh_2)$ which gives a 5-membered ring, whereas no insertion was found with $((PhO)_3P)_3RuCl(C_6H_4OP(OPh)_2)$ where a 6-membered ring would result. This may not be an effect of ring size, but may rather reflect the different electronic configuration and coordination number of these molecules.

The insertion found with some complexes containing 5-membered rings[298] militates against arguments based on ring size. $(C_6H_4CH_2NR_2)_2Pt$ contains a similar 5-membered internally metallated ring to (azb)Pt(CO)Cl, but under mild conditions coordination of one molecule of CO with displacement of nitrogen is followed by coordination of a second CO molecule and insertion.[298]



R = Et, Me

Table 11. Comparisons of carbon monoxide reactions with complexes containing internally metallated rings.

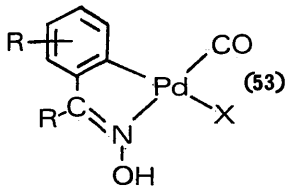
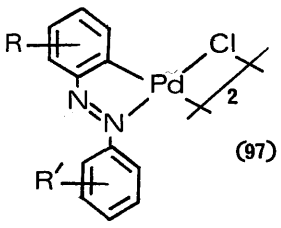
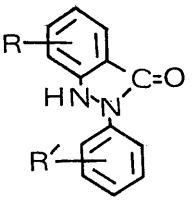
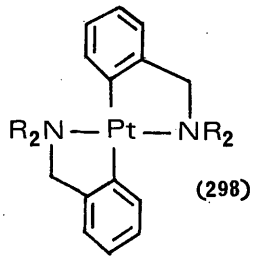
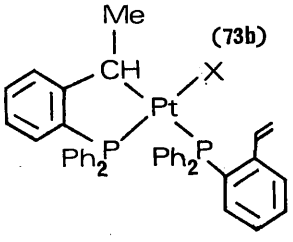
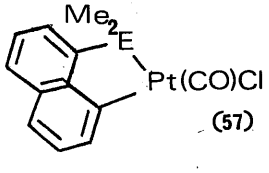
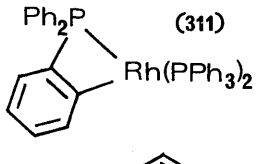
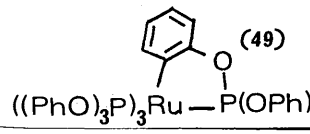
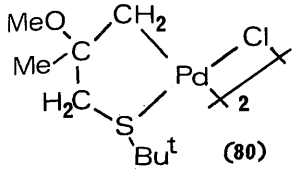
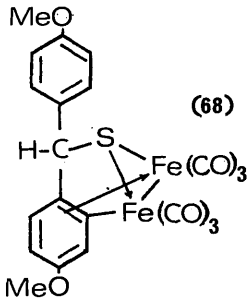
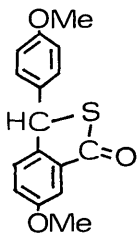
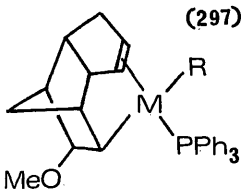
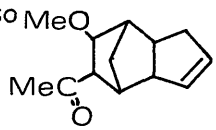
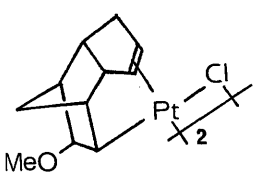
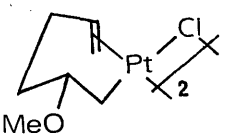
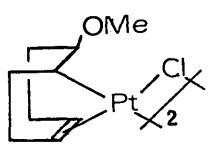
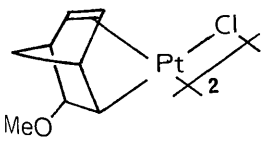
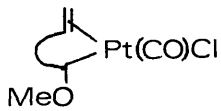
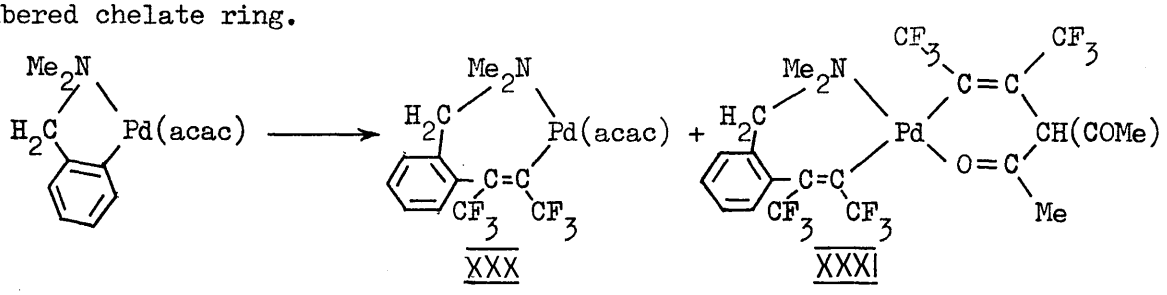
Complex(Ref.)	Pressure (atm.)	Solvent	Temperature	Remarks
	1	$CHCl_3$	R.T.	No evidence of insertion Loss of CO above 100°C X = Cl,Br,I
	150	EtOH	100°C	Decomposition to 
	100	H_2O	100°C	
	1	THF	R.T.	Insertion observed. No insertion in cis complex. Decomposition to colloidal platinum carbonyl at high temperature and pressure
	1	Various (unstated)	R.T.	No insertion observed.
	1	C_6H_6	80°C	No insertion reported. E = P,As
	13.6	C_6H_6	60°C	Insertion observed. Reaction performed with added Ph_3P
				No insertion observed.

Table 11 continued.

Complex (Ref.)	Pressure (atm.)	Solvent	Temperature	Remarks
 (80)	1	MeOH	R.T.	Decomposition to Bu^tSCH_2-C(Me)CH_2 (with low recovery) and Pd metal. No products isolated which indicate insertion has occurred.
 (68)	-	-	-	Addition of Lewis Bases, L, causes decomposition to  Iron acyl intermediate isolated when L = Ph_3P
 (297)	1	(C_6H_6) (CH_2Cl_2)	R.T.	M=Pt (R=Cl,Me,Ph insertion into ring; R=Me, insertion into Pt-Me; R=Ph, no insertion into Pt-Ph) M=Pd Decomposition to 
    (312)	1	$ChCl_3$	-20°	No insertion observed though IR indicates formation of intermediates of the type. 

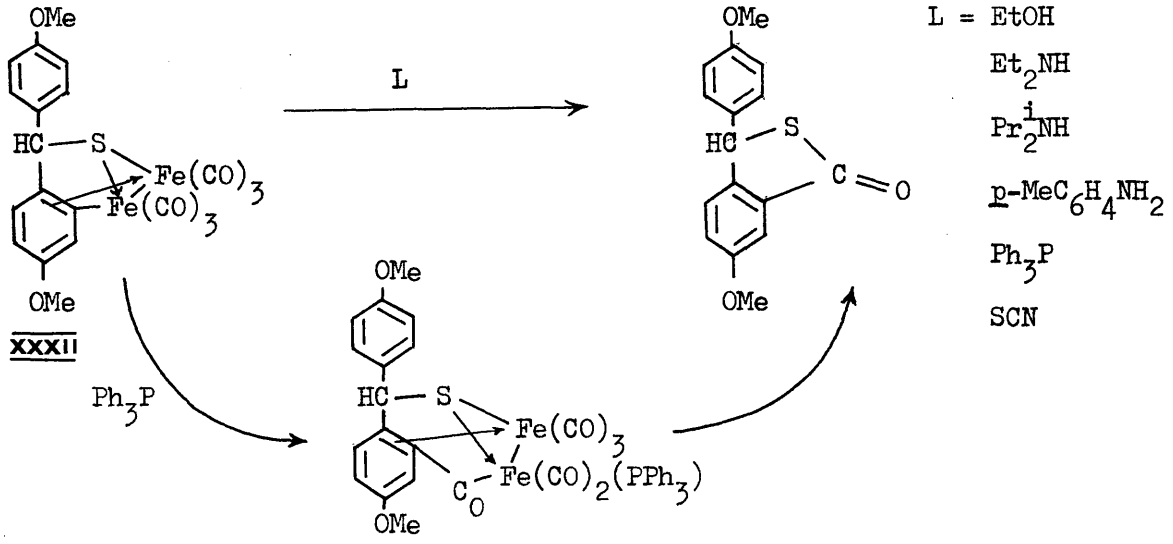
Insertion of CF_3-C=C-CF_3 into the same ring system has been reported [51] and in this case two of the products XXX and XXXI contain a seven membered chelate ring.



