

A Thesis

entitled

PALLADIUM AND PLATINUM COMPLEXES

OF

BIS(ALKYLTHIO)ALKANES

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degree of

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by

HUGO TORRENS M.

Department of Chemistry
University of Glasgow
Glasgow G 12 8QQ

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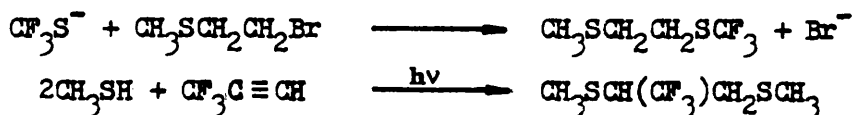
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ABSTRACT

Novel bis(alkylthio)alkanes containing fluorinated substituents in either the sulphur atoms or the bridge have been prepared by metathetical or photochemical reactions e.g.



Photolytic reactions of CH_3SSCH_3 and CH_3SH are considered to proceed via $\text{CH}_3\text{S}\cdot$ radicals.

Interaction of fluorinated bis(alkylthio)alkanes with $[\text{PdCl}_4]^{2-}$ or $[\text{PtCl}_4]^{2-}$ afforded 44 new complexes with the general formula $(\text{RSR}'\text{SR}'')\text{MX}_2$, where R and R'' = CH_3 , CF_3 , C_6F_5 ; R' = CH_2CH_2 , $\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)$, CF_2CH_2 , $\text{CH}(\text{CF}_3)\text{CH}(\text{CF}_3)$, $\text{CH}(\text{CF}_3)\text{CH}_2$; M = Pd, Pt and X = Cl, Br, I; but not all combinations were obtained.

Ligands containing both hydrocarbon and fluorocarbon sulphur substituents, e.g. $\text{CH}_3\text{SC}_2\text{H}_4\text{SCF}_3$, form 1:1 and 2:1 complexes acting as bidentate or monodentate ligands respectively. In the last case only the CH_3S grouping is coordinated and both cis and trans isomers were obtained. No reaction was found to take place between fluorinated sulphides, e.g. CH_3SCF_3 , and either palladium(II) or platinum(II) salts.

Differences in the observed chemical reactions of hydrocarbon and fluorocarbon sulphides and dithioethers towards Pd(II) and Pt(II) are discussed in relation to the sulphur-metal bond.

X-ray studies of $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ have shown that sulphur-platinum bond lengths are slightly shorter than in cis $((\text{p-C}_6\text{H}_4\text{Cl})_2\text{S})_2\text{PtCl}_2$, the most directly comparable structure known. The results have also revealed strong non bonded sulphur-chlorine interactions between pairs of centrosymmetrically related molecules.

In solution, all five membered chelate ring complexes exhibit isomerism due to inversion of configuration at sulphur. The total number of stereoisomers depends also on the substituents in the bridge. Thus for compound containing $\text{RSCH}_2\text{CH}_2\text{SR}$, $\text{RSCH(R)CH}_2\text{SR}$ and RSCH(R)CH(R)SR ligands, 2, 4 and 6 isomers are possible.

N.m.r. spectra of the anti isomers of compounds containing bis(perfluoro-alkylthio)alkanes e.g. $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ show fluorine-fluorine coupling between fluorine atoms in different sulphur substituents. This coupling is rationalized in terms of a 'through space' mechanism. N.m.r. spectra of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtClBr}$ confirm the proposed structural assignment.

The isomeric structure of most platinum compounds have also been tentatively assigned based on n.m.r. parameters.

The effect of variable concentration in the bromine substitution reaction involving $(\text{CH}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ has been monitored by n.m.r. spectroscopy. Substitution takes place, preferentially trans to the CF_3S grouping.

Variable temperature n.m.r. of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ shows that the coalescence temperature of this compound is higher than that found for the corresponding hydrocarbon analogue, probably due to the higher electronegativity and larger mass of the fluorinated substituents.

Dynamic n.m.r. studies of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtI}_2$ found two different intramolecular processes: at 183 K the bridge carbon-carbon bond rotation is sufficiently slow to detect the individual resonances arising from two diastereoisomers of a syn isomer. At high temperature the coalescence of resonances arising from anti and syn structures is discussed in terms of sulphur inversion taking place preferentially at single sulphur atoms.

Platinum chemical shifts determined for several complexes have

been found to be dependent on both the ligands present and the structure of the compounds. The values of $\delta^{195}\text{Pt}$ for different halide complexes seem to follow additive rules. Values of platinum chemical shift for different stereoisomers of a given complex are qualitatively discussed in terms of intramolecular magnetic fields.

Brief studies of reduction and ligand substitution reactions e.g. bis(cyclo-octa-1,5-diene)platinum(0) + $\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3$, were carried out in an attempt to obtain zerovalent platinum complexes with sulphur containing ligands.

CONTENTS

	page
INTRODUCTION	1
<u>A. LIGANDS</u>	
CHAPTER I Ligands	6
<u>B. COMPLEXES</u>	
CHAPTER II Structure and bonding	
Introduction	29
Discussion of results	40
Structure	49
CHAPTER III Dynamic N.M.R.	87
CHAPTER IV Platinum chemical	
shifts	114
APPENDIX A ABX spin systems	146
APPENDIX B Zerovalent platinum	
complexes	152
EXPERIMENTAL	157
REFERENCES	213

INTRODUCTION

INTRODUCTION

Transition metal complexes of bis(alkylthio)ethanes have been known for more than 70 years¹⁻⁵. During this time a continuously growing interest in these compounds has encouraged the syntheses of many new complexes⁶⁻¹⁰ and several kinetic¹¹⁻¹², crystallographic¹³⁻¹⁸ and spectroscopic¹⁹⁻²¹ studies have been published.

In recent years a large effort has been directed to the study of dynamic aspects of dithioether complexes in solution²²⁻²⁶. In 1966, Abel and co-workers²² found that instead of the single n.m.r. resonance expected from a solution of $(\text{CH}_3\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtCl}_2$, two such signals were present. The explanation of this result was based on the presence of two stereoisomers arising from the relative orientations of the methyl substituents attached to the donor sulphur atoms. Thus one syn isomer, in which both sulphur substituents are on the same side of the S-Pt-S plane and one anti isomer, where substituents are in opposite sides, were assumed to be responsible for the n.m.r. spectrum observed. An increase in temperature produced a reversible coalescence of both methyl resonances. In agreement with similar results obtained for sulphide complexes²⁷, the process observed was rationalized invoking inversion of configuration at sulphur atoms²⁵.

Similar conclusions were reached by Cross et al.^{23,26,28} after studying a large series of dithioether complexes of platinum and palladium.

By 1973, the only crystal structure known for this type of complex was that of $(\text{Pr}^i\text{SeC}_2\text{H}_4\text{SePr}^i)\text{PdCl}_2$ for which only one, syn isomer was found in the solid state¹⁴. Hunter and Massey²⁹ reported then that the observed isomerism of this compound in solution involved two different conformers of the syn structure, suggesting that the coalescence of the methylene n.m.r. resonances in the complex was the result of total chelate ring

inversion rather than the result of inversion at selenium atoms.

The suggestion that alternative processes could operate for sulphur and selenium containing compounds stimulated further studies during which inversion of configuration at selenium³⁰ atoms as well as additional examples of ring inversion^{31,32} were reported.

In 1976, however, re-examination of $(\text{Pr}^i\text{SeC}_2\text{H}_4\text{SePr}^i)\text{PdCl}_2$ and other compounds using improved instrumentation, showed conclusively that the coalescence phenomenon observed in the temperature dependent n.m.r. spectra, results from inversion of configuration about the ligand atoms and not from reversal of the chelate ring³³.

At the same time, other research groups studying different aspects of the chemistry of dithioether complexes provided valuable information. The ability of bis(alkythio)alkanes to form trans chelated compounds was studied in relation to the characteristics of the ligands³⁴. X-ray diffraction studies showed the possibility of dithioethers acting as monodentate bridging two metal atoms in complexes of tungsten³⁵. Examples of anti isomers in Cu(I) ¹⁸ and Cr(IV) ¹⁷ were also determined by crystallographic studies which also led to revision of the role of π -bonding in these compounds¹⁷. Rhodium complexes afforded one of the first examples of the dependence of metal chemical shifts on the structure of the ligand³⁶.

In contrast with the vast amount of information of hydrocarbon complexes, and although many bis(alkylthio)ethanes containing fluorine in either the sulphur substituents or the bridge have been prepared and characterised³⁷, nothing was known, before this work, of the properties of such compounds as ligands³⁸.

Unsuccessful attempts to obtain coordination compounds with fluorinated sulphides^{39,40} have been rationalized by the presence of strongly electronegative groups which, presumably, reduce the availability of the sulphur lone pairs for coordination. However, the ability of fluor-

inated thiolates to form bridges between metal atoms is well known⁴¹⁻⁴³, suggesting that sulphur atoms are able to coordinate to metals even when linked to strongly electronegative groupings.

In view of this situation, it was judged desirable to investigate further the possibility of synthesizing complexes with fluorinated dithioethers as ligands.

Having succeeded in obtaining some representative examples of such compounds the work aimed to study firstly, the effects of fluorinated substituents on the platinum-sulphur bond as reflected by bond distances, differences in coalescence temperatures and chemical reactions. Secondly the identification of each stereoisomer present in solution was attempted.

N.m.r. spectroscopy provided evidence which made it possible to identify the structures present in solutions of most compounds. In addition, conformers arising from a rigid five membered ring were observed for the first time and evidence suggesting that inversion of configuration takes place preferentially at single sulphur atoms was obtained. Finally, in view of the increasing interest on metal chemical shifts, a series of ¹⁹⁵Pt chemical shifts were measured; these values were found to be dependent on both the ligand attached to the metal centre and the structure of the complexes. The parameters obtained represent one of the largest series of isomeric platinum chemical shifts described to date.

The discussion of the results obtained during the present work are presented in four chapters dealing respectively with the syntheses of new ligands, bonding and structure of complexes, dynamic nuclear magnetic resonance and platinum chemical shifts.

The experimental techniques, and instrumentation are described in the experimental part which also includes tables with all physical data obtained.

Appendix A describe the parameters used for the solution of the ABX

system in the n.m.r. spectra of $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtX}_2$, X=Cl, Br or I and finally, appendix B presents some experimental results obtained while attempting to synthesize zerovalent platinum complexes.

CHAPTER I

LIGANDS

LIGANDS

Until 1950, compounds containing the SCF_3 moiety were unknown⁴⁴. In that year CF_3SF_5 was synthesized by fluorination of carbon disulphide with cobalt trifluoride⁴⁵ and subsequently other metal fluorides and electrochemical methods were used to prepare a large variety of fluorinated derivatives of sulphur compounds⁴⁶⁻⁴⁹ containing S(IV) or S(VI). The formation of CF_3SSCF_3 , $(\text{CF}_3\text{S})_2\text{Hg}$ and CF_3SH ⁴⁴ opened the possibility of substitution and addition reactions parallel to those of normal organic chemistry and the number of compounds containing $\text{CF}_3\text{S}-$ groups expanded rapidly⁴⁶⁻⁵⁰. The properties and practical applications⁵¹⁻⁵⁵ of these compounds encouraged the study of their chemistry which has merited several reviews⁵⁶⁻⁵⁹. The first fluorinated bis(alkylthio)alkane was reported in 1961 by Harris and Stacey⁶⁰ as a product from the reaction of trifluoromethane-thiol and hexafluoropropene.

Later, Sharp et al.^{37,61} employing photochemical reactions and Peach et al.⁶² using fluorinated thiolates greatly expanded the work on these compounds. A list of all fluorinated dithioethers known to date is presented on page 26

Some fluorinated dithioethers used in this work have been reported before; others were prepared for the first time and the discussion of preparation and properties of these new compounds forms the content of this section.

The preparation of hydrocarbon dithioethers is well documented⁶³⁻⁶⁷ and for a large range of compounds it involves simple, straightforward reactions. Such normally standard procedures, when used to obtain fluorinated analogues, often fail to produce the desired compounds and alternative routes have had to be devised. The method most frequently

used in order to obtain symmetric dithioethers involves the interaction of a suitable alkyl dihalide, normally a bromide⁶⁷, with sodium or potassium thiolates. Alternatively, reactions involving the formation of thiolates in situ⁶⁸ have been successfully used in this work, (see page 10). Similarly, fluorinated substituents at the sulphur atom have been incorporated by the reaction of the hydrocarbon halide with suitable metal thiolates^{39,62}. These methods are illustrated by reactions I, II and III in figure 1.

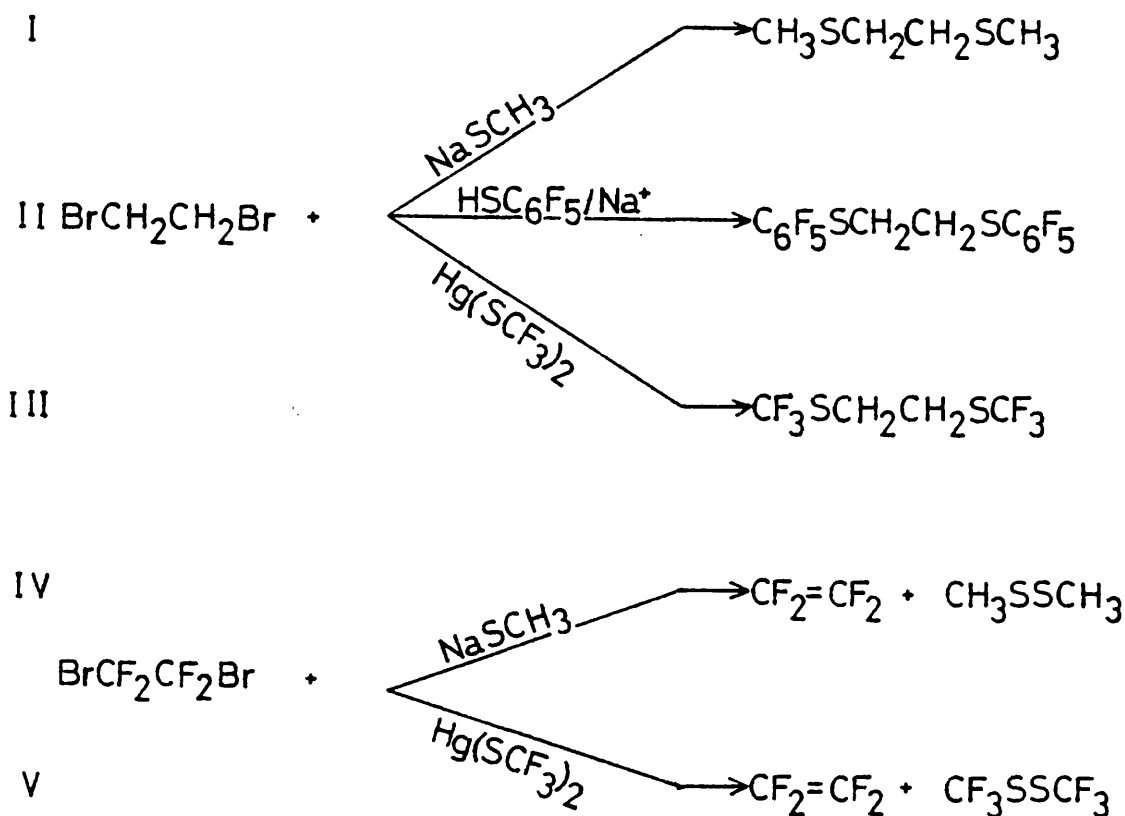
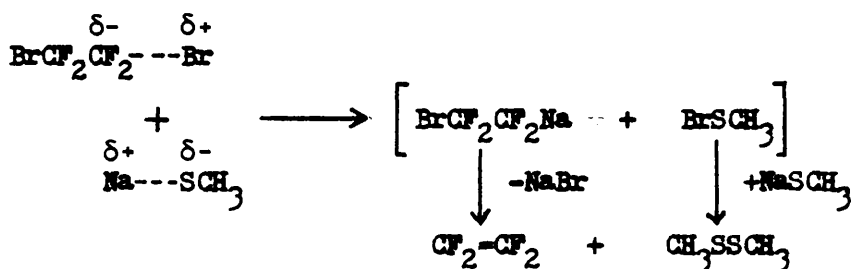


Figure 1. Reactions of 1,2-dibromoethane and 1,2-dibromo-1,1,2,2,-tetrafluoroethane.

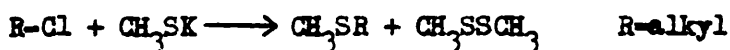
During the course of this work, attempts were made to prepare fluorinated dithioethers by following a similar procedure by reacting, for example $\text{BrCF}_2\text{CF}_2\text{Br}$ or $\text{BrCF}_2\text{CHFBr}$ and NaSCH_3 or $\text{Hg}(\text{SCF}_3)_2$ in closed systems under autogenous pressure. Under these conditions no reaction

was observed below 80°C but above this temperature both systems generated the fluoro-olefin, $\text{CF}_2=\text{CF}_2$ and $\text{CF}_2=\text{CHF}$ respectively and the corresponding disulphide as shown by reactions IV and V in figure 1.

Previously, similar reactions conducted in open systems have been also unsuccessful although no attempt was made to identify the volatile products⁶⁹. The nature of the products obtained in closed systems could be rationalized by the following pathway.



It must be emphasized that there is no experimental evidence for this scheme but the sensitivity of alkyl reactivity to the nature of the substituents is well known^{70,71}. Evidently the possibility of electrophilic displacement by the fluoroalkyl group has been greatly reduced by the fluorine substituents and according to the products obtained, it appears to act as a nucleophile. Reversal in the polarity of carbon-halogen bond, allowing initial attack on the electron deficient halide, has been suggested before^{72,73} to explain the reactions of fluorocarbon halides with bases and it is probably equally important in the present reactions. It is also relevant that the participation of CH_3SCH_3 in reactions of the type

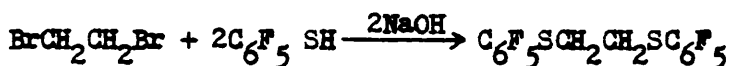


has been previously postulated⁷⁴.

Ionic reactions involving a metallic thiolate and alkyl halides are apparently limited to obtain dithioethers in which fluorinated

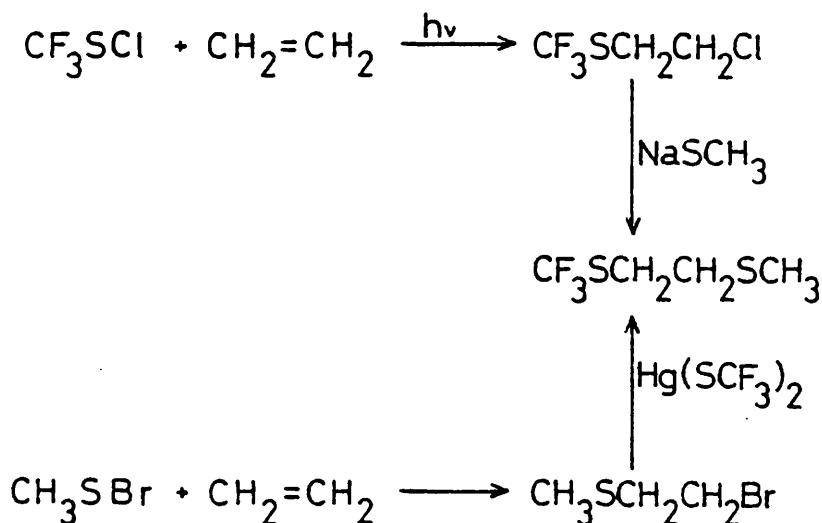
substituents are present on the sulphur atoms only or in cases of a low fluorine content of the alkyl.