XXX XXXI

Furthermore, the insertion implied by the decomposition products from the reaction of $(azbPdCl)_2$ with carbon monoxide indicates that in this case too the presence of a 5-membered ring does not preclude insertion.

Carbonyl insertion was also implied from the decomposition product, from the reaction of XXXII with a variety of Lewis Bases.[68]



XXXII

With Ph_3P the intermediate acyl complex could be isolated but was found to decompose on heating. This study contrasts with the failure to observe insertion with (azb)Pt(CO)Cl, the only other internally metallated system where the effects of Lewis Bases have been investigated. The two systems, however, are not closely enough related to draw any significant conclusions from the different behaviour.

The evidence therefore indicates that the failure of (azb)Pt(CO)Cl to undergo CO insertion is not due either to unfavourable configuration

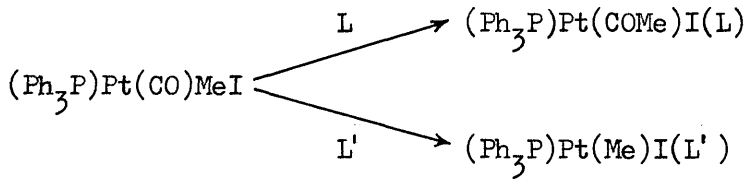
of groups about the metal or to the steric constraint of the chelate ring. Nevertheless, the specialised form of this molecule and the varied observations in other internally metallated complexes (Table 11) point to the need to base conclusions on results from the more conventional molecules $(R_3P)Pt(CO)Br(Ph)$ and $(PhMe_2P)Pt(CO)X_2$.

In each case the reaction of $(R_3P)Pt(CO)Br(Ph)$ proceeded predominantly by loss of carbon monoxide. Either replacement of CO by a Lewis Base (as with (azb)Pt(CO)Cl) or dimerisation of an intermediate species occurred. The only evidence for insertion with these complexes comes from two reactions. In the preparation of $(PhMe_2P)Pt(CO)BrPh$, formation of a small amount of the bromine bridged acyl complex, $((PhMe_2P)Pt(COPh)Br)_2$, occurred and was probably promoted by coordination of a second molecule of CO. The reaction of hydrogen with $(Et_3P)Pt(CO)Br(Ph)$ also produced a very small amount of material which, though as yet unidentified, appears to be the result of insertion. The reactions of $(PhMe_2P)Pt(CO)Cl_2$ with $(o\text{-tolyl})_2Hg$ or Ph_4Sn, gave complete insertion and the mercurial reaction seems quite general.

The predominance of substitution over insertion in the wide variety of reactions studied is difficult to rationalise. Lewis Base addition (even with compounds known to produce insertion in other systems) indicates that the nature of the added ligand is not the crucial factor. Nor does it appear that a mechanism involving oxidative addition leads invariably to insertion since the bromination reaction did not produce insertion (though the organo-mercury and tin reactions may be examples where oxidative addition does produce insertion).

A disparity between these reactions and other platinum(II) carbonyl systems is evident. When the present study was well advanced a report appeared on the interaction of $(Ph_3P)Pt(CO)MeI$ with Lewis Bases.[290] This

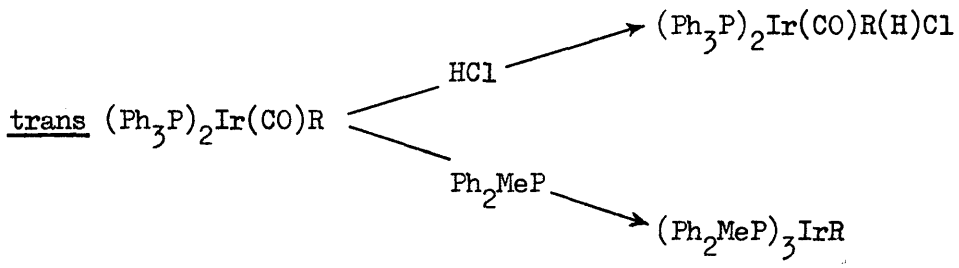
showed that carbonyl displacement or insertion may occur depending on the nature of the incoming ligand.



The evidence suggests that both steric and electronic effects are important. P donor ligands appear more likely to give rise to substitution than either nitrogen or arsenic ligands. This is probably an electronic effect. Within the range of arsenic ligands themselves, the bulkiness of the ligand was claimed to be important, insertion being favoured by increasing bulkiness.

The extent of the displacement reaction in the present work is therefore surprising. Even slow addition of $AsPh_3$ at low temperature, the conditions claimed by Mawby as most favouring insertion[290], produced only CO substitution with $(Et_3P)Pt(CO)Br(Ph)$. The reason for the disparity between these series of reactions is most probably related to the nature of the organic group bonded to the metal. The addition of Lewis Bases leading to CO insertion has been demonstrated mainly for alkyl platinum complexes[264,287]. The predominance of carbonyl substitution in the present study may, therefore, be associated with the known greater ease of insertion into platinum alkyl compared to platinum aryl bonds[288].

Two reactions of the 16-electron complex <u>trans</u> $(Ph_3P)_2Ir(CO)R$ where both oxidative addition and ligand association fail to produce insertion provide an interesting comparison. Oxidative addition of hydrogen chloride produces a stable carbonyl complex and gives no insertion or substitution. Addition of excess diphenylmethylphosphine, however, promotes loss of carbon monoxide (and replacement of Ph_3P)[314].



What is certain in the present study is that reaction, either by Lewis Base addition or oxidative addition, did invariably occur. Both processes increase the number of valence electrons to 18. It was hoped at the outset that in such cases carbon monoxide insertion would reduce the electron count at the metal by two, producing 16-electron molecules. The observed carbon monoxide loss also achieves this result though the reasons that it is the favoured process are not clear. The configuration of the intermediates and, as mentioned above, the nature of the organic group may be crucial. Since the formation of 18-electron intermediates involves population of the lowest antibonding orbital, it has been suggested[315] that if this orbital has more metal than carbonyl character then insertion will occur, while if the orbital has more ligand character then substitution will occur.

SPECTROSCOPIC EXAMINATION OF THE COMPLEXES.

IR Spectra.

The terminal carbonyl stretching mode for monocarbonyl complexes gives rise to a single band. This band has been observed for the platinum complexes described in this Chapter and the values, which fall around 2100cm^{-1}, are recorded in Table 12. The spectra of samples run as KBr discs sometimes show more than one peak and this can be attributed to solid state effects.

The complexes $(PhMe_2P)Pt(CO)X_2$ show a trend in ν(CO), Cl > Br > I which is normal for this type of complex[296] and parallels the decrease in electronegativity of the halogens. Greater retrodative π bonding from metal to CO is possible as the halogen becomes less electronegative and results in the observed decrease in ν(CO). The effect of the acceptor (or donor) properties of the halogens is less clear. Cl^- has been shown to be a π- donor[316] and the observed trend could be explained if the π - donor ability of the halogens increases down the group. If this increase does not hold then the effect must be less important than electronegativity since the opposite order of ν (CO) would be found.