$C_6F_5SCH_2CH_2SC_6F_5$ was reported by Peach et al.⁶² who prepared it by the metathetical reaction of $BrCH_2CH_2Br$ and $Pb(SC_6F_5)_2$. An improved procedure was used in this work, generating in situ the pentafluorobenzene thiolate of sodium or potassium, by the reaction

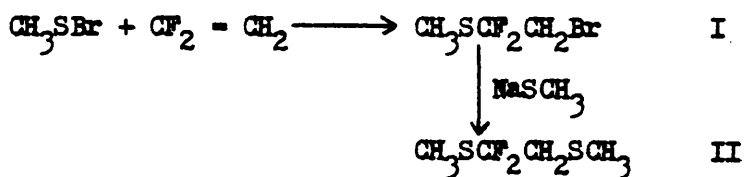


The white solid produced was characterized by i.r. (table 26); n.m.r., (table 29); and mass spectrometry (table 27).

Metathetical reactions were also used to prepare the asymmetric compounds $CF_3SCH_2CH_2SCH_3$ and $C_6F_5SCH_2CH_2SCH_3$ as follows



Preparation of $CH_3SCF_2CH_2SCH_3$ was attempted by reacting CH_3S^- and $BrCF_2CH_2Br$; this reaction however, gave the thioether $BrCF_2CH_2SCH_3$ which was not unexpected in view of the similar reactions described earlier. Two different procedures were then followed; a) a two step preparation involving the reactions



and b) the photochemical addition of dimethyl disulphide to CF_2CH_2 .

CH_3SBr and $\text{CF}_2=\text{CH}_2$ do not react at room temperature without catalyst. The choice of reaction condition was determined by the specific orientation desired. Photochemical reactions generally give rise to a mixture of products⁷⁵ in which the 'abnormal' anti-Markownikoff addition predominates; on the other hand, base catalyzed reactions are generally more selective producing mainly a Markownikoff addition⁷⁶⁻⁷⁸ across the double bond. Accordingly reaction I was carried out using sodium hydroxide as catalyst. The ^1H n.m.r. spectrum of a reaction mixture shown in figure 3, shows the presence of only one 1:3:1 triplet suggesting that the reactions proceeds almost quantitatively in one orientation and mass spectroscopic data confirmed that the product obtained was $\text{CH}_3\text{SCF}_2\text{CH}_2\text{Br}$.

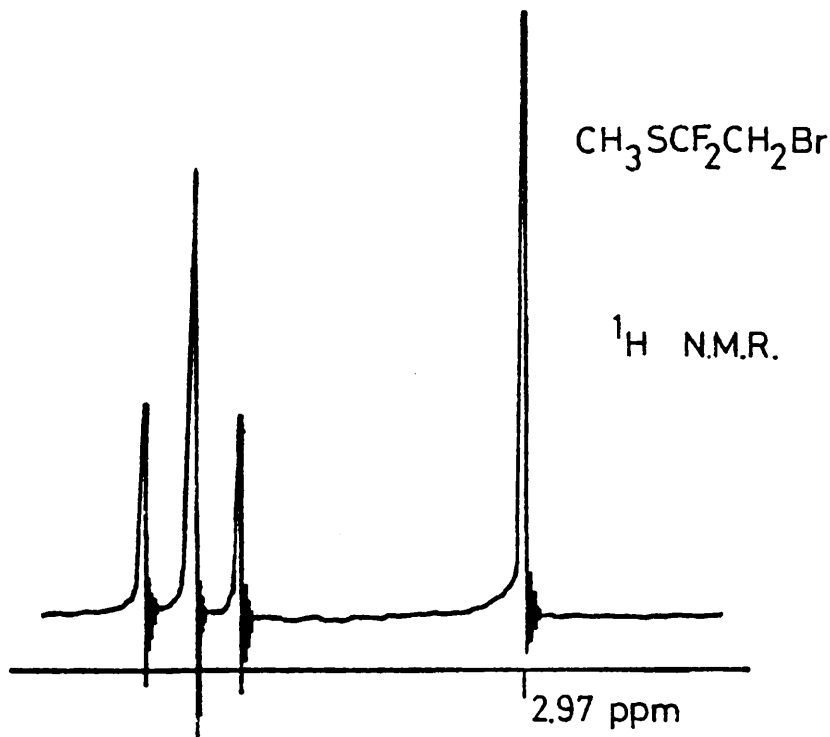


Figure 3. Proton n.m.r. spectra of $\text{CH}_3\text{SCF}_2\text{CH}_2\text{Br}$

Dimethyl disulphide⁷⁹⁻⁸¹ and its perfluorinated analogue have been reported to act as sources of radicals by homolytic rupture of the sulphur-sulphur bond. However under comparable conditions, the photochemical, gas phase reaction of both disulphides with ethylene follows different routes as illustrated by reactions I^{80,83,37} and II in figure 4. Instead of adding across the double bond, dimethyl disulphide

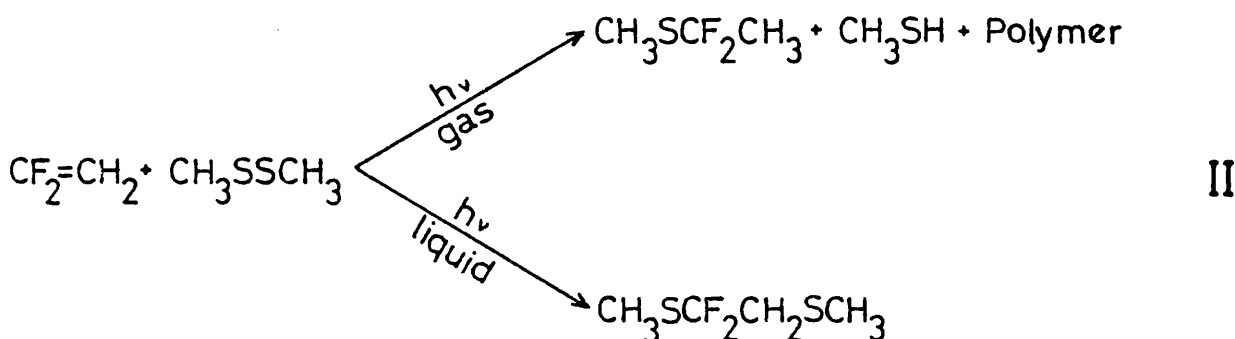
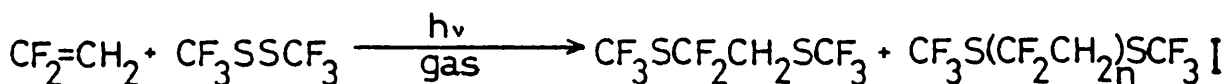
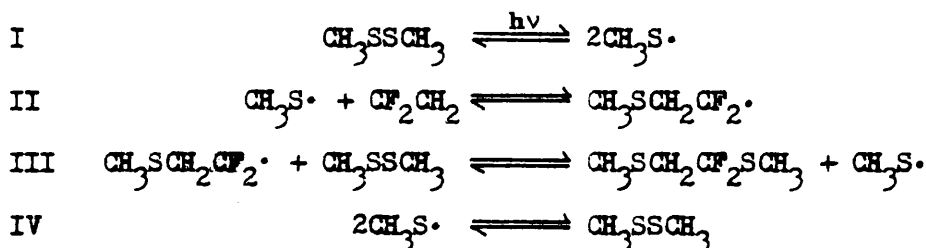


Figure 4. Photolytic reactions of disulphides.

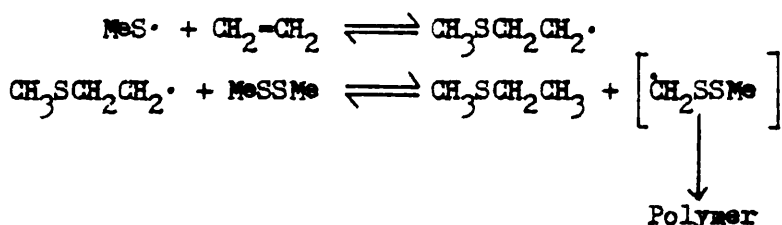
produces a complex mixture of disproportionation products but in no reaction was the direct addition found to be significant. Disproportionation and carbon-sulphur bond cleavage also occurs when the pure disulphide is irradiated in the gas phase; on the other hand, Saissman⁸¹ has demonstrated that in the liquid phase the primary process is sulphur-sulphur bond cleavage and under such conditions disproportionation is reduced to a minimum. With this evidence in mind the reaction between $\text{CF}_2=\text{CH}_2$ and dimethyl disulphide was carried out in the liquid state. A reasonable yield of the expected dithioether was obtained whereas only

traces of other products were found. A sequence of reactions leading to the products obtained is shown below^{79,80,83,84}

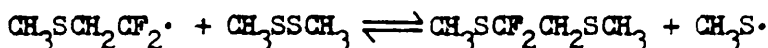
SCHEME I



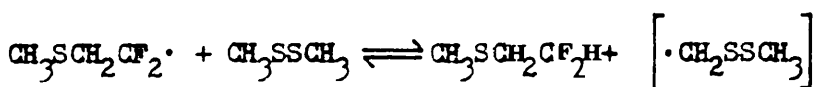
Mass spectrometry showed also the presence of $\text{CH}_3\text{SCH}_2\text{CF}_2\text{H}$. The hydrocarbon analogue has been obtained by the photochemical reaction of CH_3SSCH_3 and ethylene⁸⁰ and it is suggested to be the product of the following reactions



It is interesting that studies⁸⁵⁻⁸⁷ on free radical reactions have suggested that the ability of different substituents to stabilise radicals increases in the series $\text{Cl} > \text{F} > \text{H}$ and therefore on this basis, the intermediate radical $\text{CH}_3\text{SCH}_2\text{CF}_2\cdot$ is expected to be more stable than $\text{CH}_3\text{SCF}_2\text{CH}_2\cdot$, which is in agreement with the results obtained. Accordingly, reaction III in scheme I, seems to occur in two different ways:

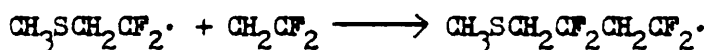


and

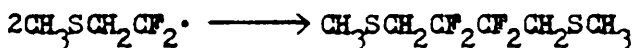


Products resulting from subsequent reactions of $\left[\cdot \text{CH}_2\text{SSCH}_3 \right]$ have not, however been identified.

In the photochemical addition of CF_3SSCF_3 to olefines³⁷, it was found that for partially and fully fluorinated derivatives there is a tendency for telomerization which is absent in the hydrocarbon analogues. In the reaction with CH_3SSCH_3 , no telomerization was found. This result is probably a consequence of the experimental conditions used; dimethyl disulphide present in a large excess has more probability of taking part in all reactions occurring during the photochemical addition and therefore, the alternative reactions



and



which would produce telomers, are minimized.

For the experimental conditions used in this work, (see page 163) the course of the reaction depends strongly on the solubility of the olefine in dimethyl disulphide used both as solvent and reactant; times of irradiation tend to be long but the reaction is nevertheless convenient for syntheses of dithioethers with fluorinated bridges which cannot be prepared by ionic methods.

Compared with the free radical addition of thiols to olefines^{88,89,91} the corresponding reactions with acetylenes have received very little attention⁹². The thermal addition of p-thiocresol to phenylacetylene giving a quantitative yield of a mixture of cis and trans isomers of p-tolyl-β-styryl sulphide⁹³ was apparently the first example of a free-radical addition of a thiol to an acetylene. Methanethiol has been reported to react with acetylene and carbon monoxide under the influence of a catalyst and pressure to give $\text{CH}_3\text{SCH}=\text{CHCHO}$ and $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$ ⁹⁴;

with $\text{HC}\equiv\text{CCH}_2\text{OH}$, under similar conditions, to give $\text{CH}_3\text{SCH}_2\text{CH}(\text{SCH}_3)\text{CH}_2\text{OH}$ ⁹⁵ and to react, under u.v. radiation and in the presence of a catalyst, with $\text{CH}_3\text{C}\equiv\text{CH}$ to afford $\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3$ ⁹⁶. No reactions have been reported between fluorinated acetylenes and CH_3SH but addition across the triple bond of these compounds have been studied for several systems 97-99 including H_2S ¹⁰⁰, alcohols¹⁰¹, phosphines^{103,104}, arsines^{104,105} and amines¹⁰¹. In this work, it was found that on u.v. irradiation in quartz apparatus in the presence of acetylenes, CH_3SH undergoes the addition reactions shown below. U.v. irradiation of CH_3SH has been shown¹⁰² to produce mainly $\text{CH}_3\text{S}\cdot$ and $\text{H}\cdot$ radicals although the carbon-sulphur bond is also cleaved in a small proportion of the reaction. The reaction of CH_3SH with acetylenes is probably a free radical reaction since there is no reaction at room temperature in the absence of irradiation. Results are summarized in table 1.

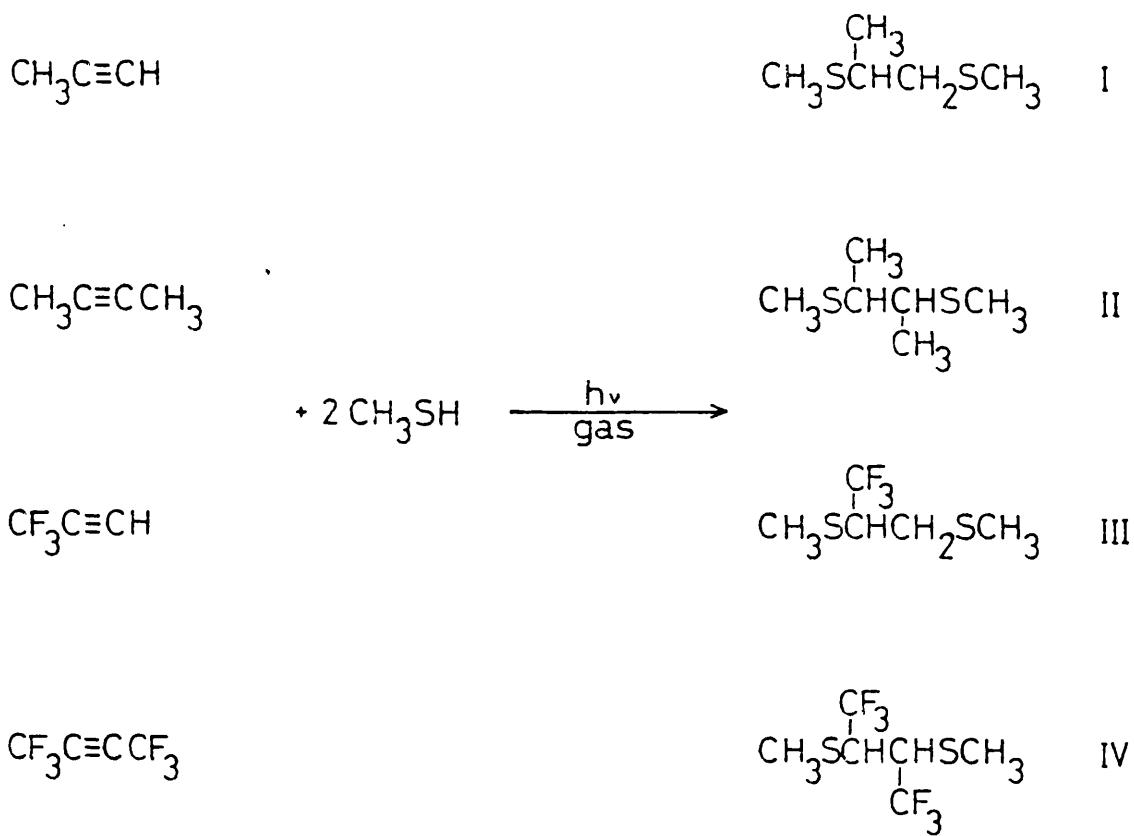


Figure 5. Photochemical addition of CH_3SH to acetylenes.

Table 1

Acetylene	Time of reaction (hrs)	Conversion of acetylene (%)	Products	bp (K/torr)
I $\text{CH}_3\text{C}\equiv\text{CH}$	12	90	$\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3^{\text{a}}$	357-358/20 357/20 ^a
II $\text{CF}_3\text{C}\equiv\text{CH}$	14	87	$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3$ $(\text{CH}_3\text{S})_2\text{CHCH}(\text{CF}_3)(\text{SCH}_3)^{\text{o}}$	351-353/18
III $\text{CH}_3\text{C}\equiv\text{CCH}_3$	16	85	$\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3^{\text{b}}$	363-364/31
IV $\text{CF}_3\text{C}\equiv\text{CCF}_3$	24	85	$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$ $(\text{CH}_3\text{S})_2\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3^{\text{o}}$	352-353/29

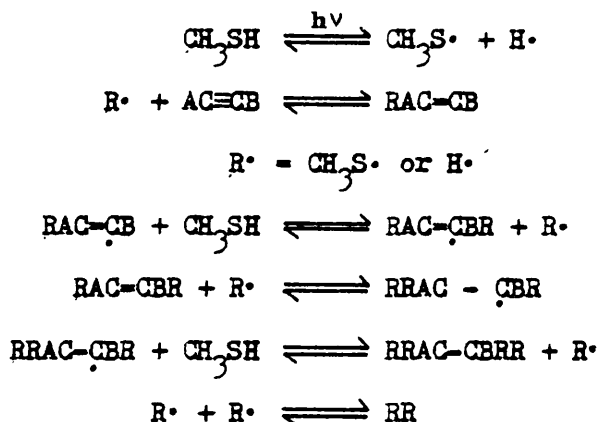
a) Compound I has been prepared by K. Griesbaum *et al.*⁹⁶ by irradiation of CH_3SH and $\text{CH}_3\text{C}\equiv\text{CH}$ in presence of *t*-butyl hydroperoxide.

b) Compound III has been prepared by G.K. Helmkamp *et al.*¹⁰⁷ treating $\text{HSCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3$ with CH_3I .

c) Not isolated

The reaction can be conveniently described in terms of the following scheme II showing the reactions between methylthiyl and hydrogen radicals with the acetylenes¹⁰².

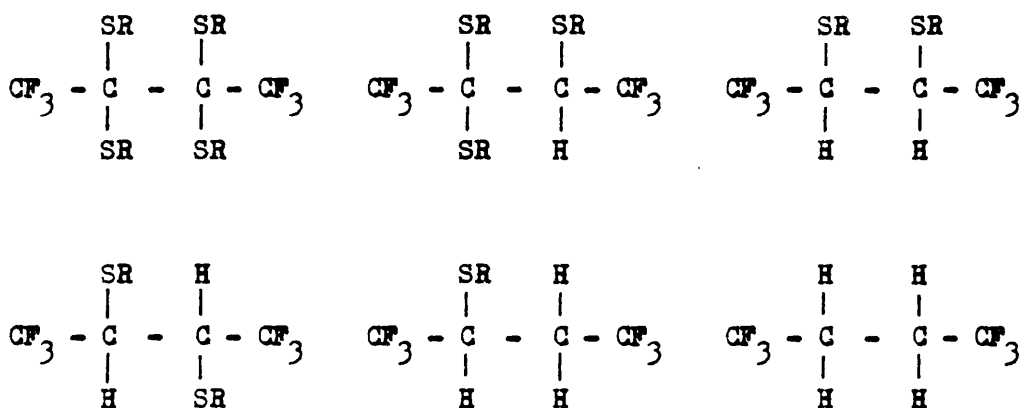
SCHEME II



It should be emphasized that the evidence for the successive steps in this scheme is based on the observed products rather than kinetic data. The sequence is an extension of similar reaction schemes for the addition of thiols to olefines⁸⁸ and radical combination or radical displacement could not be distinguished from the products obtained since both processes would produce similar combinations.

In contrast with other reactions involving addition across a triple bond⁵⁰⁻⁵³, in the reactions described here, the relative proportion of reactants had no major effect on the observed products. They were all saturated compounds and no olefinic products, as expected from one to one addition reactions, were found even though experiments with a large excess of acetylene were carried out. These results could arise from a fast reaction of the unsaturated mono-adducts with the thiol since a high reactivity of olefinic sulphides towards methanethiol has been previously observed^{100,108}. Excess of methanethiol increased the production of hydrogen and dimethyl disulphide^{102,106}.

According to scheme II, 6 or 9 different saturated products are possible depending on whether the acetylene $AC\equiv CB$ is symmetric ($A=B$) or asymmetric ($A\neq B$) respectively. For example, if $A=B=CF_3$ the following six products are possible



Experimentally products with four equal R-substituents,

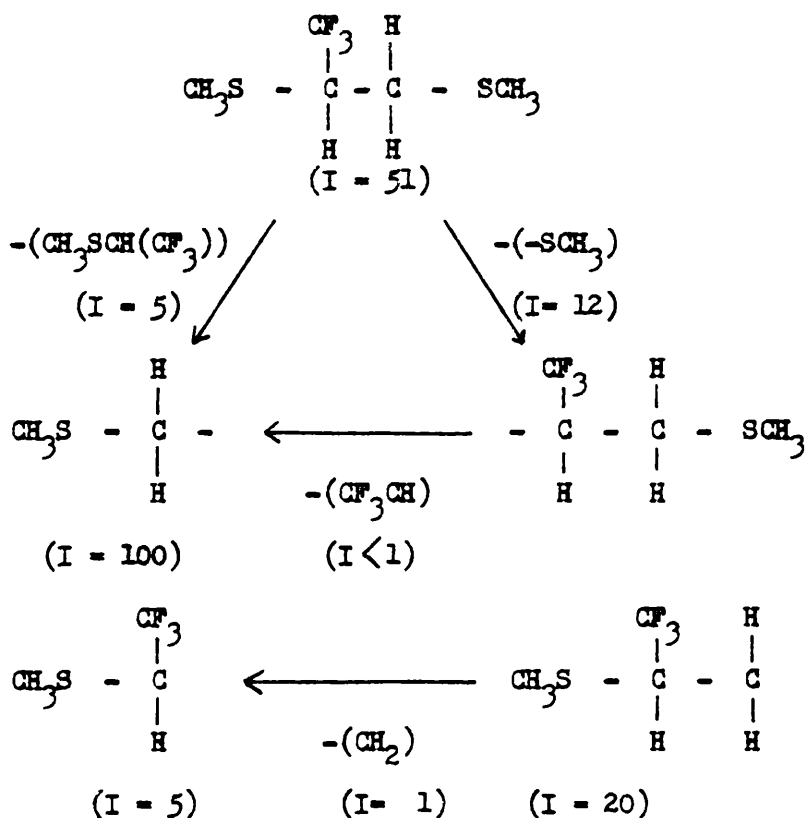
i.e. $(CH_3S)_2C(CF_3)C(CF_3)(SCH_3)_2$ and $CF_3CH_2CH_2CF_3$, were not detected.

Mass spectra of the reaction mixtures from the reactions of CH_3SH with $CH_3C\equiv CCH_3$ and $CH_3C\equiv CH$ show the highest molecular weights at $m/e = 150$ and 136 , corresponding to the molecular ions $CH_3SCH(CH_3)CH(CH_3)SCH_3^+$ and $CH_3SCH(CH_3)CH_2SCH_3^+$ respectively; the products from the reactions with $CF_3C\equiv CCF_3$ and $CF_3C\equiv CH$ however produced mass spectra in which the highest peaks occurred at $m/e = 304$ and 236 corresponding to the ions $(CH_3S)_2C(CF_3)CH(CF_3)^+$, I and $(CH_3S)_2CHCH(CF_3)SCH_3^+$, II. Compound I has only one orientation of substituents but compound II has two possible alternatives. Formulation II is suggested by the appearance of the fragment $(CH_3S)_2CH^+$ $m/e=107$. No peak for $C(CF_3)(SCH_3)_2^+$ $m/e = 175$ assignable to the alternative $CH_3SCH_2C(CF_3)(SCH_3)_2$ was found.

The proportion of the compounds just described is very small and although no attempt was made to isolate them they probably account for less than 1% of the total products. The proportion of the symmetric

double addition product was always greater than 95%.

All the methylthio derivatives show a relatively strong parent ion. For asymmetric compounds β -fission¹⁰⁹ produces two segments of different and characteristic m/e ratio, whereas symmetric dithioethers give rise to one peak from two similar fragments. One mode of breakdown appears to be loss of CH_3S group from the end of the molecule at which the carbon has a substituent other than hydrogen. Further breakdown appears to occur mainly (in terms of intensities) by successive loss of groups from this end of the molecule. An example is shown in the next diagram in which relative intensities are indicated below each observed fragment.



N.m.r. spectra of $\text{CH}_3\text{SCH(R)CH}_2\text{SCH}_3$, $\text{R} = \text{CH}_3$ or CF_3 , correspond to those expected for a rapid interconversion of rotamers¹¹⁰. The experimental spectra arises from $(2\text{A}_3 + \text{D}_3\text{NM}_2)$, $\text{R} = \text{CH}_3$ and

($2A_3 + X_3NM_2$), $R = CF_3$, systems. The spin-spin coupling along the chain, i.e. X_3NM_2 and D_3NM_2 produce complex spectra and the fine structure could not be interpreted in all cases. 1H and ^{19}F n.m.r. data are shown in table 2.

Table 2

N.m.r. parameters of $CH_3SCH(R)CH(R)SCH_3$, $R = H, CH_3$ or CF_3 .

Chemical shifts^a.

	δCH_3S	$\delta^b CH-CH_n$	δCH_3	δCF_3
$CH_3SCH(CH_3)CH_2SCH_3$ 1 3 3	2.52(1) 2.54(3)	3.12	1.77	-
$CH_3SCH(CF_3)CH_2SCH_3$ 1 3 3	2.77(1) 2.71(3)	3.60	-	-76.25
$CH_3SCH(CH_3)CH(CH_3)SCH_3$	meso 2.31 (\pm) 1.90	3.00	1.56 1.43	-
$CH_3SCH(CF_3)CH(CF_3)SCH_3$	meso 2.88 (\pm) 2.83	4.17	-	-73.5 -78.2

a) Values of 1H in ppm from external TMS. Values of ^{19}F in ppm positive to low field of external CCl_3F .

b) Approximate shift of the multiplet.

$CH_3SCH(R)CH(R)SCH_3$, $R = CH_3$ or CF_3 , having two asymmetric carbon atoms can adopt the meso and (\pm) isomeric structures shown in figure 6.

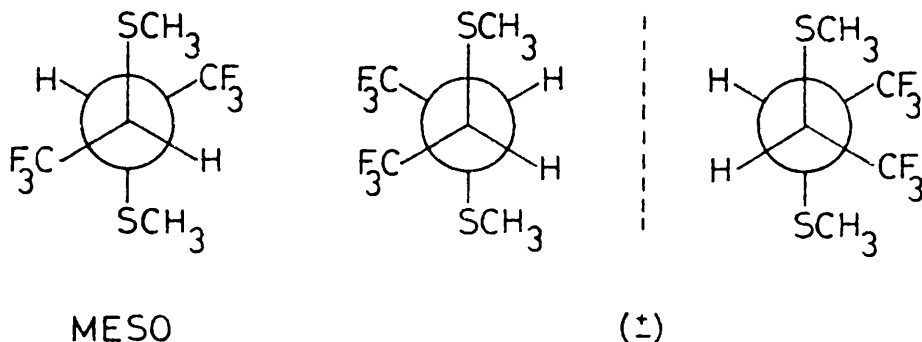


Figure 6. Meso and (\pm) isomers of $CH_3SCH(CF_3)CH(CF_3)SCH_3$.

All groups attached to the central carbon atoms in the (\pm) isomer are magnetically equivalent in any rotamer and therefore form a $2A_3 + 2(N X_3)$ system where $A = SCH_3$, $N = H$ and $X = CH_3$ or CF_3 . Groups in the meso isomer are magnetically non equivalent in two possible gauche conformations and equivalent in the trans rotamer; equivalence of these groups is not achieved by rapid rotation about the carbon-carbon bond and for the proton, taken as example, an $A_2 + 2AB$ system is expected. The experimental spectra are shown in figures 7, 8 and 9.

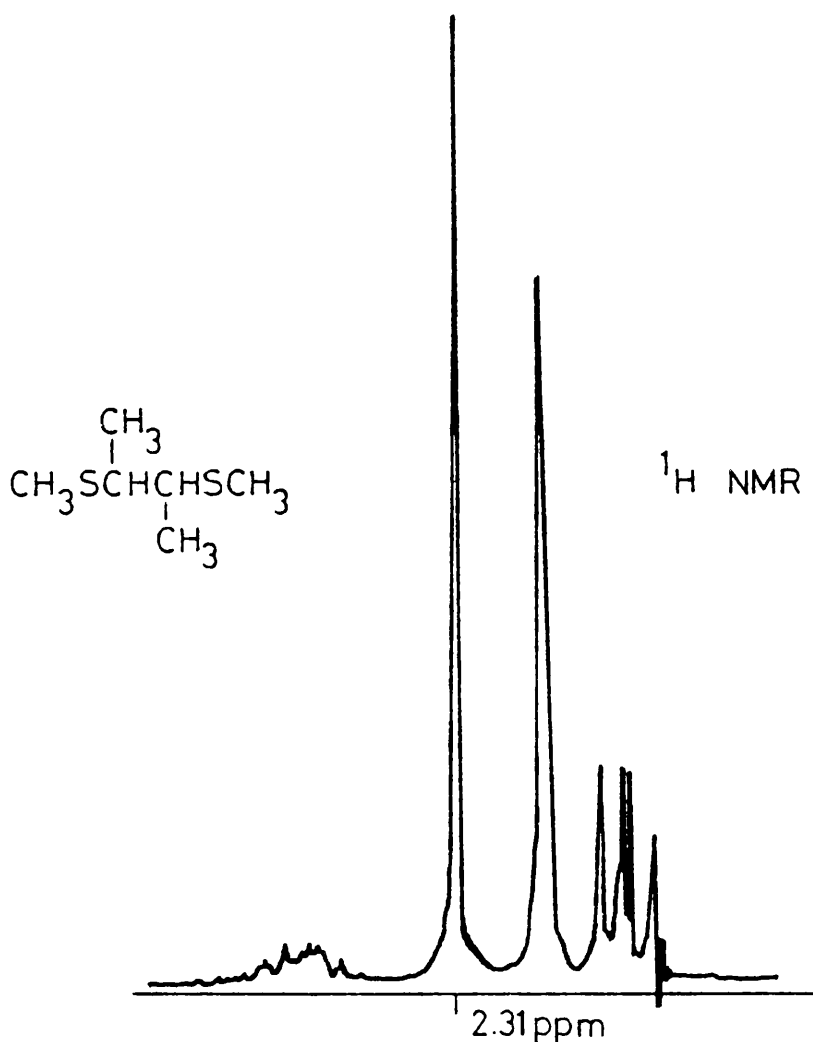


Figure 7. Proton n.m.r. spectrum of $CH_3SCH(CH_3)CH(CH_3)SCH_3$.

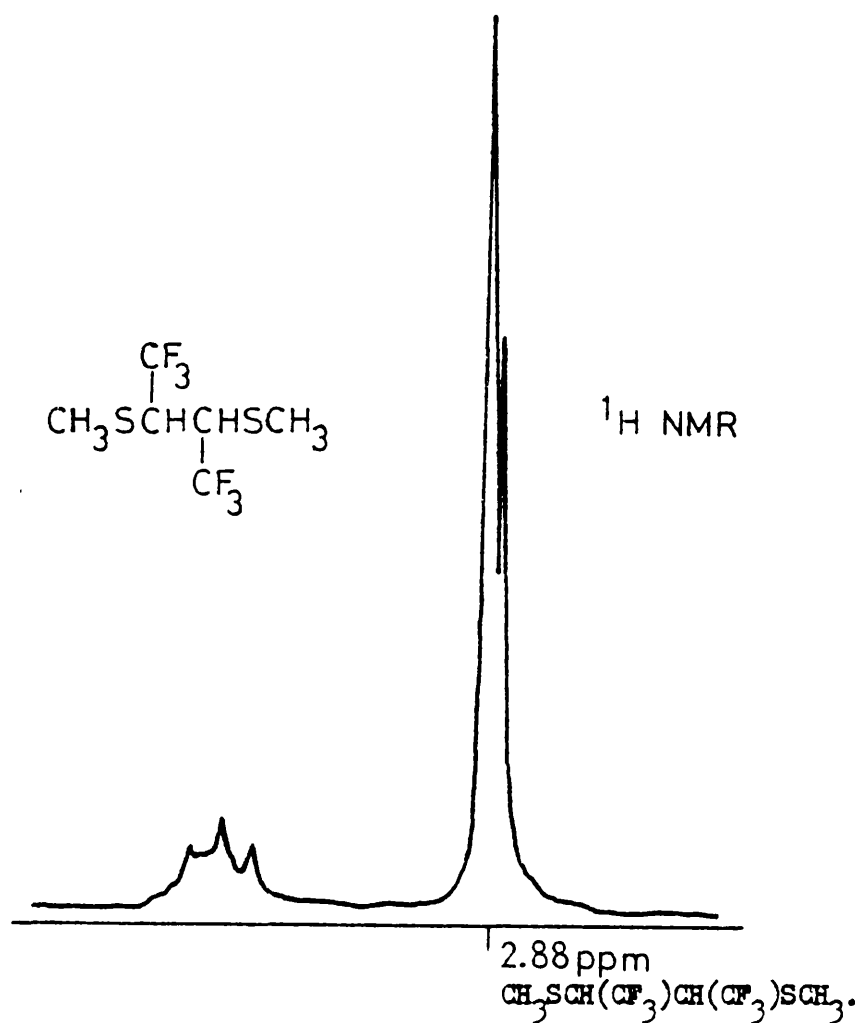


Figure 8. Proton n.m.r. spectrum of $\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$.

In different experiments the relative proportion of meso to (\pm) was always approximately 2:1 as determined by the intensities of their n.m.r. resonances. All reactions were conducted at room temperature and therefore little information on the factors affecting the addition are established. Base-induced and more significantly, free radical addition to acetylenes produce predominantly the trans ethylenic compound¹¹¹⁻¹¹⁵. Assuming that similar formation of the trans derivatives occurs in the reactions described here, the second addition could

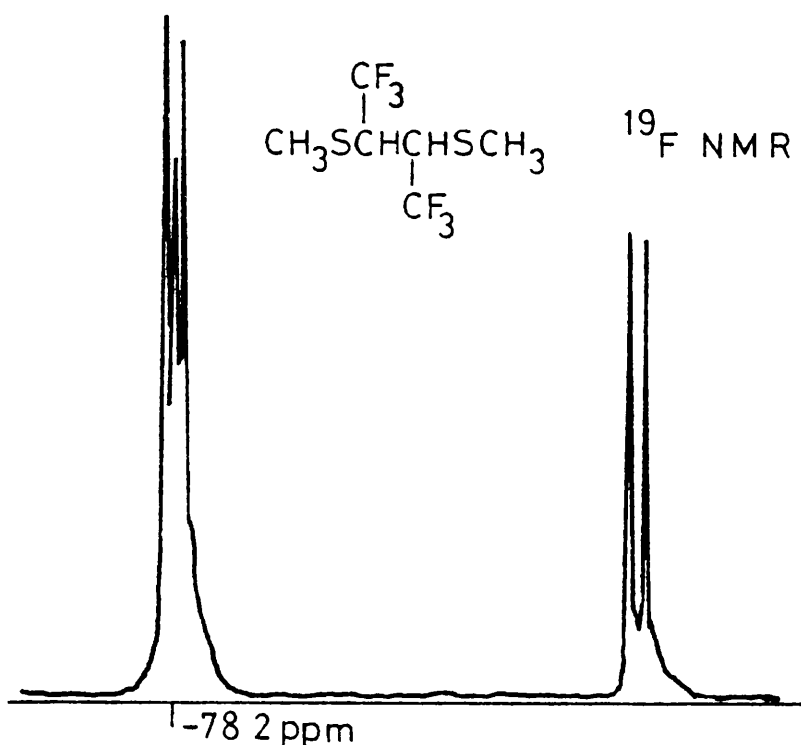


Figure 9. Fluorine n.m.r. spectrum of $\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$.

proceed by two paths, both leading to a larger proportion of meso isomer. The first model, is shown in figure 10.

The alternative mechanism requires that the radical attack on the primary olefinic adduct produces an intermediate capable of undergoing carbon-carbon bond rotation, which is normally assumed in photochemical mechanism¹¹⁶, and the final product will then be established via the most stable, probably the least crowded intermediate as shown in figure 11.