The assignment of ν (Pt-CO) for these complexes is more difficult and has not been attempted. Adams assigned this mode to two bands ~500cm^{-1} [317] This has subsequently been challenged[318] and the higher band is now identified as ν(Pt-C). For the complexes <u>cis</u> $(Et_3P)Pt(CO)X_2$ the frequency of this band decreased in the order Cl > Br > I [296] In agreement with this the complexes <u>cis</u> $(PhMe_2P)Pt(CO)X_2$ show intense sharp bands, assigned to ν(Pt-C) at 538cm^{-1}, 529cm^{-1} and 511cm^{-1} for the chloride, bromide and iodide respectively. This is the opposite order to that expected for the increase in Pt-C bond order I > Br > Cl. It is thought[318] that this reversal of order arises because the effect of

substituting a more massive halogen outweighs the increase in bond order.

These observations for ν(CO) and ν(Pt-C) mean that ν(CO) is a good reflection of M-C bond order (and trans influence) while ν(Pt-C) is not.

^{1}H NMR Spectra.

The complexes-$(PhMe_2P)Pt(CO)X_2$ (X = Cl,Br, or I) have been investigated by NMR. Insolubility proved a problem for cis-$(PhMe_2P)Pt(CO)Cl_2$ and in fact Shaw found it too insoluble to obtain its ^{1}H NMR spectrum.[200] It is found, however, that the complex is readily soluble in sym tetrachloroethane. This is a general observation that platinum complexes which are very insoluble in a range of other solvents show remarkable solubility in sym-tetrachloroethane. This solvent cannot be used with cis $(PhMe_2P)Pt(CO)I_2$ since ready loss of CO occurs, probably promoted by solvent attack.

The ^{1}H NMR spectrum of these complexes shows a doublet for the methyl resonance with platinum satellites (^{195}Pt, I=$\frac{1}{2}$, 33.8%). The parameters extracted from the spectra are presented in Table 13 and are typical of $PhMe_2P$ complexes[200]. Double irradiation experiments determined the ^{31}P and ^{195}Pt chemical shifts and established the value of ^1J(Pt-P) as well as the relative signs of ^1J(Pt-P), ^3J(Pt-H) and ^2J(P-H). The like signs of ^1J(Pt-P) and ^3J(Pt-H) and the opposite sign for ^2J(P-H) was also found for the methylphosphine complexes described in Chapter 2 and appears to be quite general for such compounds.

Solubility and stability difficulties prevented measurement ^1J(Pt-P) for the series of complexes in the same solvent. Nevertheless, no variation in the size of ^1J(Pt-P) for cis $(PhMe_2P)Pt(CO)Br_2$ was observed for determinations made in benzene or sym tetrachloroethane.

This suggests little or no solvent dependence for $^{1}J(Pt-P)$ and indicates the validity of comparisons between the series of halide complexes although different solvents were used. A decrease in the size of $^{1}J(Pt-P)$ is observed to follow the order $Cl > Br > I$ paralleling the decrease in $\nu(CO)$ observed in the IR. Since $PhMe_2P$ and CO are trans to the halogens and since both $^{1}J(Pt-P)$ and $\nu(CO)$ are a measure of trans influence it seemed likely that these two quantities would correlate well. This is demonstrated by a plot of $^{1}J(Pt-P)/\nu(CO)$ for these complexes which gives a good straight line graph (Figure 14).

A more surprising correlation between $^{1}J(Pt-P)$ and (Pt-P) bond length has been claimed by Pidcock[319]. The present bond length from the X-Ray Crystal Structure of <u>cis</u>$(PhMe_2P)Pt(CO)Cl_2$ currently in progress appears to confirm the validity of the correlation for this compound also.

<u>X-Ray Diffraction studies on $(Ph_3P)Pt(CO)Cl_2$ and $(PhMe_2P)Pt(CO)Cl_2$.</u>

Bond lengths determined by X-Ray Crystallography have been used as a measure of trans influence[104]. A high trans influence is generally ascribed to a ligand if the bond trans to it is unusually long either compared to the sum of the covalent radii or other bond lengths for the atoms in question.

The method is not without limitations. Since the bond length differences involved are very small, accurate data is required to raise these differences above the level of experimental error. Furthermore, intramolecular interactions can appreciably affect bond lengths. It appears, too, that different groups may have different sensitivity to structural trans influence. The evidence suggests that Pt-Cl bond length, for example, can distinguish between relatively small differences in ligands of high trans influence but is relatively insensitive to differences in ligands of low trans influence[104].

It is clear, therefore, that the best way to examine these effects is in a closely related series of compounds such as the square planar platinum complexes cis L_2PtXY where X may be varied while Y is kept constant or L varied while X and Y are kept constant. The compounds $(Ph_3P)Pt(CO)Cl_2$ and $(Ph_2MeP)Pt(CO)Cl_2$ prepared in the course of this work form part of such a series, and the structures have been investigated by L. Muir, K. Muir and R. Walker with a view to extending the structural data on trans influence in platinum (II) complexes. The main aspects of the structure of cis $(Ph_3P)Pt(CO)Cl_2$ have been published[320] and the important bond lengths are contained in Table 14 which also displays comparative data for other cis $(R_3P)Pt(L)Cl_2$ complexes. The significant features of the structure (which shows the expected square planar cis geometry) include the very short Pt-Cl (trans to CO) distance. This indicates that CO has a low trans influence. In fact CO has been claimed to have "no" trans influence[321]. Perhaps more significant is the short Pt-Cl (trans to P) distance and the long (Pt-P) distance compared to the weighted mean values of the corresponding distances in the other cis $(R_3P)Pt(L)Cl_2$ complexes. These differences may be interpreted in two ways. Either the CO molecule exerts a cis influence which strengthens the Pt-Cl bond and weakens the Pt-P bond, or Ph_3P forms a weaker bond to platinum and has a lower trans influence than PEt_3, PMe_3 and $PPhEt_2$. The lower trans influence of Ph_3P compared to Et_3P is indicated by values of $^1J(Pt\text{-}P)$.[107]

Detection of cis influence from Pt - Cl bond lengths indicates that the trend (if any) is opposite to that of trans influence[103] Despite the claim by Zumdahl and Drago that cis influence is comparable with trans influence[322] the bulk of evidence favours the view that the cis influence is much smaller than the trans influence. A cis influence

series has been determined from n.q.r. studies.[323] This study also indicates that Pt-Cl bond length is more sensitive to the trans ligand than the cis ligand while Cl^{35} resonance frequencies are sensitive to changes in both the cis and trans ligands. This observation makes the possible cis influence reflected by Pt-Cl bond length of $(Ph_3P)Pt(CO)Cl_2$ all the more fascinating.

The structure of $(PhMe_2P)Pt(CO)Cl_2$ has not yet reached the stage of refinement which makes comparisons meaningful.

Mass Spectra

Many of the compounds prepared in this chapter were examined by mass spectrometry. Molecular ions were observed in most cases but not for the complexes $(PhMe_2P)Pt(CO)X_2$. In these compounds the heaviest fragment corresponded to $(PhMe_2P)PtX_2$. Fragment identification was facilitated by the distinctive platinum isotope pattern (Figure 15). Fragments containing both platinum and chlorine or bromine had isotope patterns modified by the presence of these halogens as shown pictorially by Haake[329] (for Pt^+, $PtCl^+$, $PtCl_2^+$, $PtBr^+$ and $PtBr_2^+$) and in Figure 15. The peak heights of the isotope patterns in this Figure and in Figure 16 (for $PdCl_n$ (n=0-4) combinations) were calculated by computer.

Table 12. I.R. spectroscopic data for the platinum carbonyls.