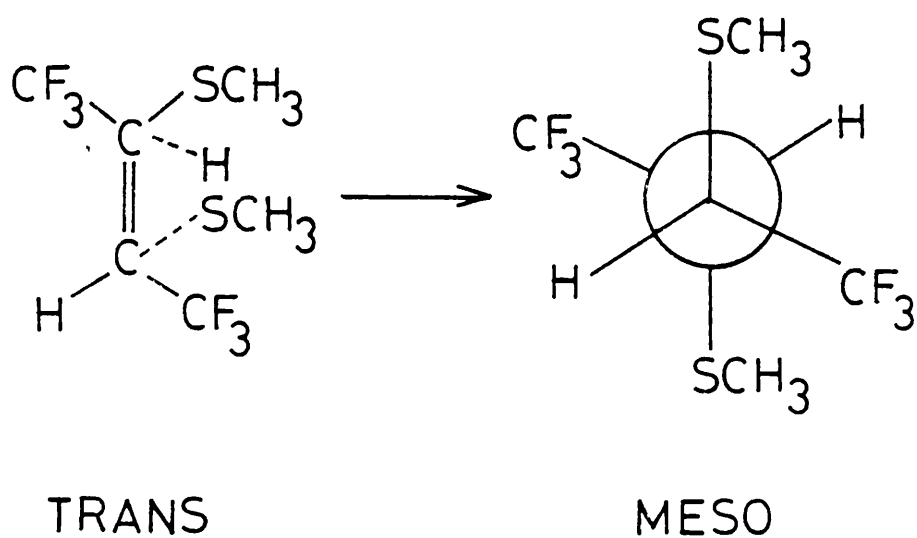
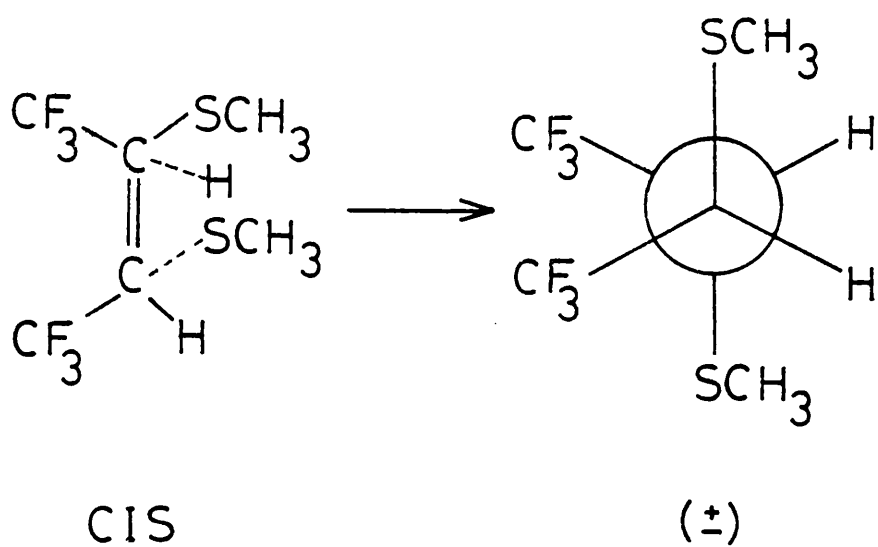


Figure 10. Reaction of CH_3SH with olefinic sulphides.

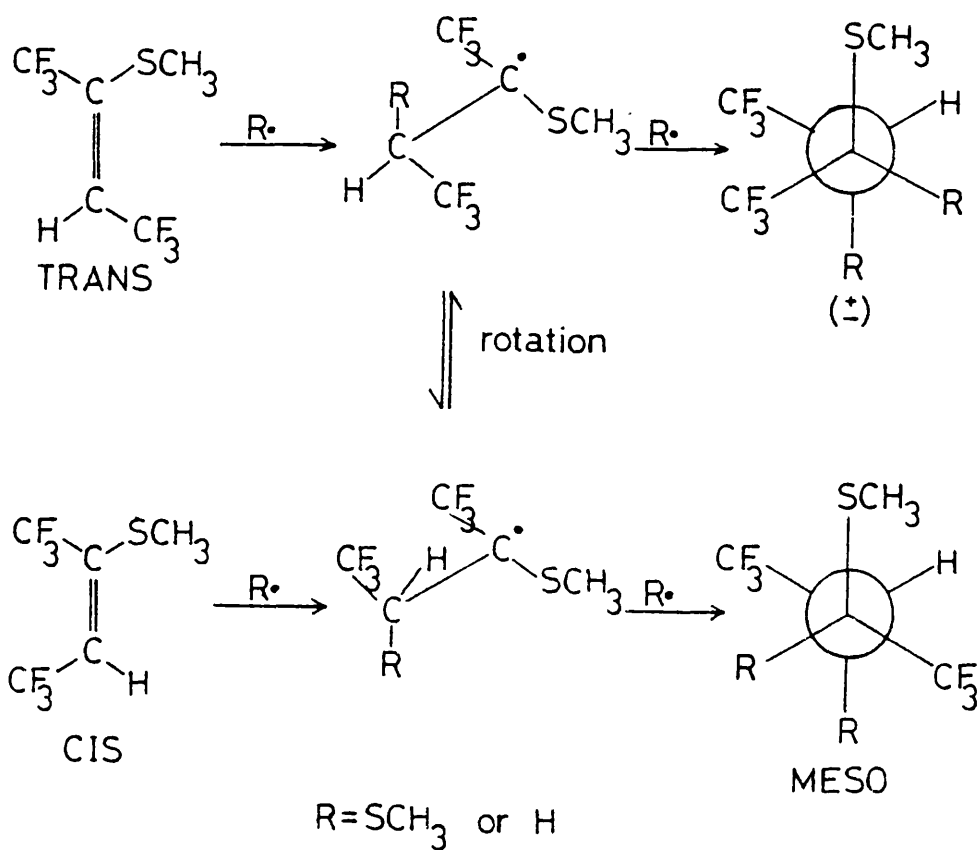


Figure 11. Free-radical of CH_3SCH to $\text{CH}_3\text{SC}(\text{CF}_3)=\text{CH}(\text{CF}_3)$

Table 3

Fluorinated compounds with the general formula RSR'SR"

No of Fluorine atoms	Compound	Preparation	Reference
2	$\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3$	A, E	this work
3	$\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$	E	this work
	$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3$	B	this work
4	$\text{CH}_3\text{SCF}_2\text{CF}_2\text{SCH}_3$	F	117
	$\begin{array}{c} \text{RSC}-\text{CSR} \\ \quad \\ \text{F}_2\text{C}-\text{CF}_2 \end{array}$ $\text{R} = \text{C}_4\text{H}_9$ $\quad = \text{CH}_2\text{COOH}$ $\quad = 2-\text{C}_{10}\text{H}_7$	C	40
5	$\begin{array}{c} \text{RSCH}-\text{CFSR} \\ \quad \\ \text{F}_2\text{C}-\text{CF}_2 \end{array}$ $\text{R} = \text{C}_4\text{H}_9$	C	40
	$\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SCH}_3$	E	this work
6	$\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$	A, E	37, 39
	$\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3$	A	37
	$\text{CH}_3\text{SC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SCH}_3$	E	118
	$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$	B	this work
	$(\text{CF}_3\text{S})_2\text{CHCH}_3$	E	39
	$\text{CF}_3\text{S}(\text{CH}_2\text{CH}_2)_n\text{SCF}_3 \quad n = 1, 2 \text{ and } 3$	E	39
	$\text{CF}_3\text{SCHBrCH}_2\text{SCF}_3$	F	39
	$\text{CF}_3\text{SCHBrCHBrSCF}_3$	F	39
	$\text{CF}_3\text{SCBr}_2\text{CH}_2\text{SCF}_3$	F	39
	$\text{CF}_3\text{SCH}=\text{CH}_2\text{SCF}_3$	F	39
	$\text{CF}_3\text{SC OSCF}_3$	F	39

table 3, continued.

No of Fluorine atoms	Compound	Preparation	Reference
8	$\text{CF}_3\text{SCF}_2\text{CH}_2\text{SCF}_3$	A	37
	$\text{CH}_3\text{S}(\text{CF}_2\text{CF}_2)_2\text{SCH}_3$	F	73
9	$\text{CF}_3\text{SCF}_2\text{CHFSCF}_3$	A	37
	$\text{CF}_3\text{SCF}_2\text{CFClSCF}_3$	A	37
	$(\text{CF}_3\text{S})_2\text{CHCH}_2\text{SCF}_3$	E	39
10	$\text{CF}_3\text{S}(\text{CF}_2\text{CH}_2)_2\text{SCF}_3$	A	37, 82
	$\text{CF}_3\text{SCF}_2\text{CF}_2\text{SCF}_3$	A	82
	$\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SC}_6\text{F}_5$	E	this work, 6:
12	$\text{CF}_3\text{S}(\text{CF}_2\text{CH}_2)_3\text{SCF}_3$	A	37
	$\text{CF}_3\text{S}(\text{CF}_2\text{CHF})_2\text{SCF}_3$	A	37
	$\text{CF}_3\text{SCF}(\text{CF}_3)\text{CF}_2\text{SCF}_3$	A, F	37, 82, 120
	$\text{CF}_3\text{S}(\text{CF}_2\text{CFCl})_2\text{SCF}_3$	A	37, 82
	$\text{CF}_3\text{S}(\text{CF}_2\text{CFBr})_2\text{SCF}_3$	A	82
14	$\text{CF}_3\text{S}(\text{CF}_2\text{CH}_2)_4\text{SCF}_3$	A	37
	$\text{CF}_3\text{S}(\text{CF}_2\text{CF}_2)_2\text{SCF}_3$	A	37, 82
15	$\text{CF}_3\text{S}(\text{CF}_2\text{CHF})_3\text{SCF}_3$	A	37
	$\text{CF}_3\text{S}(\text{CF}_2\text{CFCl})_3\text{SCF}_3$	A	37, 82
	$\text{CF}_3\text{S}(\text{CF}_2\text{CFBr})_3\text{SCF}_3$	A	82
16	$\text{CF}_3\text{S}(\text{CF}_2\text{CH}_2)_5\text{SCF}_3$	A	37
18	$\text{CF}_3\text{S}(\text{CF}_2\text{CH}_2)_6\text{SCF}_3$	A	37
	$\text{CF}_3\text{S}(\text{CF}_2\text{CHF})_4\text{SCF}_3$	A	37
	$\text{CF}_3\text{S}(\text{CF}(\text{CF}_3)\text{CF}_2)_2\text{SCF}_3$	A, F	37, 60

table 3, continued.

No of Fluorine atoms	Compound	Preparation	Reference	
18	$\text{CF}_3\text{S}(\text{CF}_2\text{CFCl})_4\text{SCF}_3$	A	37, 82	
21	$\text{CF}_3\text{S}(\text{CF}_2\text{CHF})_5\text{SCF}_3$	A	37	
24	$\text{CF}_3\text{S}(\text{CF}_2\text{CHF})_6\text{SCF}_3$	A	37	
27	$\text{CF}_3\text{S}(\text{CF}_2\text{CHF})_7\text{SCF}_3$	A	37	
40	$\text{CH}_3\text{S}(\text{CF}_2\text{CF}_2)_{10}\text{SCH}_3$	D	119	
undetermined	$\text{CF}_3\text{S}(\text{CF}_2\text{CF}_2)_n\text{SCF}_3$	$n < 2$	A	37
	$\text{CF}_3\text{S}(\text{CF}_2\text{CFCl})_n\text{SCF}_3$	$n < 4$	A	37
	$\text{CH}_3\text{S}(\text{CF}_2\text{CF}_2)_n\text{SCH}_3$	$n < 4$	D	119

A Photochemical addition to olefine; B Photochemical addition to acetylene

C Base catalysed addition to olefin; D Thermal addition to olefine;

E Metathetical reaction; F other reactions.

CHAPTER II

BONDING AND STRUCTURE

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Introduction

Platinum and palladium have a very rich and extensive chemistry which consists almost entirely of coordination compounds. Like the heavy metals that are at both sides of them in the periodic table, Pd and Pt have been classified¹²¹ as 'class b' metals, i.e., 'soft acids', according to Pearson's theory¹²².

In the series Ni, Pd, Pt the usual trends towards higher oxidation number are observed. Thus Ni(IV) is only stabilised by the use of ligands such as oxide or fluoride¹²³, while Pd(IV) is stabilised by chloride ligands in $[\text{PdCl}_6]^{2-}$ ¹²⁴. Pd(II) is however more stable relative to Pd(IV)¹²⁵, see table 4, oxidation states +2 and +4 of platinum are about equally stable.

Table 4

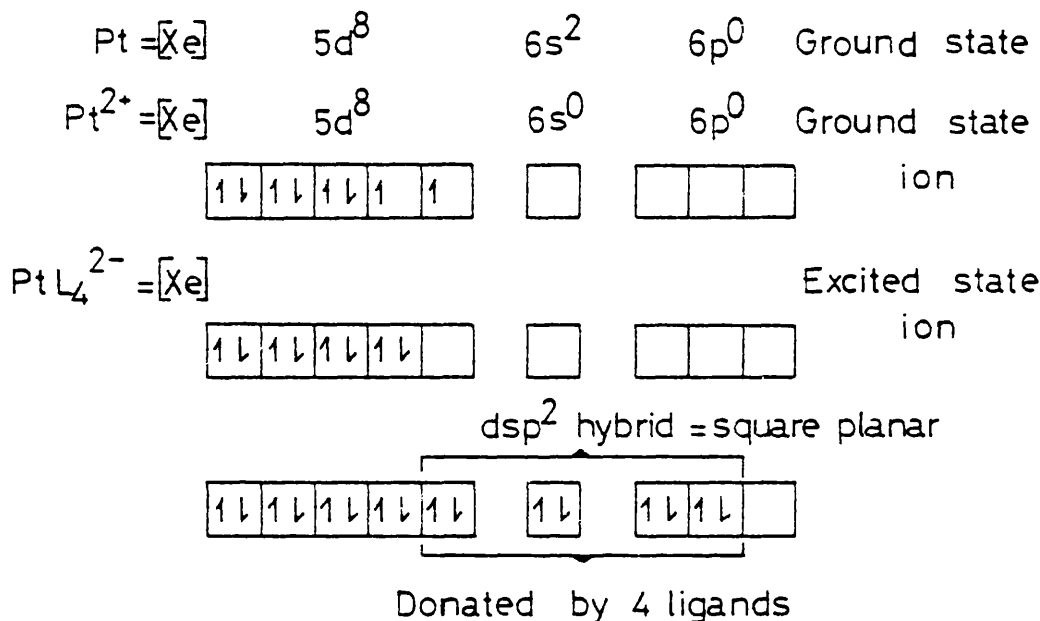
Oxidation potentials of Pt and Pd¹²⁶.

Oxidation state change	Equilibrium	Oxidation Potential (Volts)	
		Pt	Pd
$\text{M}(0) \rightleftharpoons \text{M}(\text{II})$	$\text{M} + 4\text{Cl}^- \rightleftharpoons \text{MCl}_4^{2-} + 2\text{e}$	-0.75	-0.59
$\text{M}(\text{II}) \rightleftharpoons \text{M}(\text{IV})$	$\text{MCl}_4^{2-} + 2\text{Cl}^- \rightleftharpoons \text{MCl}_6^{2-} + 2\text{e}$	-0.77	-1.26

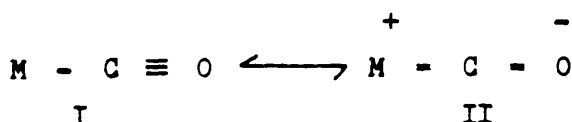
Other oxidation states found for both Pd and Pt are +1 and zero¹²⁷⁻¹³⁴. Two types of coordination are observed in Pt(0) compounds, tetrahedral^{135,136} as in $(\text{Ph}_3\text{P})_3\text{PtCO}$, and trigonal planar as in $(\text{Ph}_3\text{P})_3\text{Pt}$ ¹³⁷⁻¹⁴¹. Although reports of compounds with metal in +3 oxidation state have appeared¹³⁸, for example $\text{Pt}(\text{NH}_3)\text{I}(\text{SCN})_2$ Pt(III), these have not been authenticated yet.

Unlike complexes of Ni(II) which may be octahedral, tetrahedral or square planar, almost all those of Pd(II) and Pt(II) are square planar. This preferred stereochemistry is attributed to the increased value of the crystal-field splitting, $10Dq$, that accompanies the larger effective nuclear charge of the heavier atoms. The stability of the square planar complexes relative to tetrahedral depends on the high crystal field stabilisation energy of the d^8 systems¹⁴². In the square planar geometry the destabilisation of the $d_{x^2-y^2}$ orbital is so great that the 8 d-electrons are paired in the four low-energy d-orbitals making the complexes diamagnetic.

In terms of valence bond theory, square planar geometry can be described as follows



Thus valence bond theory assumes that ligand-metal bonds are purely dative, sigma bonds. This simplified view leads to an increase in the formal negative charge of the metal. In order to explain how electron density could be reduced, Pauling¹⁴³ suggested a partial multiple bond resonance which can be exemplified by the canonical forms I and II



In form II, electron density will be shifted from the metal to the oxygen through the overlap of a d-orbital on the metal with the p-orbital of the carbon. Interpretations in terms of molecular orbital theory assume that delocalization of metal electron density occurs via the d-orbitals of the metal and vacant orbitals in the ligands. If the formal charge at the metal is reduced, sigma bonding can be increased in a synergic mechanism.

Since the 1950's when the concept of synergic bonding in transition metal complexes was proposed¹⁴⁴⁻¹⁴⁸, the role of σ and π bonding has been continuously studied and debated¹⁴⁹⁻¹⁵².

In terms of the Chatt-Duncanson-Venanzi¹⁴⁵ model, Pt or Pd will have nine orbitals available for forming bonds, i.e., 5X5d, 1X6s and 3X6p in the case of platinum.

Two basic criteria have to be kept in mind when allocating these electronic orbitals to any particular type of bonding. The first condition refers to compatible symmetry of the bond-forming orbitals. In a square planar platinum complex, for example, sigma bonds require the use of $5d_{x^2-y^2}$, $5d_{z^2}$, $6p_x$, $6p_y$ and $6s$ ¹⁵³. The remaining atomic orbitals, namely the $5d_{xy}$, $5d_{xz}$, $5d_{yz}$ and $6p_z$, will be available to form a different bond in a system of π molecular orbitals with ligand orbitals of corresponding symmetry.

The second consideration regarding the atomic orbitals ability for bond formation is related to the orbital energies, usually indirectly referred to as orbital overlap, which also have to be comparable if strong bonds are to be formed. It must be noted that whereas orbital symmetry requirements will be invariant within the series Ni, Pd, and Pt, the energy factors will depend on the particular element considered. One of the consequences derived from the orbital energy requirements for π bond formation is that overlap of orbitals is less effective with lighter elements than with the heavier ones due to the larger

contraction of 3d-orbitals compared with that of 5d-orbitals. Accordingly, the observed tendency towards formation of π bonding is greater for platinum than it is for palladium. On the other hand strongest σ bonds should be formed between elements of the same row in the periodic table. A pictorial representation of a ligand-metal bond is given in figure 12.

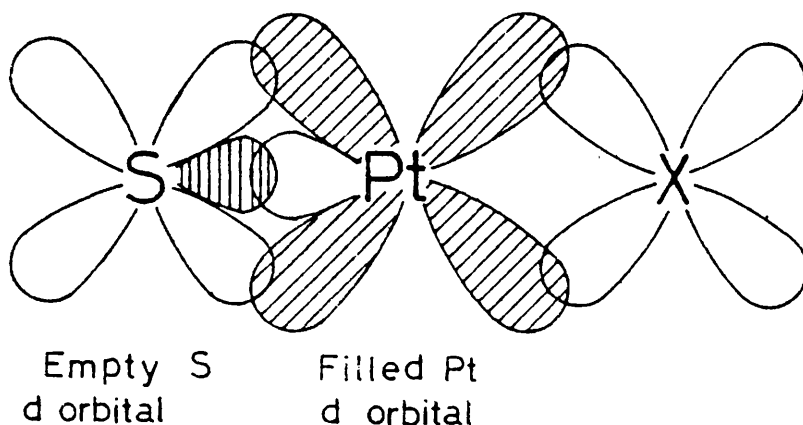


Figure 12. Postulated $d_{\pi} - d_{\pi}$ bonding.

If both symmetry and energy requirements are met, the ligand donor atom is assumed to donate a pair of electrons to the metal through the sigma system; simultaneously the metal can direct part of its electron density to the empty orbitals of the ligand in what has been called 'back donation' or 'back bonding'.

In theory, the σ -bond may range from a strong bond with complete sharing of the lone pair and transfer of one negative electronic charge to the acceptor metal atom, to a weak bond with little transfer of charge and, trivially, to a non-bonding situation with no charge transfer¹⁵⁴. On the other hand, the transfer of charge involved in π -bonding can have a lower limit of zero if, for example, the metal is bonded to an atom which has no vacant orbitals in its valency shell for 'back bonding' formation¹⁵⁵. The upper theoretical limit will also be the transfer of one electronic charge, the attainment of which has been suggested in

such bonds as Pt-PF₃ and Pt-CO.

In valence bond terms, coordination compounds of sulphur, with an outer electronic configuration of 3s², 3p⁴, are formed by the donation of one or two of the sulphur sp³ hybrid orbitals containing a lone pair of electrons.

In addition, sulphur has vacant d-orbitals which, if energetically compatible, could accept electron density from filled d-orbitals on the metal in a d_π-d_π bonding.

Several reports on the role of π bonding in sulphur-containing compounds have reached what are apparently opposite conclusions: i.r. studies on mercapto derivatives of transition metal carbonyls have assumed that increased CO stretching frequencies can be explained by a significant π character of the M-SR bond¹⁵⁶⁻¹⁵⁹. However, mass spectral studies¹⁶⁰ of the ionisation potential of ligands in (Fe(CO)₃X)₂ X=PR₂, SR, have suggested that sulphur ligands are less efficient σ donors and, surprisingly, more efficient π acceptors than phosphorus ligands, on the other hand, the relative π acceptor ability of sulphides has been reported to be less effective than that of phosphines¹⁶¹. X-ray diffraction studies for complexes containing bridging-SR groups indicated some^{162,163} multiple bond character although it has been judged to be totally absent in some metal(II)-sulphur bonds¹⁶⁴.

This situation is not necessarily a problem however, since neither the bond strength nor the relative participation of σ and π bonding are invariable properties of the sulphur-metal bond. The characteristics of a M-S bond will also depend on the nature of other ligands attached to the metal and substituents bonded to sulphur.

Relevant to the work described in this thesis is the effect on the sulphur-metal bond of highly electronegative substituents attached to the sulphur atom. Two effects can be expected: firstly the electron withdrawing properties of the substituent will reduce the availability

of the sulphur lone pair by contracting the hybrid lone pair orbitals closer to the sulphur atom¹⁶⁵. Indicative of this fact are the marked tendency for fluorinated thiolates of transition metals to form stable monomers. In contrast, sulphur atoms in their hydrocarbon analogues form readily a coordination bond with additional molecules producing dimers¹⁶⁶⁻¹⁶⁸ and polymers¹⁶⁹. Secondly the electronegative group will promote transfer of electron density into the vacant sulphur 3d-orbitals from metal d-orbitals of appropriate energy. Therefore, if the sulphur-metal bond is considered purely in terms of the σ bonding, the effect of the electronegative substituents at the donor atom will be a weakening of the bond; on the other hand, if the complementary π bonding is also considered, the result would probably be the restoration of part of the bond strength. The overall effect however is far from predictable.

Trans effect and trans influence.

The intensive studies developed in the USSR on coordination compounds of platinum, led to the discover of the first stereospecific displacement reaction in 1926. In that year, Chernyaev¹⁷⁰ found that Pt(II) compounds underwent substitution reactions in which the position adopted by the entering ligands depended on the ligands already present in the complexes. It was noted in particular, that different ligands had different effect on the substitution of the trans ligands. The concept of trans effect was used to designate the labilization of ligands trans to other, trans directing ligands, since substitution reactions did not always give the thermodynamically most stable product¹⁷¹.

The property of a ligand of being a trans-director can originate in two ways. A ligand can be a trans-director if it weakens the bond trans to itself or if the ligand stabilises the transition state of a substitution reaction¹⁷².

In order to differentiate between these two situations the term

trans effect was later restricted specifically to the kinetic effect and was defined as: 'the effect of a coordinated group on the rate of substitution reactions of ligands opposite to it'.¹⁷³ A new term, trans influence, was defined as: 'the extent to which the ligand weakens the bond trans to itself'.¹⁷⁴ Trans effect and trans influence are therefore different, well-defined, phenomena and although they are often related by postulating trans influence as an operative mechanism of trans effect¹⁷⁵ other pathways to explain trans effect have been suggested.¹⁷⁶⁻¹⁷⁸

Recently, great attention has been given to the particular type of metal and ligand orbitals used in bonding in an effort to rationalize both concepts. A large π character has often been associated with a large trans influence^{179,180} but the inverse statement (i.e. large trans influence indicating large π bonding) is not necessarily correct, since it is known that hydride and alkyl groups which are exceptionally good trans directors¹⁸¹ cannot π bond. Although most authors approach the interpretation of trans influence from a sigma bond only^{151,174,182,186} point of view, a more complete explanation will probably have to include both σ and π bonding^{183,184}.

The simplest representation of trans influence with a sigma bond approach is the polarization theory of Grinberg¹⁸⁵.

Grinberg suggested that in a symmetrical complex such as $\left[\text{PtCl}_4 \right]^{2-}$, represented by A in figure 13, since all bonds are equivalent the metal-ligand dipoles will all be identical and cancel each other. On the other hand if one ligand is substituted by a more polarizing one it will induce a non compensated dipole at the metal.

The dipoles of the polarizing ligand pL and the metal will attract each other strengthening the pL-metal bond and simultaneously, the dipoles of the trans ligand and the metal will repel each other weakening the trans L-metal bond.

Modern views of Grinberg's theory in terms of molecular orbital

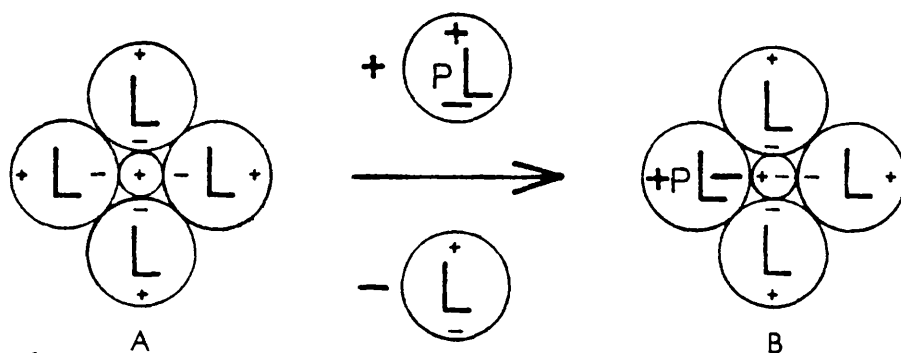


Figure 13. Grinberg model of trans influence

theory assume a similar situation but replace the purely electrostatic interactions by an unequal overlap of the ligand orbitals with the metal orbitals along the $PL-M-L$ bonds¹⁷⁶ or with the $d_{x^2-y^2}$ orbitals^{182,186}. The polarization theory indicates that large and polarizable metal atoms will show greatest trans influence. Accordingly, for Ni, Pd and Pt the order of polarizability²¹⁷ and that of trans influence are identical being $Pt(II) > Pd(II) > Ni(II)$. It also must be noted that the polarization theory emphasizes the role of inductive effects which can be very important in fluorinated compounds (see page 9)

The second approach to trans influence involving π bonding, is shown in figure 14. It assumes that two trans ligands competing for the d electrons of the metal, will arrive at the situation in which the stronger π bond will dominate the π bonding, weakening the bonding of the trans group. It is assumed that cis group do not compete in this manner since they each use a different d-orbital¹⁸⁷. Both models attempt to explain the same fact, namely the extent to which the ligand weakens the bond trans to itself. In this sense its measure should ideally rely on bond energies or alternatively on bond lengths parameters which are unfortunately very seldom available. Other parameters often related to trans influence are spin-spin coupling constants¹⁸⁸⁻¹⁹⁰ and

i.r. frequencies¹⁹¹⁻¹⁹³.

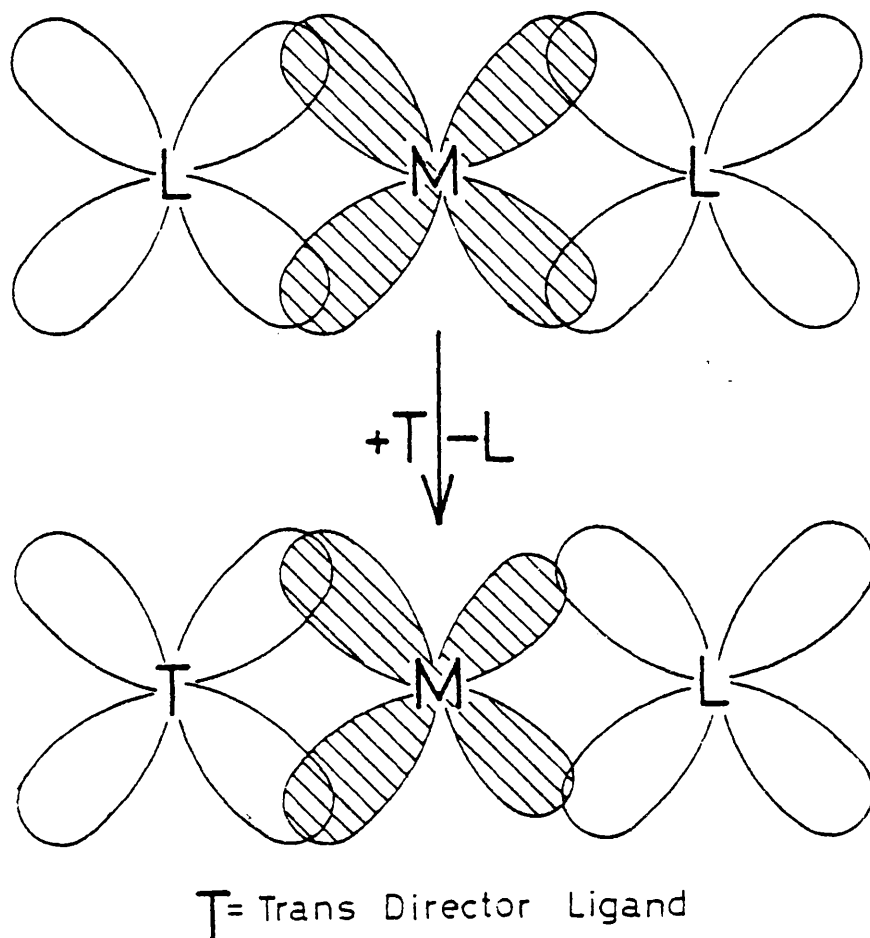


Figure 14. Postulated effect of a trans director ligand on the $d_{\pi}-d_{\pi}$ bonding.

Chelate effect.

Finally, use will be made of the term 'chelate effect' and therefore a short discussion of this effect is included in this section.

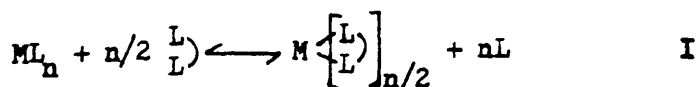
In 1952 Schwarzenbach¹⁹⁴⁻¹⁹⁶ showed that the stability of a metal chelated compound is considerably greater than that of an analogous compound which contains fewer or no chelate rings. This extra stability is termed the chelate effect. There is no unique explanation for the effect; in fact the enhanced stability of complexes containing chelated rings has been attributed to a large variety of factors. Resonance

stabilization is thought to be responsible for the formation of the six membered rings of acetylacetonate complexes¹⁹⁷, rigid chelated ligands like olefinic diphosphines form more stable complexes than their saturated diphosphines analogues presumably because the greater rotational freedom of the latter ligands encourages partial dissociation^{198,199}. It has also been pointed out²⁰⁰ that the more favorable heat of reaction which occurs in the formation of metal chelate compounds compared to the heats observed in similar complexes containing no chelate rings can be interpreted as the result of repulsive forces between the polar groups bound to the metal; in simple complexes interligand repulsions can be of great importance whereas in chelating ligands the bridge between these dipoles holds the donor groups together in opposition to the repulsive forces. Thus the formation of a metal chelate involves a more favorable heat of reaction because it is not necessary to bring together ions or dipoles with like charges.

The effects just described depend on the specific system studied; in addition to these effects there is an entropy factor common to all chelate compounds which is normally regarded as the origin of the chelate effect²⁰¹.

Considering the differences in the dissociation processes of the mono and bidentate ligands shown in figure 15 it is clear that if a metal ligand bond is broken in a chelated and a non-chelated compound the probability of the now free monodentate ligand to reforming the bond is less than that of the dissociated donor atom in the chelating ligand atom which has been retained near the metal atom bonding the other end of the molecule.

Experimentally the equilibrium



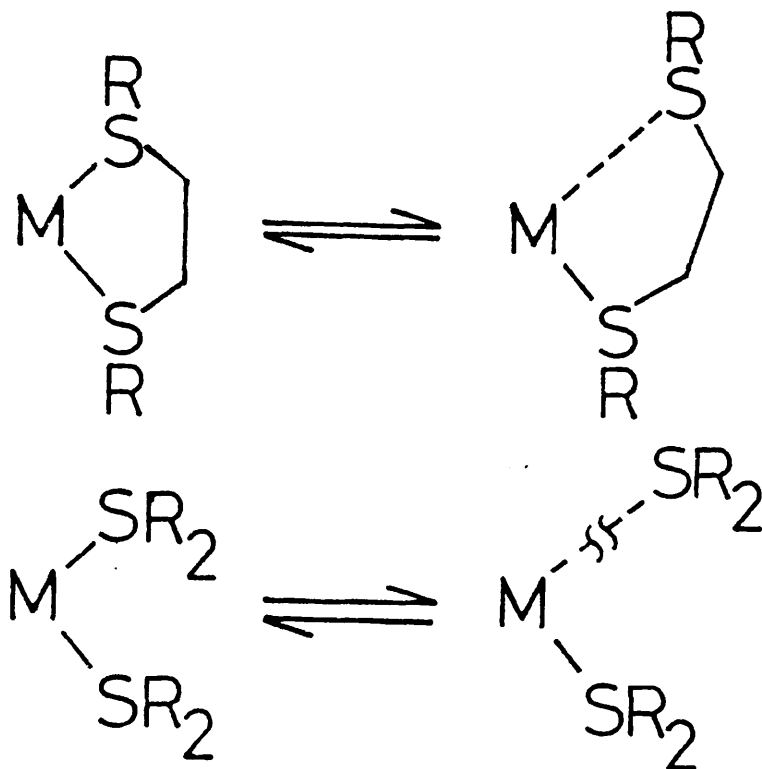


Figure 15. Dissociation of monodentate and bidentate ligands.

has been studied with a large variety of ligands^{11,202}, particularly with ammonia and amines^{203,204}. The change in entropy for the reaction I will be proportional to the difference in the number of molecules present in the system. Entropy favours the formation of the chelate complex and the reaction proceeds to the right as observed experimentally.

Discussion of results

The chelated complexes prepared during the course of this work are indicated in table 5 together with their colours.

All syntheses were carried out in a very similar way by reaction of the ligand with a suitable metallic salt (generally N₂MX₄, where N=K or Na; M=Pd or Pt; and X=Cl, Br or I) in a solvent system which depended on the relative solubilities of both ligand and metal salt.

Table 5

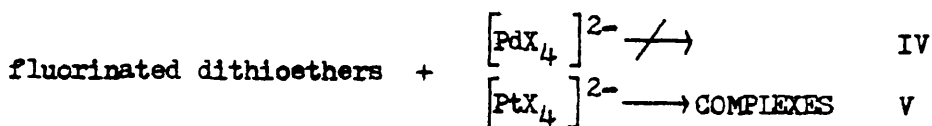
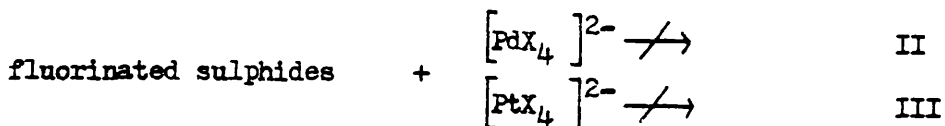
Chelated Pd(II) and Pt(II) complexes with fluorinated dithioethers. (Ligand) MX_2 M=Pd, Pt; X=Cl, Br, I.

Ligand	Platinum			Palladium		
	Cl	Br	I	Cl	Br	I
$CF_3SCF_2CH_2SCF_3$						
$CF_3SCH_2CH_2SCF_3$	yellow	yellow				
$CF_3SCH(CH_3)CH_2SCF_3$	yellow	yellow				
$C_6F_5SCH_2CH_2SCF_3$	yellow	yellow	brown			
$CH_3SCF_2CH_2SCH_3$	yellow	yellow	brown	yellow	orange	violet
$CH_3SCH(CF_3)CH_2SCH_3$	yellow	yellow	brown	yellow	orange	violet
$CH_3SCH(CF_3)CH(CF_3)SCH_3$	yellow	yellow	brown	yellow	orange	violet

Most complexes were obtained from aqueous-acetone solutions from which the complexes crystallized on standing for variable periods. By this procedure no reaction was found to take place between $CF_3SCF_2CH_2SCF_3$ and either platinum or palladium salts. None of the ligands containing the CF_3 moiety produced the expected complexes with palladium, as shown in table 5 by the shaded spaces. It has already been mentioned that unsuccessful attempts to prepare metal complexes with $CF_3SCH_2CH_3$ and $C_2HClF_3SC_2H_4OH$ have been published^{39,40} and during the course of this work attempts to prepare compounds with CH_3SCF_3 and CF_3SCF_3 also

failed. Because the reaction conditions were all very similar, it is clear that there is a marked difference between the reactivity of platinum(II) and palladium(II) towards fluorinated ligands.

The following reactions summarize the above information.



The discussion that follows is focussed firstly, on the different results obtained with fluorinated dithioethers and fluorinated sulphides and secondly, on the different results from the reactions of fluorinated dithioethers with palladium(II) and platinum(II).

If a fluorinated sulphide is represented by the general formula SRR' , I, where one or both R substituents are fluorinated groups, a dithioether is a specific sulphide in which one substituent is also a sulphide.

The sulphur atom in I will probably have similar electronic properties in any series of sulphides as long as the nature of the groups directly attached to it do not change substantially. For example, it is reasonable to assume that bonding properties of sulphur in CF_3SCH_3 , $\text{CF}_3\text{SCH}_2\text{CH}_3$ and $\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ are all similar; yet, under the conditions used in this work, only the last compound formed platinum(II) complexes. If the assumption of invariant electronic properties in the mentioned series of compounds is correct, the different results obtained for sulphides and dithioethers could be rationalized by their different coordination possibilities. In contrast to the monodentate sulphides, the potentially chelating dithioethers could form metal complexes if

additional stabilization is gained by chelate ring formation.