Compound	(CO) (cm^{-1})	Medium
$(C_6H_5N_2C_6H_4)Pt(CO)Cl$[a]	2114	$CHCl_3$
	2118	C_6H_6
$(PhMe_2P)Pt(CO)Cl_2$[b]	2110	$CHCl_3$
$(PhMe_2P)Pt(CO)Br_2$	2105	$CHCl_3$
$(PhMe_2P)Pt(CO)I_2$	2093	$CHCl_3$
$(PhMe_2P)Pt(CO)Br(Ph)$	(2090 (2108	C_6H_6
$(Et_3P)Pt(CO)Br(Ph)$	(2090 (2108	C_6H_6
$((PhMe_2P)Pt(COPh)Cl)_2$	1628	KBr
$((PhMe_2P)Pt(COPh)Br)_2$	1629	KBr
$((PhMe_2P)Pt(COC_6H_4\text{-}o\text{-}Me)Cl)_2$	1625	KBr

[a] ν(Pt-Cl) = 298cm^{-1} (KBr disc)

[b] ν(Pt-Cl) = 348,300cm^{-1} (KBr disc)

Table 13. ^{1}H, ^{31}P and ^{195}Pt parameters for cis $(PhMe_2P)Pt(CO)X_2$ complexes.

Compound	Chemical Shift					Coupling Constants(Hz)		
	$^{1}H(Me)$	^{31}P		^{195}Pt		$^{2}J(P-H)$	$^{3}J(Pt-H)$	$^{1}J(Pt-P)$
	τ	$\Xi(^{31}P)/Hz$[d]	p.p.m.[e]	$\Xi(^{195}Pt)/Hz$[d]	p.p.m.[f]			
cis$(PhMe_2P)Pt(CO)Cl_2$[a]	7.74[c]	24,288,127	+ 13.0	12,845,331	+ 611	12.0	37.0	2844
cis$(PhMe_2P)Pt(CO)Br_2$[a]	7.88	24,288,194	+ 10.3	12,842,162	+ 858	12.0	38.0	2810[a] 2810[b]
cis$(PhMe_2P)Pt(CO)I_2$[b]	8.48	24,288,078	+ 15.1	12,835,241	+ 1398	12.0	38.0	2745

[a] $Cl_2CHCHCl_2$ solution [b] C_6H_6 solution [c] $CDCl_3$ solution [d] Resonance frequency at a polarising field strength such that the T.M.S. resonance is exactly 60 MHz [e] Positive shift indicates a resonance to high field of H_3PO_4 reference ($\Xi(^{31}P)$ = 24,288,444 Hz) [f] Positive shift indicates a resonance to high field of cis $(Me_2S)_2PtCl_2$ reference (ref. 277) ($\Xi(^{195}Pt)$ = 12,853,188 Hz).

Table 14. Comparative Bond Lengths (A) in cis-$PtCl_2L(R_3P)$ Complexes.*

L	R_3P	Pt-Cl (trans L)	Pt-Cl (trans P)	Pt-P	Ref.
PMe_3	PMe_3	2.376(12)[a]	2.376(12)[a]	2.248(9)[a]	324
C(OEt)NHPh	PEt_3	2.365(5)	2.368(7)	2.240(8)	325
$C(NPhCH_2)_2$	PEt_3	2.362(3)	2.381(3)	2.234(3)	326
CNPh	PEt_3	2.333(12)	2.365(11)	2.238(8)	325,327
CNEt	$PPhEt_2$	2.314(10)	2.390(8)	2.244(8)	328
Weighted means		-	2.379(3)	2.237(2)	
CO	PPh_3	2.277(3)	2.342(3)	2.279(3)	