$\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3$ has been found to act either as bidentate or monodentate ligand. In complexes where this ligand is monodentate, the preferred coordination site is the CH_3S^- group; no evidence was found for the occurrence of monodentate complexes in which coordination occurred through the CF_3S^+ end of the ligand and indeed, there is no unambiguous example known of CF_3SR compound acting as monodentate ligand. Hydrocarbon dithioethers^{205,206} and diphosphines²⁰⁷ with the general formula $\text{RPR}'\text{PR}''$, are known to form both chelate complexes or binuclear compounds in which the ligand is bonded to both metal centres as a monodentate ligand; none of the ligands in this work produce complexes having a $\text{CF}_3\text{S-Pt}$ bond, other than chelate complexes. It is also interesting that $\text{CF}_3\text{SCF}_2\text{CH}_2\text{SCF}_3$ does not react with either palladium(II) or platinum(II) under the conditions used in this work. The increased fluorine substitution around one of the donor atoms in this ligand appears to diminish still further the donor ability of sulphur and the observed lack of reactivity would suggest that, in this case, the increased stability gained by the chelate effect is insufficient to compensate the electronic effect. Much more information on the coordination chemistry of fluorinated dithioethers and related ligands is needed before final conclusions can be reached but apparently, $\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3$ is very near the border-line as a ligand just capable of forming stable complexes with palladium(II) or platinum(II). This fact is also apparent from the results of halide substitution reactions. The order of increasing trans influence for halides is $\text{I} > \text{Br} > \text{Cl}$ ¹⁸³; correspondingly a successive weakening of the sulphur-platinum bond is expected on a step-wise substitution of chlorine by bromine or iodine. Experimentally, bromide substitution in $(\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ is easily carried out, but a similar reaction with iodide produces decomposition of the complex giving the free ligand and PtI_2 as products. As expected no reaction takes place

between $\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3$ and K_2PtI_4 . Interestingly, when the electronegativity of the sulphur substituents is decreased, as in the substitution of CF_3 by C_6F_5 groups, i.e. $\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SC}_6\text{F}_5$, the iodine complex of platinum(II) is obtained although still no reaction take place with palladium(II). These results contrast with the existence of iodide derivatives for all complexes of hydrocarbon dithioethers. Variations of spin-spin coupling constants in series of similar compounds are commonly related to the bond strength^{208,209} and on this basis the results shown in table 6, could reflect also a weakening of the sulphur metal bond in the bromide complex as compared with the chloride compound.:

Table 6.

Differences of platinum-fluorine coupling constants in chlorine and bromide complexes.

Compound	$J \text{ (Pt-F)}^a$		$\Delta J \text{ (Pt-F)}$
	X=Cl	X=Br	
$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtX}_2$			
Isomer A	60.0	57.7	2.3
Isomer B	57.7	55.0	2.7
$(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtX}_2$			
Isomer A	68.7	66.0	2.7
	54.0	52.8	1.2
Isomer B	65.5	-	-
	54.0	-	-
Isomer C	53.0	-	-
	62.0	60.1	1.9
Isomer D	59.0	57.2	1.8
	59.0	57.2	1.8

a) In Hz.

Thermal decomposition of complexes with ligands containig the CF_3S

moiety occur at higher temperatures than for hydrocarbon analogues as shown in table 7.

Table 7

Decomposition temperatures, °C.

I	$(\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3)\text{PtCl}_2$	248
II	$(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$	241
III	$(\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$ ²³	235
IV	$(\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3)\text{PtBr}_2$	234
V	$(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$	247

Thermal decomposition takes place depositing PtCl_2 with liberation of the ligand.

Although it has been suggested²¹⁰ that in π bonded compounds the energy required to produce decomposition is increased compared with a non- π bonded compound, the increase in the decomposition temperature of compound I relative to II, is more likely to reflect larger packing energies than bonding parameters since, as discussed later, (page 53) X-ray data of compound V suggest the presence of strong intermolecular interactions in the solid state. This electrostatic interaction between sulphur and chlorine of neighboring molecules is attributed to the electron-withdrawing character of the fluorinated substituents at sulphur and therefore a similar situation is likely to be present for compound I.

The second part of this discussion concerns the reactions IV and V which suggest a different reactivity between palladium(II) and platinum(II) towards fluorinated dithioethers.

Since a more effective sigma bonding is expected between atoms of the same or of the nearest row in the periodic table²¹¹, the preparation of platinum(II) complexes but failure to synthesize the

corresponding palladium(II) compounds indicates that other factors are also involved.

One of these factors is presumably the participation of π bonding. The greater ability of platinum as compared with palladium to form π bonds is well known²¹². Furthermore, the presence of fluorinated substituents at the sulphur donor atoms, is assumed to enhance the participation of π bonding in the sulphur metal bond.

If fluorinated dithioethers of platinum(II) are indeed stabilized by π bonding, the parameters related to the metal sulphur bond are expected to reflect this situation by comparison with corresponding parameters of hydrocarbon analogues. Specially relevant to this point are the results of the X-ray diffraction study of $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{CF}_3)_2)\text{PtCl}_2$ ²¹³ shown in figure 16.

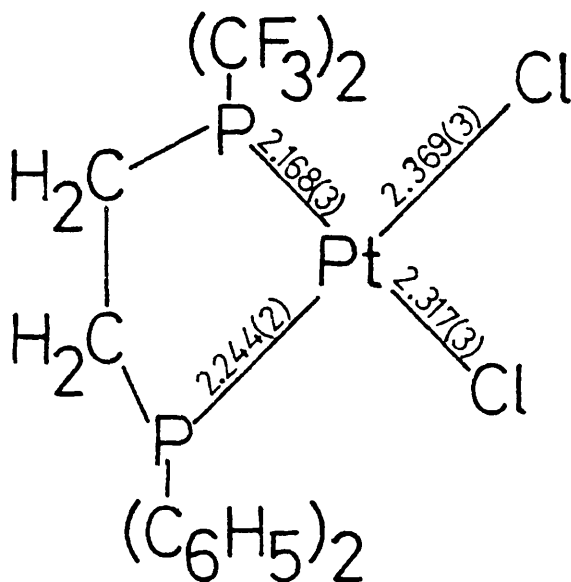


Figure 16. Structure of $((\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2)\text{PtCl}_2$

The Pt-P bond lengths are greatly affected by the nature of the substituents attached to the donor atom; the Pt-PPh₂ bond is comparable with those found in other phosphines but the significantly shorter

Pt-P(CF₃)₂ bond distance is attributed to the larger electron-withdrawing ability of the trifluoromethyl groups enhancing the metal-phosphorus π bonding.

In order to obtain precise information on the metal-sulphur bond, an X-ray diffraction study of (CF₃SCH(CH₃)CH₂SCF₃)PtCl₂ was carried out (see page 51). S-Pt and Cl-Pt bond lengths are listed in table 8 together with corresponding data for compounds containing the S-Pt-Cl skeleton.

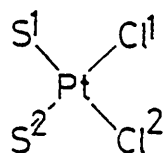
Unfortunately comparisons with other dithioether complexes of platinum(II) cannot be made since there is no structural information available. This fact makes it difficult to assess the influence of the electron-withdrawing trifluoromethyl groups on the metal ligand bond.

The most directly comparable structure is that of cis((ClC₆H₄)₂)₂PtCl₂ I²¹⁴, since compounds II and III have two different (sulphur and nitrogen) donor atoms and their structural parameters are less accurately determined²¹⁵.

The mean Pt-Cl bond lengths in IV of 2.293(5)⁰Å is shorter than in I, 2.300(5)⁰Å, and it is at the lower end of the range of terminal Pt(II)-Cl distances which spans from 2.26⁰Å to 2.45⁰Å²¹⁶. The Pt-S distances of 2.239(3) and 2.260(3) in IV are also shorter than the mean Pt-S distance of 2.285(7) in I. Therefore, crystallographic data suggest that trans influences of ligands in compounds I and IV are very similar both being relatively weak and that trifluoromethyl groups in (CF₃SCH(CH₃)CH₂SCF₃)PtCl₂ induce a contraction of the Pt-S bond length, compared with I, of 0.03-0.05⁰Å. Although the information is insufficient to confirm that π bonding is responsible for the contraction of the platinum-sulphur bond in IV, it supports this suggestion. In relation to this point it is important to consider that in terms of σ bonding only, the presence of electron-withdrawing substituents at sulphur is expected to weaken the Pt-S bond, contrary to the experimental results.

Table 8

Interatomic Distances (Å)



COMPOUND		S ¹ -Pt	S ² -Pt	Cl ² -Pt	Cl ¹ -Pt
I	(p C ₆ H ₄ Cl) ₂				
		2.292(6)	2.278(7)	2.298(7)	2.301(6)
II		2.26	—	2.31	—
		2.25	—	2.30	—
IV		2.260(3)	2.239(3)	2.290(4)	2.295(3)

Therefore the different behaviour of Pt(II) and Pt(II) towards fluorinated dithioethers can be rationalized by the greater tendency of platinum (II) than palladium (II) to form π bonds. In addition the

larger polarizability of Pt(II), is likely to add an electrostatic component to the sulphur-platinum bonding system²¹⁷. Electrostatic interactions between electron-deficient sulphur atoms and negatively charged chloro ligands are assumed to be responsible for the strong interactions between pairs of centrosymmetrically related molecules of $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ in the solid state (see page 53). The inductive effect, represented in figure 17, is also compatible with the relatively short Pt-Cl distance observed since all electric charges on

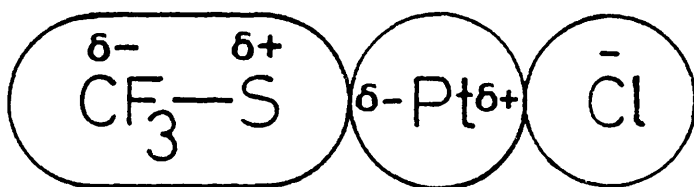


Figure 17. Electrostatic interaction between platinum and the CF_3S grouping.

this model (unlike the three-dipole system in figure 13) would produce attractive interactions.

The evidence available is consistent with the participation of the chelate effect on the stabilization of complexes containing bis(perfluoro-alkythio)alkanes. It also suggests that the π bonding component in the Pt-S bond is increased from $\text{R} = \text{p-C}_6\text{H}_4\text{Cl}$ to $\text{R} = \text{CF}_3$ although the difference is probably small.

Structure.

In 1966 Abel et al.²² reported the proton n.m.r. of $(\text{MeSC}_2\text{H}_4\text{SMe})\text{PtCl}_2$ showing the presence of two resonances, interpreted as arising from two distinct pairs of equivalent methyl substituents which, on increasing the temperature, converged and eventually

coalesced to a sharp signal in a reversible process. These results were explained by the presence, in solution, of two different isomers shown in figure 18.

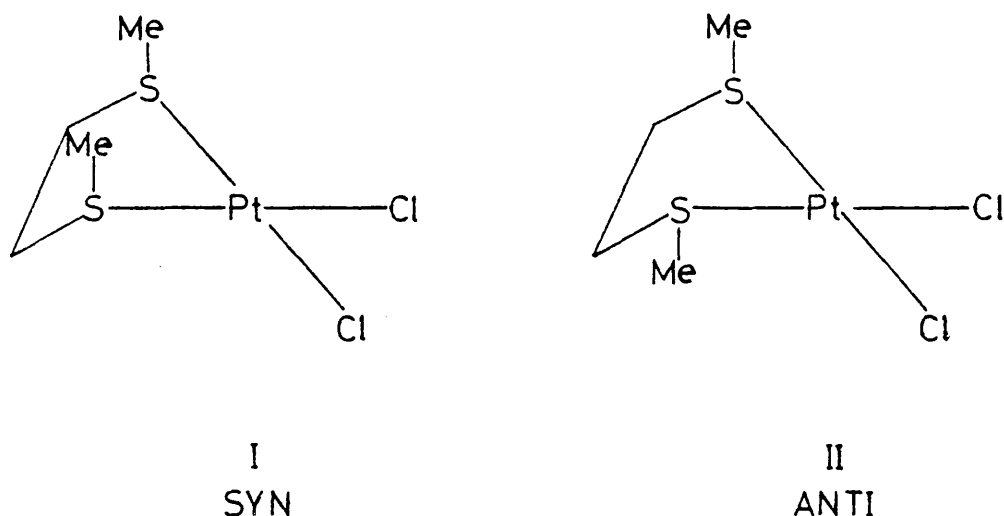


Figure 18. Stereoisomers of $(\text{MeSC}_2\text{H}_4\text{SMe})\text{PtCl}_2$

In structures I and II a different molecular environment around the methyl groups is produced and two absorptions are generated. At the same time, the chemical equivalence of substituents within each isomer is maintained and both absorptions appear as singlets. The dynamic process observed was explained by the interconversion of isomers which at and above the coalescence temperature is faster than the n.m.r. time scale producing an averaged signal.

Since this first report, several studies on the possible mechanisms for isomeric interconversion and to measure barriers of inversion have been carried out for a large series of closely related dithio²³⁻²⁶ and diselenoether^{31,32,218,219} complexes. By far the major part of these studies are conducted with solutions where, generally, mixtures in equilibrium of both isomers are obtained; surprisingly however, very little is known about which specific structures are the origin of a

given set of spectroscopic parameters obtained from those solutions. The following discussion presents the results of the first X-ray crystallographic study of a platinum dithioether complex, corresponding to $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ and it also includes the n.m.r. parameters of the complexes reported which are discussed in relation to the structure adopted by the compounds in solution.

X-ray crystallographic studies of $(\text{Pr}^i\text{SeC}_2\text{H}_4\text{SePr}^i)\text{PdCl}_2$, I¹⁴; $(1-(1, 4\text{-di-tert-butyl-4-chloro})\text{butadienyl})(\text{CH}_3\text{SC}_2\text{H}_4\text{SCH}_3)\text{PdCl}_2$, II¹⁵ and $[(\text{CH}_3\text{SC}_2\text{H}_4\text{SCH}_3)_2\text{Cu}]^{+2}$, III¹⁸ have shown the presence of only one syn isomer whereas the anti structure has been established for the complexes cis-dichloro-(1,10-diaza-4,7,13,16-tetraoxa-21,24-dithia-bicyclo [8,8,8] hexacosane)palladium(II), IV²²⁰; $[(\text{CH}_3\text{SC}_2\text{H}_4\text{SCH}_3)_2\text{Cu}]^{+1}$, V¹⁸ and $(\text{C}_2\text{H}_5\text{SC}_2\text{H}_4\text{SC}_2\text{H}_5)\text{Cr}(\text{CO})_4$, VI¹⁷.

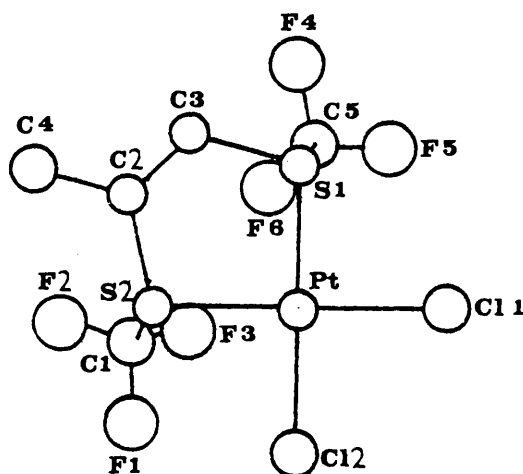


Figure 19. Structure of $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$

The single crystal X-ray diffraction study of the complex $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$, carried out by Drs K.W. Muir, Lj. Monojlovic-Muir and T. Solomon¹⁶ of this department, showed that the complex crystallises with the syn structure. The molecular structure of the complex is

Table 9

Interatomic Distances (\AA) and Angles ($^\circ$)

A) Bond Lengths		D) Interbond Angles	
Pt - S(1)	2.239(3)	S(1) - Pt - S(2)	90.6(1)
Pt - S(2)	2.260(3)	S(1) - Pt - Cl(1)	178.2(1)
Pt - Cl(1)	2.295(3)	S(1) - Pt - Cl(2)	88.7(1)
Pt - Cl(2)	2.290(4)	S(2) - Pt - Cl(1)	89.9(1)
S(1) - C(3)	1.83(1)	S(2) - Pt - Cl(2)	179.0(1)
S(1) - C(5)	1.84(1)	Cl(1) - Pt - Cl(2)	90.8(1)
S(2) - C(1)	1.82(1)	Pt - S(1) - C(3)	102.9(4)
S(2) - C(2)	1.85(1)	Pt - S(1) - C(5)	106.6(5)
C(2) - C(3)	1.50(2)	C(3) - S(1) - C(5)	101.5(7)
C(2) - C(4)	1.53(2)	Pt - S(2) - C(1)	106.2(5)
C(1) - F(1)	1.30(2)	Pt - S(2) - C(2)	105.0(4)
C(1) - F(2)	1.32(2)	C(1) - S(2) - C(2)	97.6(7)
C(1) - F(3)	1.33(2)	S(2) - C(2) - C(3)	109.2(9)
C(5) - F(4)	1.31(2)	S(2) - C(2) - C(4)	110.4(10)
C(5) - F(5)	1.28(2)	C(3) - C(2) - C(4)	111.0(11)
C(5) - F(6)	1.29(2)	S(1) - C(3) - C(2)	115.5(9)
B) Intramolecular Non-Bonded Distances		S(2) - C(1) - F(1)	110.2(10)
F(3) ... F(6)	2.817(14)	S(2) - C(1) - F(2)	111.1(11)
S(1) ... Cl(2)	3.167(5)	S(2) - C(1) - F(3)	114.5(10)
S(2) ... Cl(1)	3.218(5)	F(1) - C(1) - F(2)	105.6(12)
S(1) ... S(2)	3.199(4)	F(1) - C(1) - F(3)	107.6(13)
Cl(1) ... Cl(2)	3.264(5)	F(2) - C(1) - F(3)	107.4(12)
C) Intermolecular Contact Less than the Sum of the van der Waals Radii		S(1) - C(5) - F(4)	108.9(11)
S(1) ... Cl(1)	3.352(5)	S(1) - C(5) - F(5)	108.0(11)
S(2) ... Cl(2)	3.382(5)	S(1) - C(5) - F(6)	114.4(10)
Pt ... Pt	3.417(1)	F(4) - C(5) - F(5)	108.8(12)
Cl(1) ... C(2)	3.560(14)	F(4) - C(5) - F(6)	107.0(12)
Cl(1) ... C(3)	3.693(14)	F(5) - C(5) - F(6)	109.6(14)
Cl(1) ... C(4)	3.793(15)		

illustrated in figures 19 and 20 and structural parameters are listed in table 9.

The compound crystallises in the monoclinic system, space group $P2_1/2$, with four molecules in a unit cell of dimensions $a = 7.557(2)$, $b = 12.942(2)$, $c = 12.340(2)\text{\AA}$, $\beta = 91.42(2)^\circ$.

As expected, molecules of $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ exhibit cis-square planar coordination at the platinum atoms. The methyl group is pseudo-equatorial with respect to the chelate ring. The crystal packing involves strong interactions between pairs of centrosymmetrical

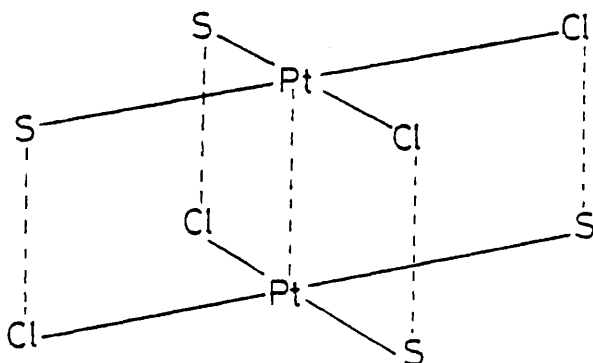


Figure 20. Interactions between centrosymmetrical molecules.

molecules. In each pair, the metal ligand bonds are eclipsed, the metal-sulphur bonds of one molecule being parallel to the metal chlorine bonds of the other. This orientation leads to $\text{Cl}\cdots\text{S}$ separations of 3.38 and 3.35\AA . On the other hand the $\text{Pt}\cdots\text{Pt}$ separation is 3.42\AA . The platinum atoms are displaced 0.002\AA from the PtS_2Cl_2 plane, away from each other whereas the displacement of the atoms $\text{S}(1)$, $\text{S}(2)$, $\text{Cl}(1)$ and $\text{Cl}(2)$ are respectively 0.028, 0.012, 0.035 and 0.016\AA in the opposite direction. Therefore this suggests an electrostatic interaction between electron deficient sulphur atoms and chloro ligands.

The $\text{Pt}\cdots\text{Pt}$ distance (3.42\AA) is longer than the typical lengths of Pt-Pt single bonds in platinum(II) ($2.77\text{--}2.87\text{\AA}$)^{221,222}. It is also

longer than the corresponding distance in $\left[\text{Pt}(\text{NH}_3)_4 \right] \left[\text{PtCl}_4 \right]$ (Magnus's green salt) $(3.25\text{\AA})^{223}$ for which a semi-empirical M.O. calculation indicated that the order of the covalent Pt-Pt bond is about 0.04^{224} . Therefore, bonding between platinum atoms in the crystal of $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ appears to be, if any, very small.

Other features of interest in the molecular structure of $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ include the orientation of the carbon-fluorine bonds involving the atoms F(3) and F(6). These atoms point inwards and almost towards each other with a resulting non bonded distance of 2.82\AA . This distance is larger than the van der Waals diameter of fluorine (2.70\AA). The S-C-F angles involving the atoms F(3) and F(6) are both ca 5° larger than the others S-C-F angles. These parameters are probably significant in relation to the fluorine-fluorine coupling constants between adjacent CF_3 groups as discussed in page 56

Nuclear magnetic resonance is a powerful tool in stereochemical studies and has been successfully used in configurational and conformational analysis of metal complexes^{225,226}. Previous configurational studies of dithio and diseleno ether complexes have been based predominantly on this technique and it is therefore surprising that very little has been achieved in correlating specific structures with the spectroscopic parameters that these structures produce.

It appears that the only cases where such an assignment has been established, correspond to the chelate complexes $(\text{Pr}^i\text{SeC}_2\text{H}_4\text{SePr}^i)\text{MX}$; $\text{M}=\text{Pd}$, $\text{X}=\text{Cl}_2$; $\text{M}=\text{Cr}$, Mo and W , $\text{X}=(\text{CO})_4$ and $(\text{PhCH}_2\text{SC}_2\text{H}_4\text{SCH}_2\text{Ph})\text{M}(\text{CO})_4$, $\text{M}=\text{Cr}$, Mo and W , reported during the course of this work^{26,33}.

The assignment is based on the detection of spin-spin coupling constants indicative of a preference for axial or equatorial positions of the methylene bridge protons, which indicates that the observed signal is generated by an anti isomer. Similar studies have been carried out

before on the conformational preferences of some diphosphines and diarsine metal complexes²²⁷⁻²³⁰. In general an accurate method of spectral simulation is needed to obtain the relevant parameters. In a more direct way, the spectrum of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ provided the same evidence.

Figure 21 shows the 94.1 MHz proton decoupled, fluorine n.m.r. spectrum

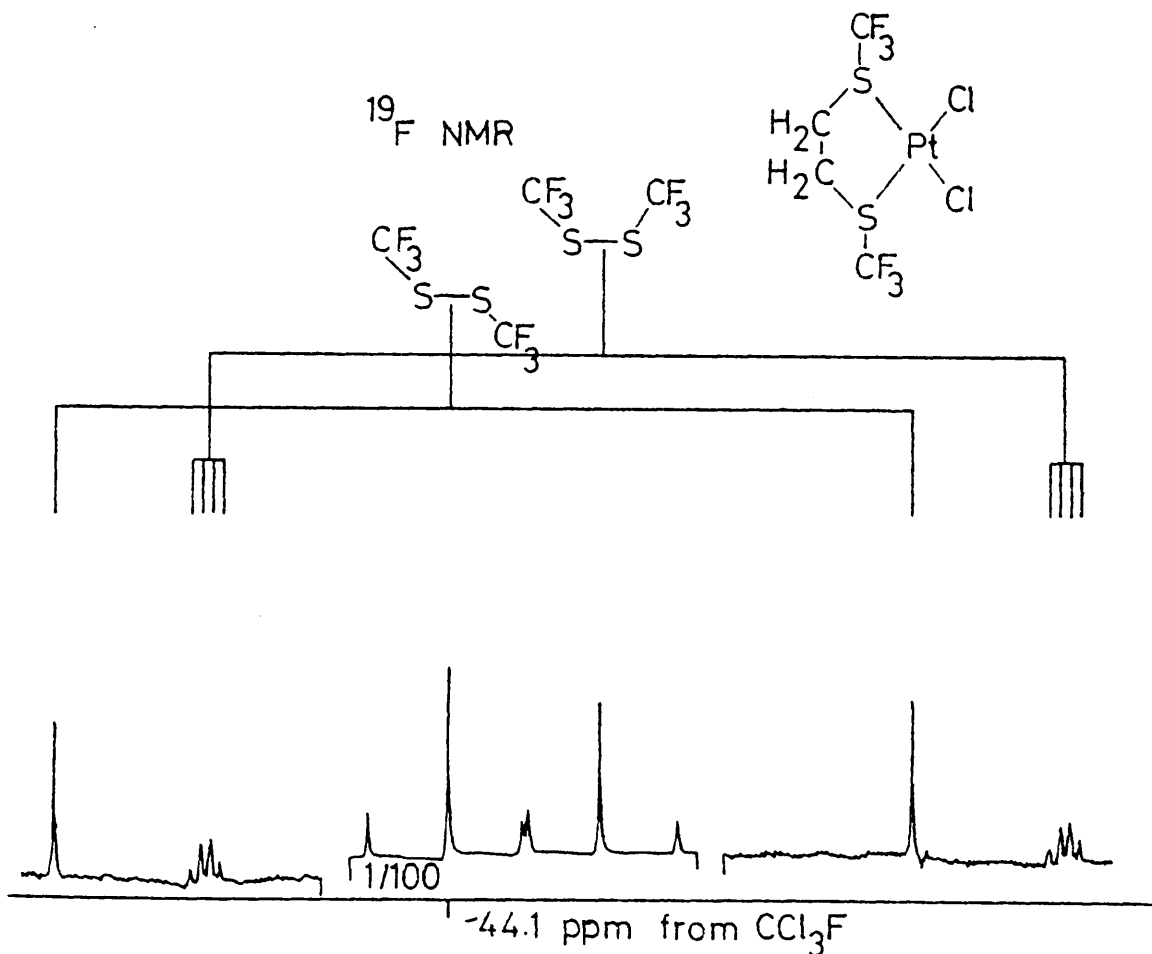


Figure 21. ^{19}F n.m.r. spectrum of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ showing ^{13}C satellites.

of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ at room temperature. The central part of the spectrum consists of two triplets in which the resonances have a 1:4:1 ratio. Each central absorption arises from species containing non-magnetically

active platinum and both signals have a pair of satellites produced by coupling between fluorine and ^{195}Pt ($I=\frac{1}{2}$, 33% abundance). A triplet is present for each syn and anti isomer in which the trifluoromethyl groups are equivalent. Since the relative intensities of these triplets are different the population of each isomer is not equal, showing that one configuration is favoured over the other.

In general fluorine chemical shifts are distributed over a wider range of values than corresponding proton chemical shifts are, but otherwise the spectrum in figure 21 is quite similar to those obtained for protons at the donor atom substituents, in complexes with the general formula $(\text{RER}'\text{ER})\text{PtX}_2$ where $\text{E}=\text{S}$ or Se , and R and R' are hydrocarbon groups²³.

Unlike their hydrocarbon analogues, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ - and other fluorinated complexes as well, vide infra - display a different multiplicity for the ^{13}C satellites of each isomer²³¹. As shown in figure 21 the ^{13}C satellites (enlarged a hundred times at each side of the normal spectrum) show a doublet of quartets for the high field signal. Effectively the ^{13}C can be thought of, as an element of asymmetry and the resultant effect is the observation of only one substituent of each isomer. This effect allows spin-spin coupling between fluorine atoms in different CF_3 groups to be observed for one configuration, whereas it was found to be absent in the other.

The transmission of spin-spin coupling is currently explained in terms of two different mechanisms, namely 'through bonds',²³² which depends on the electronic characteristics of the chemical bonds between the spin-spin coupled atoms, and 'through space',²³³ in which atoms which are at the extremes of a relatively large number of bonds but are, physically relatively close to one another, display a spin-spin coupling larger than that expected if it were transmitted through the electronic system²⁷⁰.

The experimental spectrum described, shows that spin-spin coupling between the sulphur substituents is present only for a specific

structure. Since it is unlikely that the different spatial arrangement of the trifluoromethyl groups would modify the electronic distribution to the extent of producing spin-spin coupling only in one orientation, preventing it completely in the other, the origin of such coupling is more adequately explained in terms of a 'through space' mechanism involving only the geometric arrangement of the coupled atoms²³⁴. By invoking this mechanism, it is evident that only the isomer in which substituents are orientated on the same side of the S-Pt-S plane has the necessary spatial requirements to display fluorine-fluorine coupling. It is therefore possible to assign the low field resonance to the anti isomer, in which the substituents are too far apart to show any ^{19}F - ^{19}F coupling, whereas the resonance at higher field is assigned to the syn isomer as shown in figure 21.

A more direct method of introducing an element of asymmetry to detect, directly, the spin-spin coupling between CF_3 groups, is the substitution of one of the ligands trans to the donor atoms. This has been achieved by preparing the mixed chloride-bromide complex.

The corresponding fluorine n.m.r. spectrum (figure 22) shows the expected doublet of singlets of equal intensity corresponding to each of the now distinct CF_3 groups of the anti isomer and, in addition, two quartets again with the same intensity, originated by the coupled trifluoromethyl groups of the syn isomer.

It is very difficult to generalize these structural assignments to compounds for which no direct evidence is available; nevertheless the similarity between the ratios of isomeric population of complexes listed in table 10 could be taken as an indication that a specific structure is always predominant. From molecular models it can be seen that an anti isomer minimizes the steric and electrostatic interactions between the sulphur substituents - or between the lone pairs - the anti form being indeed the predominant isomer in the complexes for which

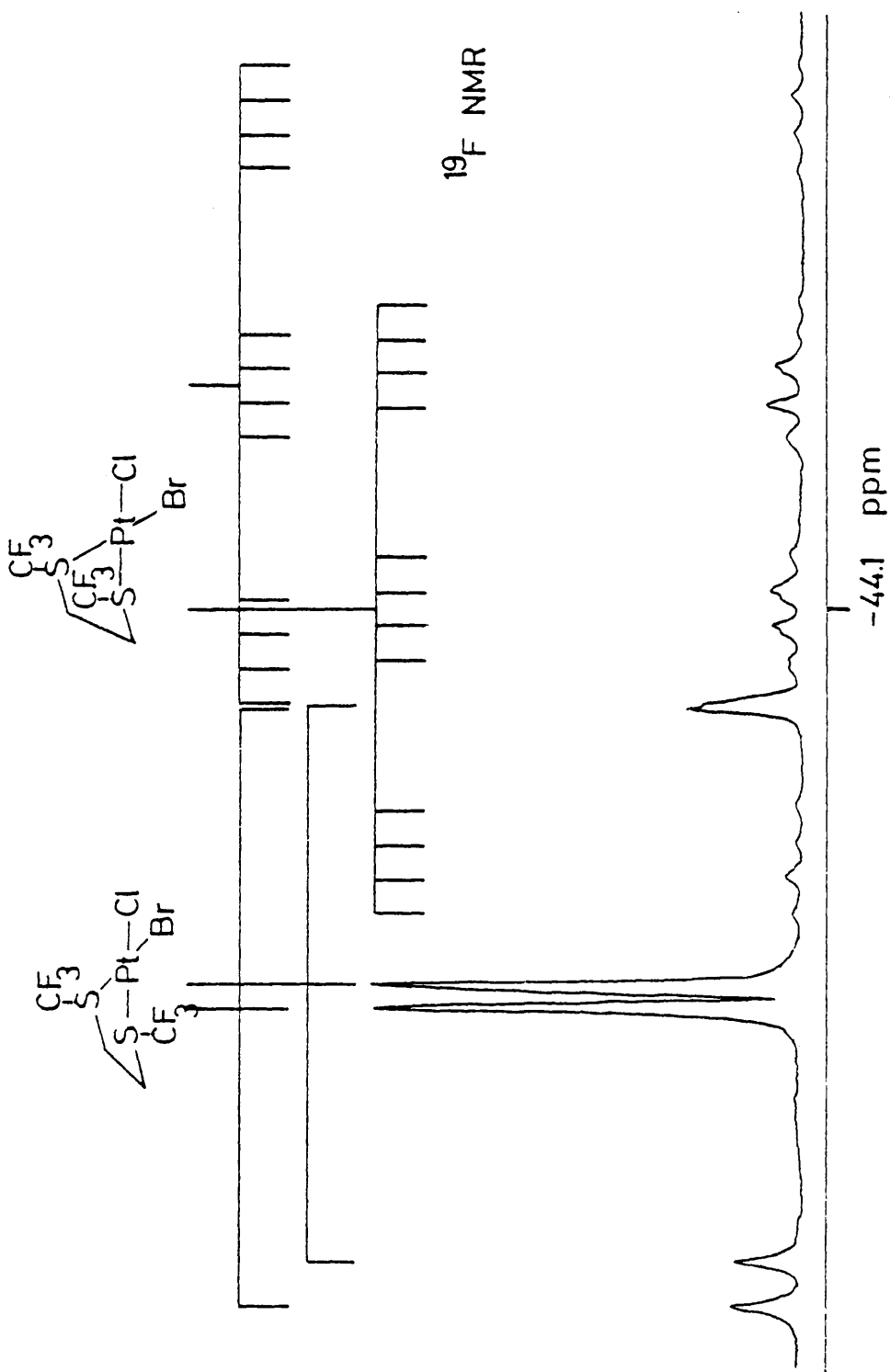


Figure 22. ^{19}F n.m.r. spectrum of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtClBr}$

direct evidence is available.

Table 10

Relative population of isomers

Compound/Isomer	relative %
$(CF_3SC_2H_4SCF_3)PtCl_2$	
syn	35
anti	65
$(CF_3SC_2H_4SCF_3)PtClBr$	
syn	35
anti	65
$(CF_3SC_2H_4SCF_3)PtBr_2$	
syn	28
anti	72
$(CF_3SC_2H_4SCH_3)PtCl_2$	
A	70
B	30
$(CH_3SCF_2CH_2SCH_3)PtCl_2$	
A	58
B	42
$(CH_3SCF_2CH_2SCH_3)PtI_2$	
A	54
B	46

a) from integration of n.m.r. resonances.

Therefore it seems reasonable to suggest tentatively, that the relative population of isomers, for compounds of the type described in this section, can be used to assign the anti structure to the more abundant isomer.

A complete description of the proton n.m.r. of $(CF_3SCH_2CH_2SCF_3)PtCl_2$ would be given by the superposition of two $(AA'BB'X_3Y_3Z + AA'BB'X_3Y_3)$ systems, where $A=B=^1H$, $X=Y=^{19}F$ and $Z=^{195}Pt$. The first term in these

systems correspond to compounds containing ^{195}Pt and each system correspond to a different isomer.

In the free ligand no detectable proton-fluorine coupling is found but in the complex, the anti isomer shows $^4J(\text{H-F})=4\text{Hz}$; therefore, as

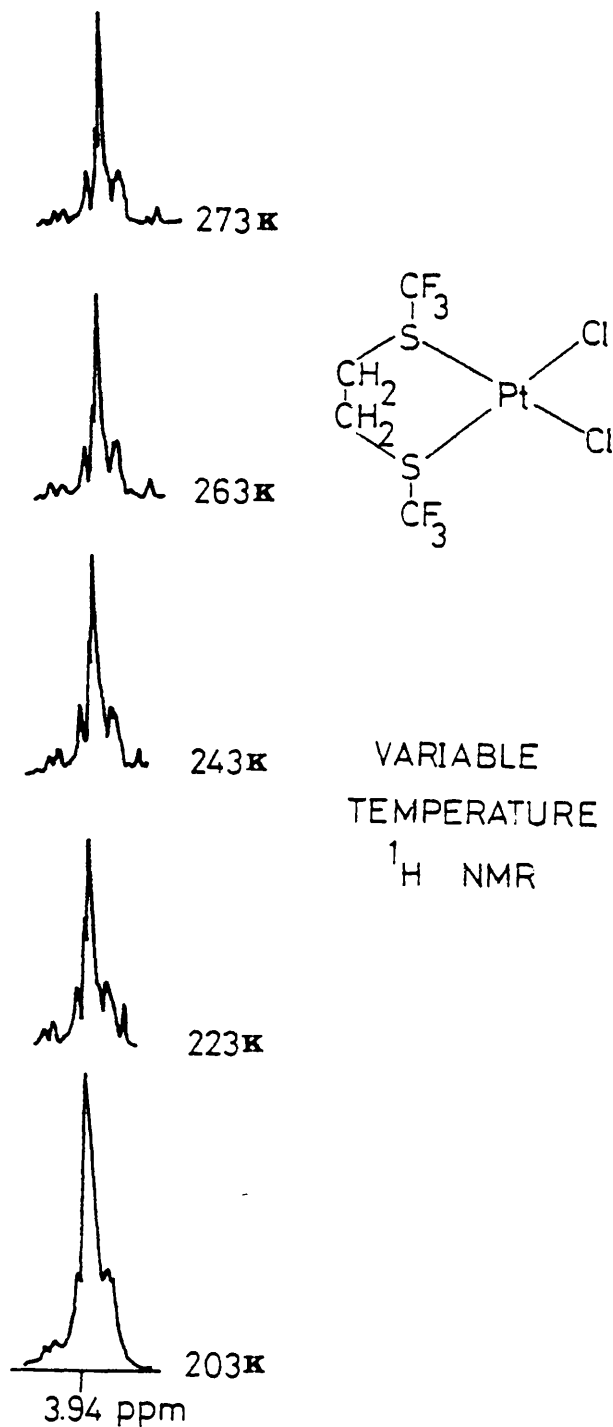


Figure 23. Low temperature proton n.m.r. spectra of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$

far as the proton n.m.r. is concerned, the magnetic systems in the complexes can be defined as $(AA'BB'X_3Y_3Z + AA'BB'X_3Y_3)$, (anti) plus $(AA'BB'Z + AA'BB')$ (syn).

In practice, the experimental 60MHz proton spectrum shows an unresolved multiplet (figure 23) which is basically unchanged after decreasing the temperature down to 203K, showing that at this temperature ring fluxion is still very rapid in the n.m.r. time scale.

In general all ^1H n.m.r. results found for the compounds reported here show the same poor resolution giving very little opportunity of detailed analysis and therefore they will not be discussed further.