[a] Mean values

* Reproduced from Ref. 320

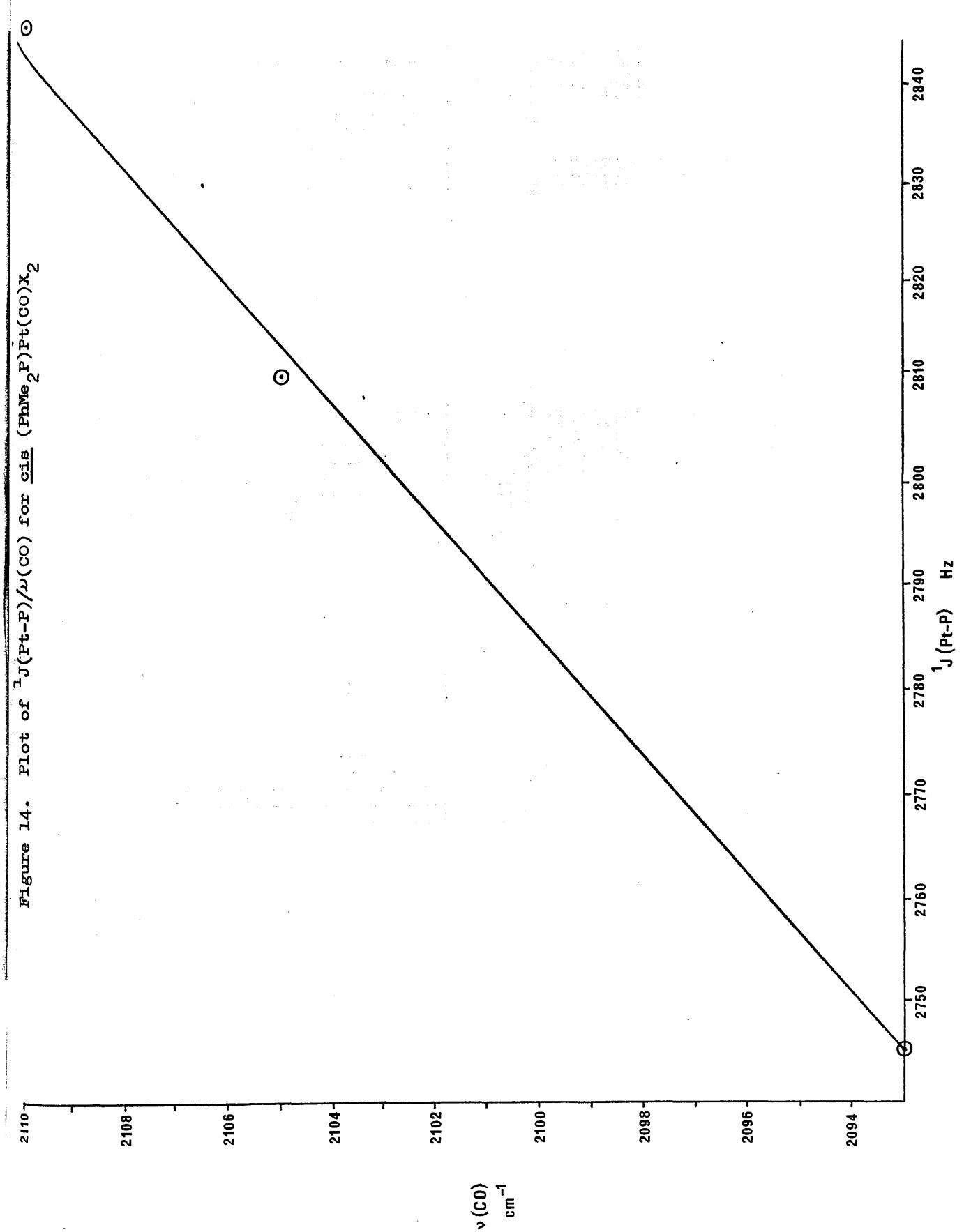
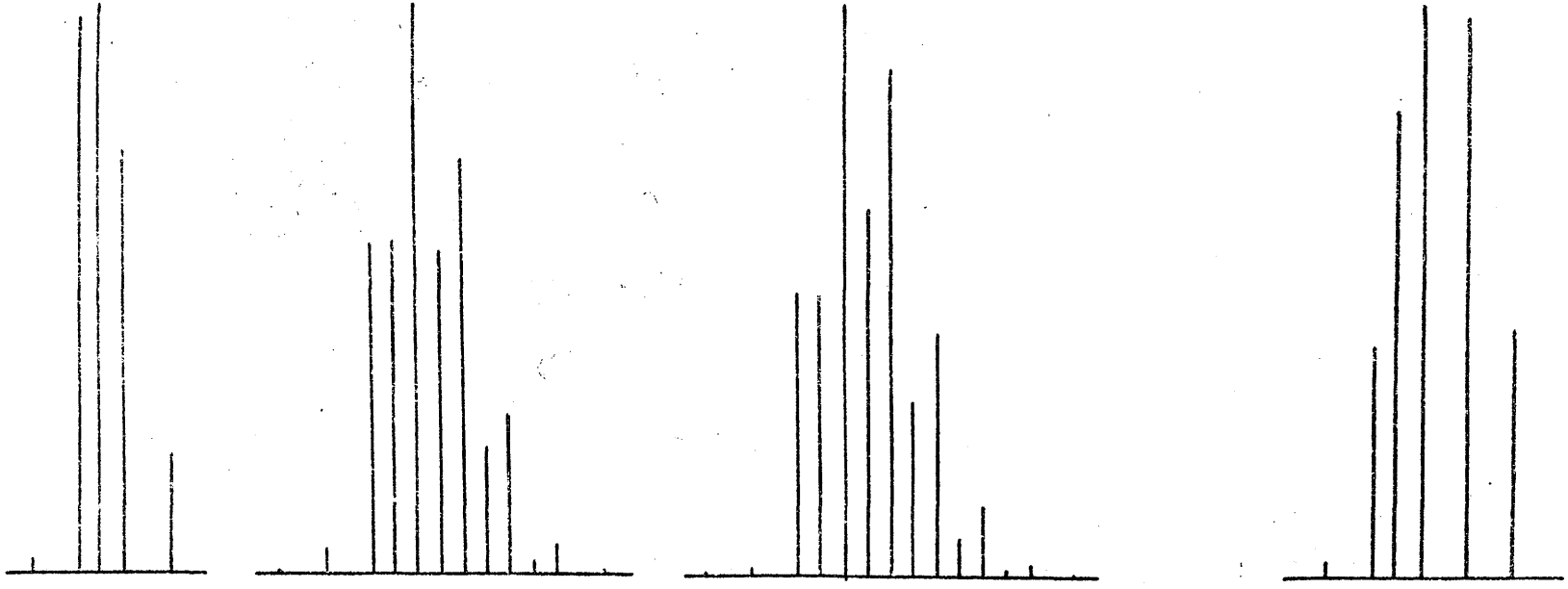
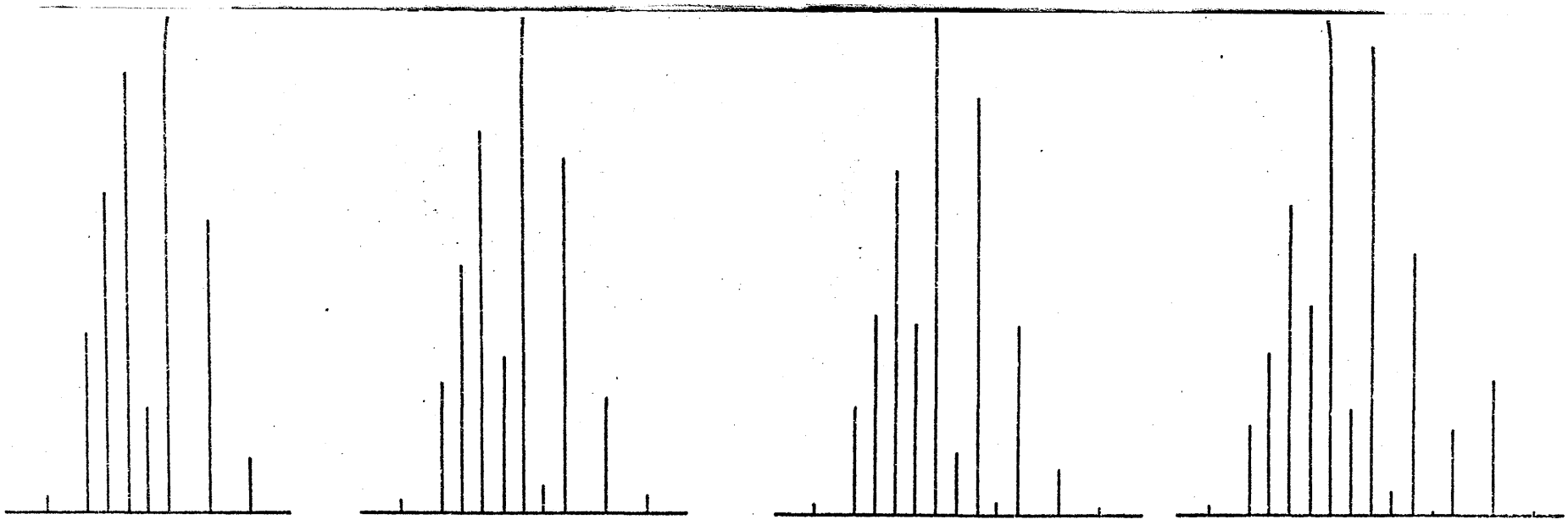


Figure 14. Plot of $^{1}J(Pt-P)/\nu(CO)$ for cis $(PhMe_2P)Pt(CO)X_2$

Figure 15. Isotope combinations for platinum and chlorine, and isotope pattern of palladium.



Pt		$PtCl_3$		$PtCl_4$		Pd	
Mass	Abundance(%)	Mass	Abundance(%)	Mass	Abundance(%)	Mass	Abundance(%)
190	0.0127	295	0.0221	330	0.0186	102	0.96
191	0.000	296	0.0000	331	0.0000	103	0.00
192	0.78	297	1.3774	332	1.1639	104	10.97
193	0.000	298	0.0000	333	0.0000	105	22.23
194	32.9	299	58.5198	334	49.5683	106	27.33
195	33.8	300	58.7595	335	49.3947	107	0.00
196	25.3	301	100.0000	336	100.0000	108	26.71
197	0.000	302	57.1103	337	64.0111	109	0.00
198	7.21	303	73.3383	338	88.8843	110	11.81
		304	18.5024	339	31.1072		
		305	27.9768	340	43.4911		
		306	1.9981	341	6.7187		
		307	5.4425	342	12.1943		
		308	0.0000	343	0.5442		
		309	0.4262	344	1.8405		
				345	0.0000		
				346	0.1161		



Pd Cl

Mass	Abundance(%)
137	2.7001
138	0.0000
139	31.7290
140	62.5241
141	86.8644
142	20.2564
143	100.0000
144	0.0000
145	57.5464
146	0.0000
147	10.7615

$Pd Cl_2$

Mass	Abundance(%)
172	2.1071
173	0.0000
174	25.4434
175	48.7928
176	75.8095
177	31.6155
178	100.0000
179	5.1214
180	70.1909
181	0.0000
182	22.9473
183	0.0000
184	2.7208

$Pd Cl_3$

Mass	Abundance(%)
207	1.6916
208	0.0000
209	20.9746
210	39.1719
211	67.4793
212	38.0724
213	100.0000
214	12.3346
215	82.3604
216	1.3320
217	36.6790
218	0.0000
219	8.1528
220	0.0000
221	0.7077

$Pd Cl_4$

Mass	Abundance(%)
242	1.3882
243	0.0000
244	17.6615
245	32.1445
246	60.9498
247	41.6564
248	100.0000
249	20.2436
250	94.1707
251	4.3723
252	51.9949
253	0.3541
254	16.4416
255	0.0000
256	2.7482
257	0.0000
258	0.1881

EXPERIMENTAL.

Preparation of chloro-carbonyl(2-(phenylazo)phenyl)platinum(II).

Di-μ-chloro-di-(2-(phenylazo)phenyl)diplatinum (0.0978g, 1.2m moles) was dissolved in benzene (100ml) and carbon monoxide bubbled through the solution. After 4 hours the solution had developed an orange colour and a solution IR showed the presence of a single peak at 2118 cm^{-1}. Benzene was removed under vacuum (0.1mm Hg) leaving an orange powder (0.1010g, 98%).

An analytically pure sample was prepared by adding hexane, saturated with carbon monoxide, to a freshly prepared benzene solution of the sample. Carbon monoxide was slowly bubbled through the solution and the addition of hexane was continued until orange crystals of chloro-carbonyl(2-(phenylazo)phenyl)platinum(II) formed (M.p. 116-136°C(dec). Found: C,35.77; H,2.16; N,6.41% $C_{13}H_9OPtCl$ requires C,35.51; H,2.06; N,6.37%).

Carbonylation of di-μ-chloro(2-(phenylazo)phenyl)dipalladium.

(a) In Benzene. Carbon monoxide was bubbled through a suspension of di-μ-chloro(2-(phenylazo)phenyl)dipalladium (0.4995g, 7.7m moles) in benzene (175ml). After 68 hours the precipitate, which was yellow in colour, was removed by filtration (0.3392g, 5.3m moles) and washed with petroleum ether giving a dark yellow residue of starting material.

Concentration of the yellow filtrate by rotary evaporation produced cream material identified by comparison with an authentic sample as 1H-2phenyl-3indazolone(0.07g, 2% M.p. 189-194°C lit[97] 204-205°C)

(b) In DMSO. Di-μ-chloro(2-(phenylazo)phenyl)dipalladium (0.8072g, 1.3m moles) was dissolved in freshly distilled DMSO (50ml) with heating. Carbon monoxide was passed through the solution at room temperature for 5 hours. The solution was added to water (200ml) and extracted with

ether (2x500ml). Filtration of this extract removed black colloidal material (0.2189g). The filtrate was dried ($MgSO_4$) and solvent removed. Sublimation of the fawn product (80°C/closed vacuum at 0.1mm Hg) produced very small amounts of azobenzene, colourless crystals of dimethylsulphone (0.001g, IR identical with an authentic sample. Found: M(Mass Spectrum) 94.008_7 $C_2H_6SO_2$ requires 94.008_8) and 1H-2phenyl-3indazolone (0.2043g, 39% M.p. 204-206°C lit 204-205°C [97] Found: M(Mass Spectrum) 210 $C_{13}H_{10}N_2O$ requires 210).

Carbonylation of di-μ-chloro(2-(3',5'-dibromophenylazo)4-chlorophenyl)-dipalladium.

Di-μ-chloro(2-(3',5'-dibromophenylazo)4-chlorophenyl)dipalladium (0.1443g 0.13m moles) was dissolved in freshly distilled DMSO (25ml) with heating. Carbon monoxide was passed at room temperature for 1 hour. The colour of the solution changed from maroon to brown during the reaction. The DMSO solution was added to water (200ml) and extracted with ether (4x200ml). The straw coloured ether extract was dried ($MgSO_4$) filtered and the ether removed giving a pale fawn product which was recrystallised from chloroform to give ivory coloured crystals of 1H-2(3',5'dibromophenyl)-6chloro-3indazolone (0.0259g, 50% M.p. 235-240°C Found: C,39.06; H,2.20% M(Mass Spectrum ^{35}Cl, ^{79}Br) 400 $C_{13}H_7Br_2ClN_2O$ requires C,38.80; H,1.75% M 400)

Reactions of chloro-carbonyl(2-(phenylazo)phenyl)platinum(II).

(a) With triethylphosphine. Chloro-carbonyl(2-(phenylazo)phenyl)-platinum(II) (0.0914g, 0.21m moles) was dissolved in benzene (25ml) under a nitrogen atmosphere. Triethylphosphine (1.2ml) was added by syringe. There was no visible colour change to the orange solution. The solution was set aside for 1 hour at room temperature then heated at 60°C for

10 minutes. Removal of solvent by rotary evaporation left an orange viscous liquid which smelled strongly of phosphine. Petroleum ether (B.p. 40-60°C) was added and on standing orange prisms formed, identified by comparison with an authentic sample as trans-chloro-(2-(phenylazo)phenyl)bis(triethylphosphine)platinum(II) (0.1063g, 80% M.p. 127-130°C)

(b) With diphenylmethylphosphine. Addition of diphenylmethylphosphine (0.0426g, 0.21m moles) in benzene (20ml) to a solution of chloro-carbonyl-(2-(phenylazo)phenyl)platinum(II) (0.0919g, 0.21m moles) in benzene (20ml) gave an immediate colour change from orange to maroon. Removal of solvent and recrystallisation from ethanol produced maroon crystals, identified by comparison with an authentic sample as chloro-diphenylmethylphosphine(2-(phenylazo)phenyl)platinum(II) (0.1085g, 83% M.p. 196-198°C)

(c) With isobutylamine. Addition of isobutylamine (0.0157g, 0.22m moles) in benzene (5ml) to a solution of chloro-carbonyl-(2-(phenylazo)phenyl)platinum(II) (0.0822g, 0.19m moles) in benzene (20ml) produced an immediate colour change from orange to maroon. Removal of solvent and recrystallisation from ethanol produced maroon needles, identified by comparison with an authentic sample as chloro-isobutylamine (2-(phenylazo)phenyl)platinum(II) (0.0396g, 45% M.p. 140-150°C(dec). Found: C,39.88; H,4.24; N,8.61% $C_{16}H_{20}N_3PtCl$ requires C,39.63; H,4.16; N,8.66%)

(d) With triphenylarsine. Chloro-carbonyl(2-(phenylazo)phenyl)-platinum(II) was prepared in situ by bubbling carbon monoxide through a suspension of di-μ-chloro-di-(2-(phenylazo)phenyl)diplatinum

(0.0100g, 0.012m moles) in benzene (5ml) for 4 hours. A solution IR of the resultant orange solution showed the characteristic ν(CO) band at 2118cm^{-1}. The solution was cooled to ~ 10°C and this temperature maintained during the dropwise addition of a solution of triphenylarsine (0.0085g, 0.027m moles) in benzene (2.5ml). The addition was followed by IR. The band at 2118cm^{-1} diminished in intensity and no band in the acyl carbonyl region was observed. The reaction was accompanied by a colour change to maroon. Removal of solvent and recrystallisation from ethanol produced maroon crystals of chloro-triphenylarsine-(2-(phenylazo)phenyl)platinum(II) (0.0145g, 84%. M.p. 245-247°C Found: C,49.64; H,3.62; N,4.11% $C_{30}H_{24}N_2AsPtCl$ requires C,50.19; H,3.37; N,3.90%)

Formation of di-μ-chloro-di-(2-(phenylazo)phenyl)diplatinum.

In solution. When a benzene solution of chloro-carbonyl-(2-(phenylazo)phenyl)platinum(II) was heated to reflux or allowed to stand for long periods at room temperature maroon crystals formed.

In absence of solvent. A few crystals of chloro-carbonyl-(2-(phenylazo)phenyl)platinum(II) were heated in an open vessel at 90°C for 1 hour. A colour change to maroon was observed.

In both cases the maroon product was identified, by comparison of its IR spectrum with an authentic sample, as di-μ-chloro-di-(2-(phenylazo)phenyl)diplatinum.

Preparation of (dimethylphenylphosphine)platinum complexes.

Preparation of cis dichlorobis(dimethylphenylphosphine)platinum(II)

Platinous chloride (8.2402g, 31.1m moles) and dimethylphenyl-phosphine (8.8153g, 62.4m moles) were refluxed under nitrogen for 19 hours.

The cream crystalline material produced was filtered. Recrystallisation from methanol gave colourless crystals of cis dichloro(dimethylphenylphosphine)platinum(II) (15.604g, 92%. M.p. 193-195°C, lit[200] 199-200°C)

Preparation of dichloro-di-μ-chloro-bis(dimethylphenylphosphine)-diplatinum(II)

Platinous chloride (1.2637g, 4.8m moles) was added to a solution of cis dichlorobis(dimethylphenylphosphine)platinum(II) (2.5605g, 4.7m moles) in sym tetrachloroethane (100ml). The solution was refluxed under nitrogen for 4 hours. No $PtCl_2$ remained and the solution was deep orange coloured. (If the temperature of the solution was just below the B.p. of sym tetrachloroethane, the reaction was incomplete even after 16 hours). The solution was filtered and reduced in volume, by rotary evaporation, to 15ml. Addition of hexane caused the precipitation of canary yellow crystals of dichloro-di-μ-chloro-bis(dimethylphenylphosphine)diplatinum(II) (1.728g, 89%. M.p. 233-237°C, lit[200] 215-230°C(dec). Found: C,23.81; H,2.98% $C_{16}H_{22}P_2Pt_2Cl_4$ requires C,23.66; H,2.73%).

Preparation of dibromo-di-μ-bromo-bis(dimethylphenylphosphine)-diplatinum(II)

Metathesis of dichloro-di-μ-chloro-bis(dimethylphenylphosphine)-diplatinum(II) using lithium iodide gave pale orange crystals of dibromo-di-μ-bromo-bis(dimethylphenylphosphine)diplatinum(II) (83%, M.p. 202-205°C)

Preparation of di-iodo-di-μ-iodo-bis(dimethylphenylphosphine)-diplatinum(II)

Dichloro-di-μ-chloro-bis(dimethylphenylphosphine)diplatinum(II) (1.2878g, 1.6m moles) in methanol (250ml) was refluxed for 30 minutes

with lithium iodide (1.1850g,8.9 m moles). Filtration of the orange product and recrystallisation from chloroform gave glistening orange-red crystals of di-iodo-di- μ -iodo-bis(dimethylphenylphosphine)diplatinum(II) (1.1689g, 80%. M.p. 275-277°C, lit 275-277°C[280] Found: C,16.41, H,2.00; I,43.05% $C_{16}H_{22}P_2Pt_2I_4$ requires C,16.37; H,1.89; I,43.23%).

Preparation of di- μ -bromo-diphenyl-bis(dimethylphenylphosphine)diplatinum(II).

Dibromo-di- μ -bromo-bis(dimethylphenylphosphine)diplatinum(II) (6.3040g, 6.4m moles) was added to benzene (100ml) under nitrogen. An ether solution of phenyl lithium (40ml/0.305 molar) was added dropwise to the stirred solution over a period of 30 minutes. The colour of the solution darkened gradually to black and some material remained unreacted. No solid material remained after stirring for a further 2½ hours, and Gilman's Colour Test showed all the phenyl lithium had been consumed.

Nevertheless, 100ml of water was added and the organic layer separated, dried (anhydrous $MgSO_4$), filtered and the solvent removed. A semi-crystalline, dark brown, oily material remained. Extraction with acetone and concentration to 5ml gave, on cooling, firstly colourless crystals thought to be diphenylbis(dimethylphenylphosphine)platinum (0.1287g, 3% M.p. 214-216°C) followed by fawn crystals of di- μ -bromo-diphenyl-bis(dimethylphenylphosphine)diplatinum(II) (1.0065g, 16%. M.p. 204-206°C Found: C,34.54; H,3.52; Br,16.36% $C_{28}H_{32}P_2Pt_2Br_2$ requires C,34.30; H,3.39; Br,16.30%)

Preparation of cis dichloro-carbonyl(dimethylphenylphosphine)platinum(II)

Carbon monoxide was passed through a stirred suspension of dichloro-di- μ -chloro-bis(dimethylphenylphosphine)platinum(II) (1.4098g, 1.8m moles) in benzene(50ml). After 15 minutes the solution was clear

and colourless. The reaction was continued for a further 2 hours and a mass of colourless microcrystalline material formed. Removal of solvent by rotary evaporation and recrystallisation of the residue from benzene produced colourless prisms of cis dichloro-carbonyl(dimethylphenylphosphine)platinum(II) (1.2357g, 82%. M.p. 176-188°C, lit 181-190°C(dec)[200] 184-191°C[280] Found: C,25.51; H,2.77; Cl,17.02% $C_9H_{11}POPtCl_2$ requires C,24.97; H,2.74; Cl,16.62%)

Preparation of cis dibromo-carbonyl(dimethylphenylphosphine)platinum(II).

In a similar way, dibromo-di-μ-bromo-bis(dimethylphenylphosphine)-platinum(II) (1.3528, 1.4m moles) reacted with carbon monoxide in benzene (50ml) to produce colourless prisms of cis dibromo-carbonyl(dimethylphenylphosphine)platinum(II) (1.2136g, 83%. M.p. 249-259°C)

Preparation of cis di-iodo-carbonyl(dimethylphenylphosphine)platinum(II)

Carbon monoxide was passed through a stirred suspension of di-iodo-di-μ-iodo-bis(dimethylphenylphosphine)platinum(II) (0.4692g, 0.4m moles) in toluene (15ml) for 3 hours. Addition of an equal volume of hexane resulted in the formation of yellow needles of the product. Cooling the solution produced a little starting material and more yellow crystalline cis di-iodo-carbonyl(dimethylphenylphosphine)platinum(II) (0.3122g, 64%. M.p. 92-97°C, lit[280] 92-94°C. Found: C,18.03; H,1.96; I,40.93%. $C_9H_{11}POPtI_2$ requires C,17.55; H,1.93; I,41.21%)

Reactions of the carbonyl complexes.

Formation of di-iodo-di-μ-iodo-bis(dimethylphenylphosphine)diplatinum(II).

(a) A solution of cis dichloro-carbonyl(dimethylphenylphosphine)platinum(II) (1.0040g, 2.2m moles) and lithium iodide (3.338g, 29 m moles) in acetone

(40ml) was refluxed for 20 minutes. The solution changed from colourless through pale green and yellow to a deep orange colour. The solution was filtered and solvent removed leaving an orange residue. This product was washed with water and ether. The yellow water washings darkened very quickly and deposited after 8 hours an unidentified material with a silvery sheen.

Recrystallisation of the product from acetone yielded orange crystals identified, by comparison with an authentic specimen, as di-iodo-di-μ-iodo-bis(dimethylphenylphosphine)diplatinum(II) (0.7735g, 61%. M.p. 275-277°C)

(b) Solutions of cis dichloro-carbonyl(dimethylphenylphosphine)platinum(II) in sym tetrachloroethane at room temperature or benzene when heated deposited orange-red material identified by comparison with an authentic sample as di-iodo-di-μ-iodo-bis(dimethylphenylphosphine)diplatinum(II) (M.p. 275-277°C)

Interaction of $((PhMe_2P)PtBr(Ph))_2$ and CO.

Di-μ-bromo-diphenylbis(dimethylphenylphosphine)diplatinum (0.9000g, 0.9m moles) was dissolved in benzene (50ml). Carbon monoxide was bubbled through the fawn coloured solution. After 1½ hours the colour of the solution had paled slightly and the IR spectrum contained two new bands at 2090cm^{-1} and 2108cm^{-1}. After a total of 4½ hours, hexane (presaturated with CO) was added to the cooled benzene solution through which the CO flow was maintained. This caused precipitation of a pale green viscous oil which showed both terminal and acyl carbonyl bands. Addition of more hexane caused precipitation of a cream powder identified as starting material.

Addition of hexane to the viscous oil caused it to solidify.

Recrystallisation from benzene produced two sets of crystals which were identified from a further recrystallisation as starting material (M.p. and IR spectrum identical with an authentic sample) and colourless crystals di-μ-bromo-dibenzoylbis(dimethylphenylphosphine)diplatinum (0.0935g, 10% M.p. 154-156°C, IR spectrum corresponds closely with that of $((PhCO)(PhMe_2P)PtCl)_2$ Found: M(Mass Spectrum ^{79}Br, ^{195}Pt) 1034 $C_{30}H_{32}Br_2O_2P_2Pt_2$ requires M 1034).

Reactions of $(Et_3P)Pt(CO)Br(Ph)$.

With Br_2. $(Et_3P)Pt(CO)Br(Ph)$ was prepared in situ by passing CO through a solution of $((Et_3P)PtBr(Ph))_2$ (0.1405g, 0.15m moles) in benzene (15ml) for 1 hour. The solution was left for 18 hours and the passage of CO was repeated for a further $1\frac{1}{2}$ hours. The IR spectrum contained two bands of equal intensity at 2090cm^{-1} and 2108cm^{-1}.

To this solution was added, dropwise, a solution of bromine (0.048g, 0.15m moles) in benzene (3ml). The addition was accompanied by a decrease in the carbonyl IR bands. After 5 minutes a yellow precipitate appeared. This was filtered and washed with benzene to produce yellow microcrystalline di-μ-bromo-dibromo-phenylbis(triethylphosphine)diplatinum(IV) (0.1401g, 75% M.p. 207-208°C Found: C,23.17; H,3.25% $C_{24}H_{40}Br_6P_2Pt_2$ requires C,22.98; H,3.21%)

With $AsPh_3$ a) In Benzene. $(Et_3P)Pt(CO)Br(Ph)$ was prepared in situ by passing CO through a solution of $((Et_3P)PtBr(Ph))_2$ (0.0514g, 0.05m moles) in benzene (5ml) for 1 hour. Two peaks of equal intensity appeared in the IR spectrum 2090cm^{-1} and 2108cm^{-1}. No increase in intensity was observed on passing CO through the solution for a further 2 hours and no change was detected in the spectrum 16 hours after the CO flow was stopped.

$AsPh_3$ dissolved in benzene (10ml) was added to the cooled solution

of $(Et_3P)Pt(CO)Br(Ph)$. The addition was monitored by IR spectroscopy which showed that the addition was accompanied by the disappearance of the terminal carbonyl bands. No evidence for the formation of an acyl carbonyl complex was obtained. Slow evaporation of solvent produced colourless crystals whose IR spectrum was compatible with the formulation of the product as $(Et_3P)Pt(AsPh_3)BrPh$ (0.0652g M.p. 171-178°C)

(b) In Dichloromethane. Passing CO through a solution of $((Et_3P)PtBr(Ph))_2$ (0.0384g, 0.04m moles) in dichloromethane (5ml) again produced two terminal carbonyl bands in the IR spectrum, though in this case they were not fully resolved. Addition of $AsPh_3$ produced the same observations as those described above.

With H_2. $(Et_3P)Pt(CO)Br(Ph)$ was prepared in situ by passing CO through a solution of $((Et_3P)PtBr(Ph))_2$ (0.1198g 0.12m moles) in benzene (15ml) for $1\frac{1}{2}$ hours. Bubbling hydrogen through this solution gave no decrease in intensity of ν(CO) after 15 minutes. A gradual decrease did occur, however, after longer reaction time and was accompanied by the growth of a broad band at 1740cm^{-1}. After 5 hours the original carbonyl bands had disappeared. Slow evaporation of solvent produced fawn coloured crystals which were washed with petroleum ether (B.p. 40-60°C) and identified as $((Et_3P)PtBr(Ph))_2$ (0.1056g M.p. 184-186°C) Evaporation of the petroleum ether washings gave an oil whose IR spectrum in benzene solution showed a strong broad peak at 1740cm^{-1}. The identity of this oil had not yet been established.

With $HgBr_2$. $(Et_3P)Pt(CO)Br(Ph)$ was prepared in situ from $((Et_3P)PtBr(Ph))_2$ (0.1677g 0.18m moles) in benzene (15ml). Mercuric bromide (0.1282g 0.36m moles) in benzene (20ml) was added. The carbonyl bands of $(Et_3P)Pt(CO)Br(Ph)$ were observed to decrease in intensity and disappeared after 24 hours. No acyl carbonyl bands were observed during

the reaction and the IR spectrum of the product produced by slow evaporation of solvent was compatible with a mixture of $HgBr_2$ and $((Et_3P)PtBr(Ph))_2$.

Reactions ofcis dichloro-carbonyl(dimethylphenylphosphine)platinum.

With $(o\text{-}MeC_6H_4)_2Hg$. Di(o-tolyl)mercury (0.4615g, 1.2m moles) was added to a suspension of dichlorocarbonyl(dimethylphenylphosphine)-platinum(II) (0.5158g, 12m moles) in benzene (50ml). The suspension was stirred and after 1 hour gave a clear, colourless solution. 24 hours stirring produced a cream coloured precipitate (0.3743g). This was removed by filtration. Recrystallisation from benzene produced pale yellow clusters of di-μ-chloro-di(o-methylbenzoyl)bis(dimethyl-phenylphosphine)platinum(II) (0.1880g, 15% M.p. 215-217°C) Found: M(Mass Spectrum ^{35}Cl, ^{195}Pt) 974 $C_{32}H_{36}Cl_2O_2P_2Pt_2$ requires M 974)

With Ph_4Sn. A suspension of dichlorocarbonyl(dimethylphenylphosphine)-platinum(II) (0.2789g, 6.5m moles) and tetraphenyltin (0.2693g, 6.3m moles) in toluene (15ml) was stirred under nitrogen for 7 hours. At no time did the solution become clear. The ivory precipitate was filtered and the pale orange filtrate reduced in volume to 10ml by rotary evaporation. After 6 hours an unidentified brick red powder (0.0567g, no melting below 300°C Found: C,17.59; H,2.62%) was filtered from this solution.

Recrystallisation of the ivory precipitate from toluene gave colourless needles of di-μ-chloro-dibenzoylbis(dimethylphenylphosphine)-diplatinum(II) (0.29g, 94% M.p. 220-222°C. Found: C,38.11; H,4.13% $C_{30}H_{32}Cl_2O_2P_2Pt_2$ requires C,38.03; H,3.40%)

Reaction of dibromo-di-μ-bromo-diphenylbis(triethylphosphine)platinum with bromine.

A solution of bromine (0.0198g, 0.13m moles) in benzene (3ml)

was added to a solution of $((Et_3P)PtBr(Ph))_2$ in benzene (10ml). Fine orange needles precipitated after 2 minutes. The solution was left for 18 hours. It is thought that less precipitate was present after this time. The material was filtered and its IR spectrum was found to be identical to the product formulated as $((Et_3P)PtBr_3Ph)_2$ (0.0228g, 14% M.p. 205-207°C)

Interaction of $((Et_3P)PtBr_3(Ph))_2$ with solvents.

In $Cl_2CHCHCl_2$. A sample of $((Et_3P)PtBr_3(Ph))_2$ was refluxed in sym-tetrachloroethane for 17 hours. Addition of petroleum ether produced orange microcrystalline prisms of $((Et_3P)PtBr_2)_2$ (M.p. 207-208°C)

In CH_2Cl_2. A sample of $((Et_3P)PtBr_3Ph)_2$ was refluxed in methylene chloride for 24 hours. The solvent was removed using a rotary evaporator leaving $((Et_3P)PtBr_2)_2$ which was extracted with petroleum ether. G.L.C. examination of this solution showed only a peak corresponding to bromobenzene.

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