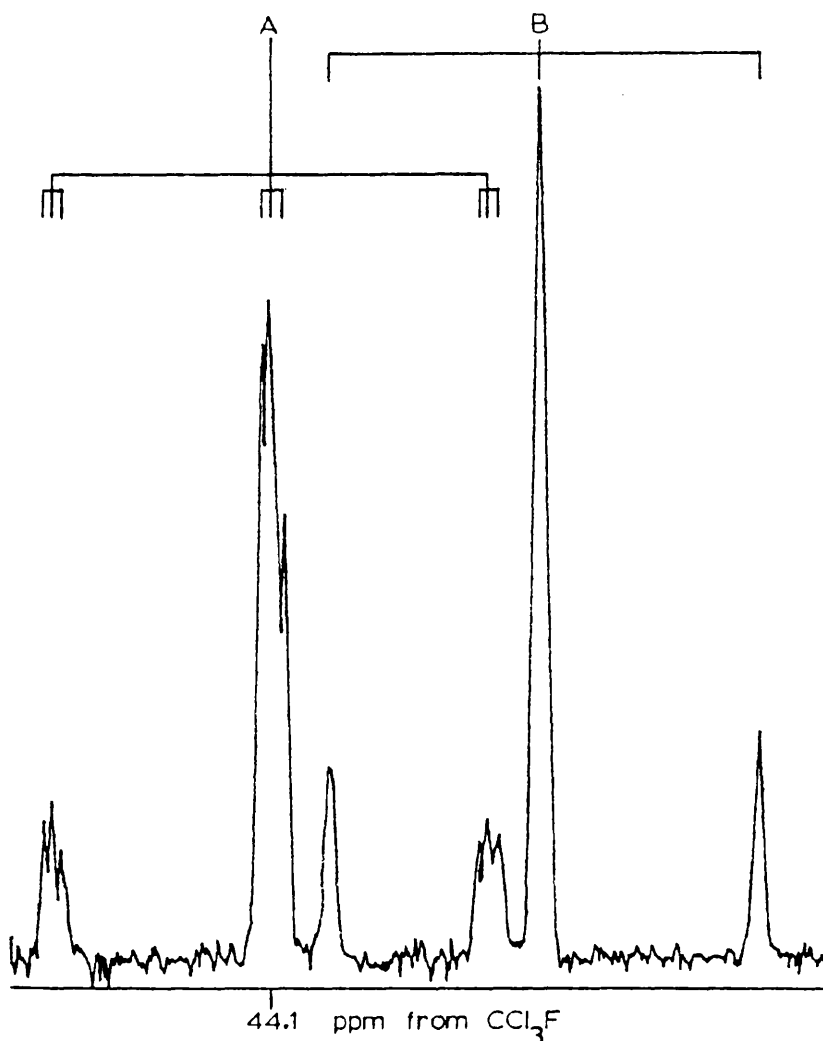
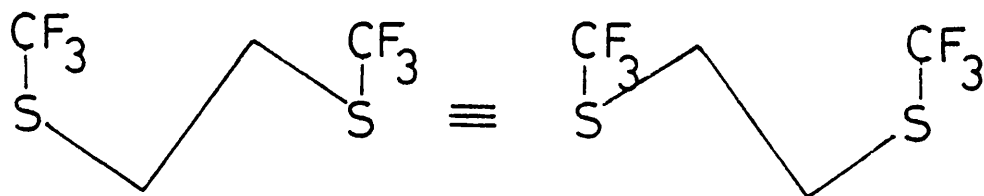
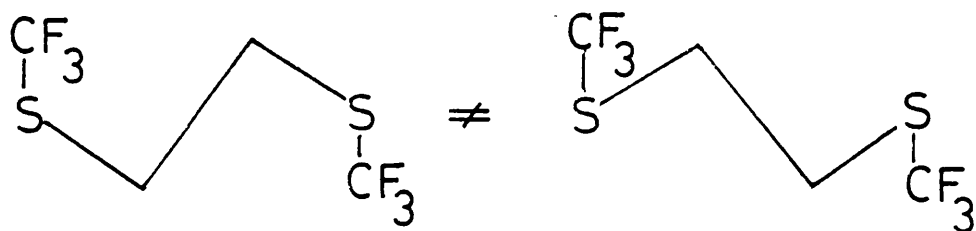


Figure 24. ^{19}F n.m.r. spectrum of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$.

Spin-spin coupling between fluorine and bridge protons is informative with regard to the conformational behaviour of the 5 membered ring. From the non-decoupled ^{19}F n.m.r. spectrum of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$, shown in figure 24, it is seen that only the anti isomer shows ^1H - ^{19}F coupling. The absence of a similar spin-spin coupling in the syn form can be rationalized by the fact that both of its possible conformers are identical,



and a rapid exchange of sites in the bridge effectively averages the molecular environmentⁿ precluding the observation of spin-spin coupling. For the anti isomer however, two distinct conformers are possible



A situation of fast exchange would also average the relative positions of the bridge; in this case however the energy and therefore the population of each conformer will probably be different and an increased population of one conformer would have the net effect of increasing the relative contribution of those spin-spin coupling constants

characteristic of a particular conformation. Unfortunately very little information is available²³⁵ regarding the angular dependence of $^4J(\text{F-C-S-C-H})$ and therefore there is no real basis to suggest which conformer is likely to be present in a larger proportion. Nevertheless the detection of this conformational equilibrium confirms the original structural assignment based on ^{19}F - ^{19}F coupling constants.

A different case where syn and anti isomers are expected to be present is represented by the complexes $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtX}_2$, $\text{X}=\text{Cl}$, Br or I .

Newman diagrams along the carbon-carbon bond for the syn and anti isomers and the corresponding conformers of $(\text{MeSCF}_2\text{CH}_2\text{SMe})\text{PtX}_2$ are shown in figure 25.

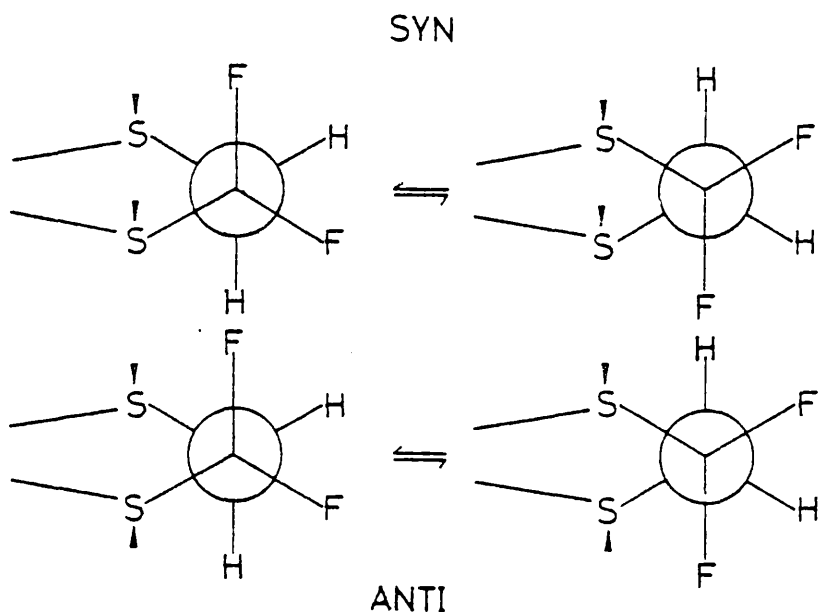


Figure 25. Newman projection along the bridge.

Restricted rotation about the carbon-carbon bond produces a pair of chemically non-equivalent fluorine atoms on each static conformer.

Rapid oscillation of the bridge between the more stable²³⁶ staggered conformations would simplify the expected n.m.r. system by

averaging the resonances of each fluorine between axial and pseudo-equatorial positions, making rotamers of each isomer indistinguishable, but, as shown in figure 26, the non equivalence of fluorine atoms will prevail.

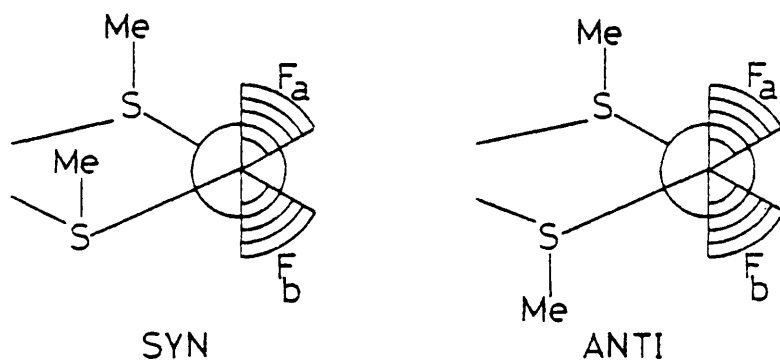


Figure 26. Averaged conformations of the bridge.

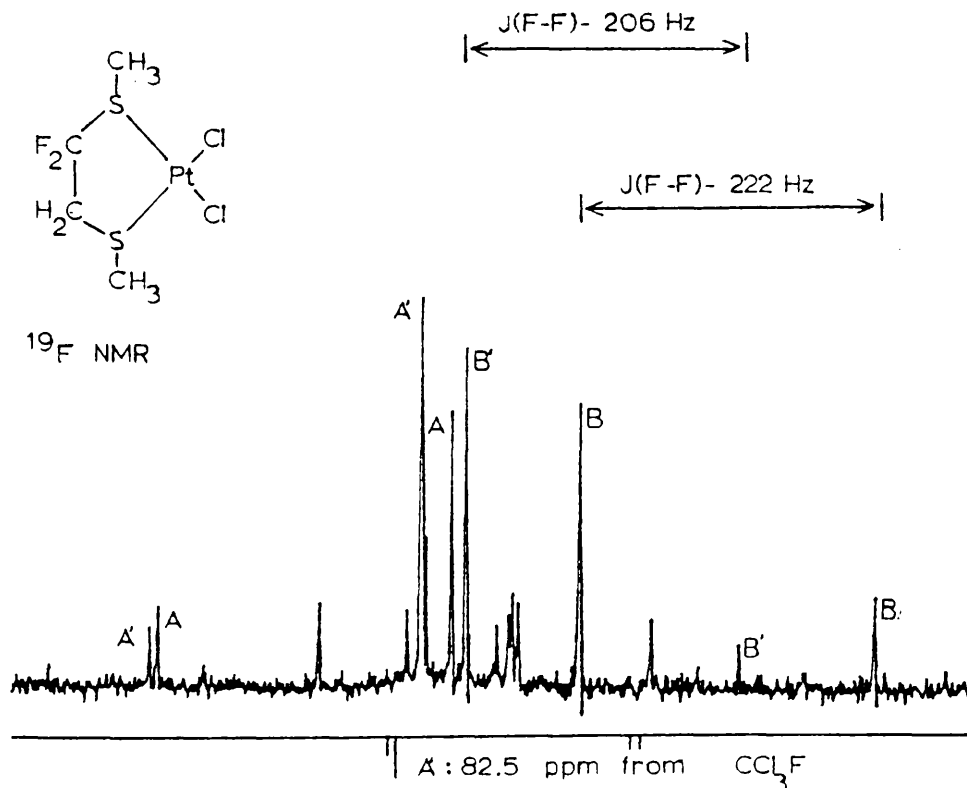


Figure 27. ^{19}F n.m.r. spectrum of $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$ showing two AB systems.

Assuming that coupling between methyl protons and the rest of the nuclei is zero the expected n.m.r. spectra would contain two (ABMX + ABMN) superimposed patterns, - syn and anti isomers - where $A=B=^1\text{H}$; $M=N=^{19}\text{F}$ and $X=^{195}\text{Pt}$. Figure 27 shows the 94.1 MHz, ^{19}F n.m.r. of $(\text{MeSCF}_2\text{CH}_2\text{SMe})\text{PtCl}_2$. By heteronuclear proton decoupling, the system has been further simplified to a (ABX + AB) pattern for each isomer. The solution of an ABX system is not trivial although it can be easily resolved by analytical expressions^{237,238}. The solutions for all but the isomer B of the bromide complex are given in appendix A and the relevant n.m.r. parameters are shown in table 11.

Table 11

N.m.r. parameters for $(\text{MeSCF}_2\text{CH}_2\text{SMe})\text{PtX}_2$ compounds.

Compound	$\delta^{19}\text{F}^a$	$J(\text{F-F})^b$	$J(\text{Pt-F})^b$
<hr/>			
$(\text{MeSCF}_2\text{CH}_2\text{SMe})\text{PtCl}_2$			
Isomer A	-84.6 -82.2	222	114.0 60.0
Isomer B	-83.5 -82.2	206	29.0 184.0
$(\text{MeSCF}_2\text{CH}_2\text{SMe})\text{PtBr}_2$			
Isomer A	-85.1 -81.4	223	118.0 43.0
Isomer B ^c		205.5	
$(\text{MeSCF}_2\text{CH}_2\text{SMe})\text{PtI}_2$			
Isomer A	-86.3 -79.9	225	113.5 22.5
Isomer B	-84.5 -82.8	206	155.5 27.5
<hr/>			

a) p.p.m. positive to low field of external CCl_3F .

b) Hz.

c) see appendix A.

As expected, fluorine atoms in each compound show relatively well separated chemical shifts, their coupling constants being in agreement

with other geminal ^{19}F - ^{19}F couplings reported^{239,240}.

On halide substitution, the magnitude of platinum-fluorine coupling constants reflect the increased halide trans influence on going from Cl to I. Simultaneously, geminal fluorine-fluorine coupling constants increase. Although these changes are not unexpected, since both parameters are presumably affected by the same electronic system, the mechanism leading to increments in $J(\text{F-F})$ is not clear. The differences in $J(\text{Pt-F})$ coupling constants between fluorine atoms of a given isomer depend on their relative position with respect to the sulphur substituents. In addition the differences in $J(\text{Pt-F})$ can reflect conformational variations; Cullen et al.²²⁸ have studied the conformational equilibrium, shown in figure 28, for several diarsine complexes.

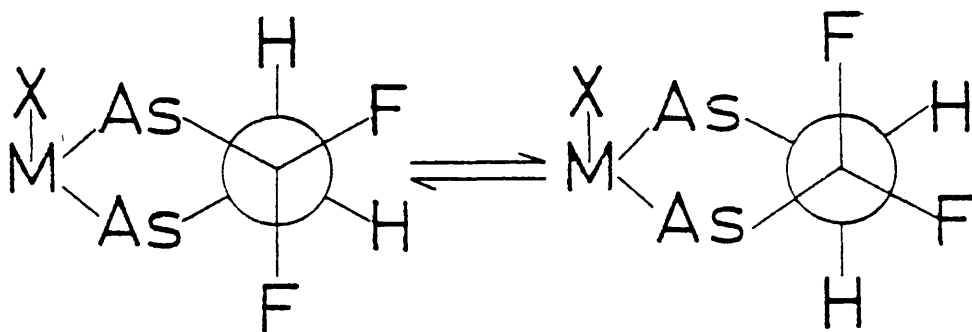


Figure 28. Conformations of a diarsine complex.

Although n.m.r. parameters were insufficient to identify a favoured conformer, the equilibrium was found to be dependent on solvent and temperature thus indicating that different populations of rotamers can be induced. It is probable that a similar situation is present for the present complexes and therefore $J(\text{Pt-F})$ can be considered to be affected by both ring fluxion and inversion, although at room temperature probably the predominant contribution would be that associated with the relative positions of the methyl and fluorine

substituents. An important difference between systems such as $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtX}_2$, I, and those discussed previously is that for both syn and anti isomers of I, each rotamer is chemically distinct as shown in figure 29.

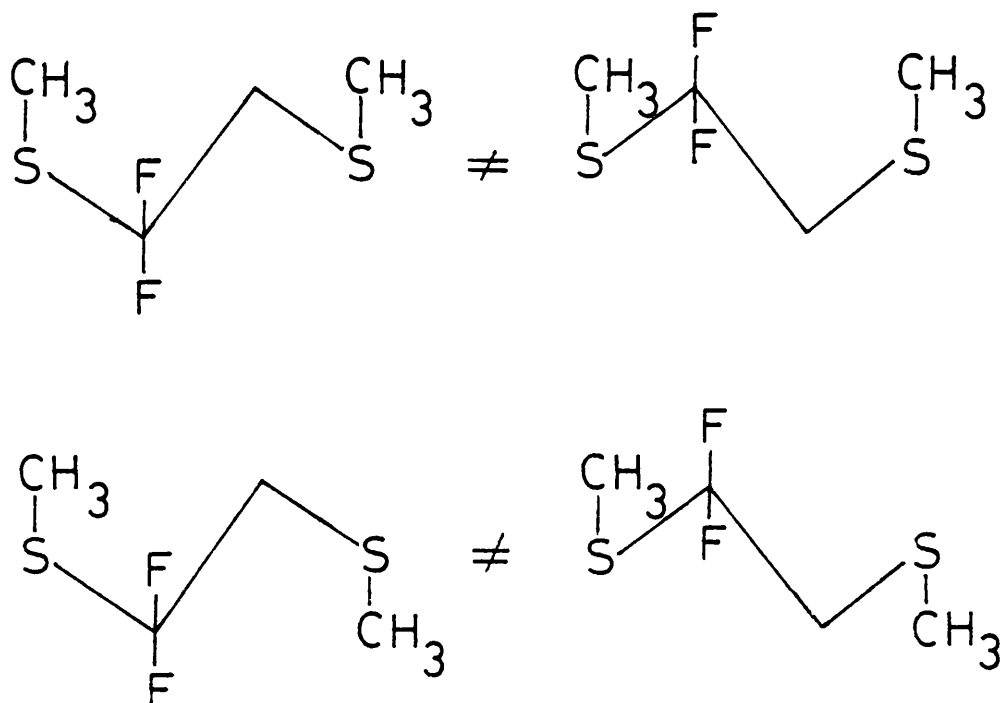


Figure 29. Rotamers of $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtX}_2$

Unfortunately no appreciable changes in the spectra of these compounds were found when the temperature was reduced to -90°C , indicating that carbon-carbon bond rotation at this temperature is still very rapid, thus precluding the distinction between each isomer. Furthermore, since both isomers can have a preferentially populated rotamer, there is no possibility of a structural assignment based on either $^4J(\text{H-S-C-F})$ or $J^{\text{vic}}(\text{F-F})$ at room temperature.

In order to determine the configurational distribution of asymmetric compounds in solution, the following compounds were studied: $(\text{RSC}(\text{R}')\text{CH}_2\text{SR})\text{PtX}_2$, $\text{R}=\text{CF}_3$, $\text{R}'=\text{CH}_3$, $\text{X}=\text{Cl}$, Br ; $\text{R}=\text{CH}_3$, $\text{R}'=\text{CF}_3$, $\text{X}=\text{Cl}$, Br , I ; $\text{R}=\text{R}'=\text{CH}_3$, $\text{X}=\text{Cl}$, Br , I .

Although some complexes with asymmetric chelating diphosphines and diarsines are known²⁴¹⁻²⁴³ no dithioether analogues have been reported prior to this work. For five membered ring complexes with group V donor atoms, the bridge substituent seems to determine the favoured conformer adopted by these compounds in solution^{229,242}. Dithioethers differ from diphosphines and diarsines in that in the latter compounds, there is no change in the number of isomers regardless on whether the bridge is symmetric or asymmetric, whereas for dithioether ligands dissimilar substituents on the bridge change the possible number of isomers in solution. Figure 30 shows the possible stereoisomers of $(CF_3SCH(CH_3)CH_2SCF_3)PtCl_2$.

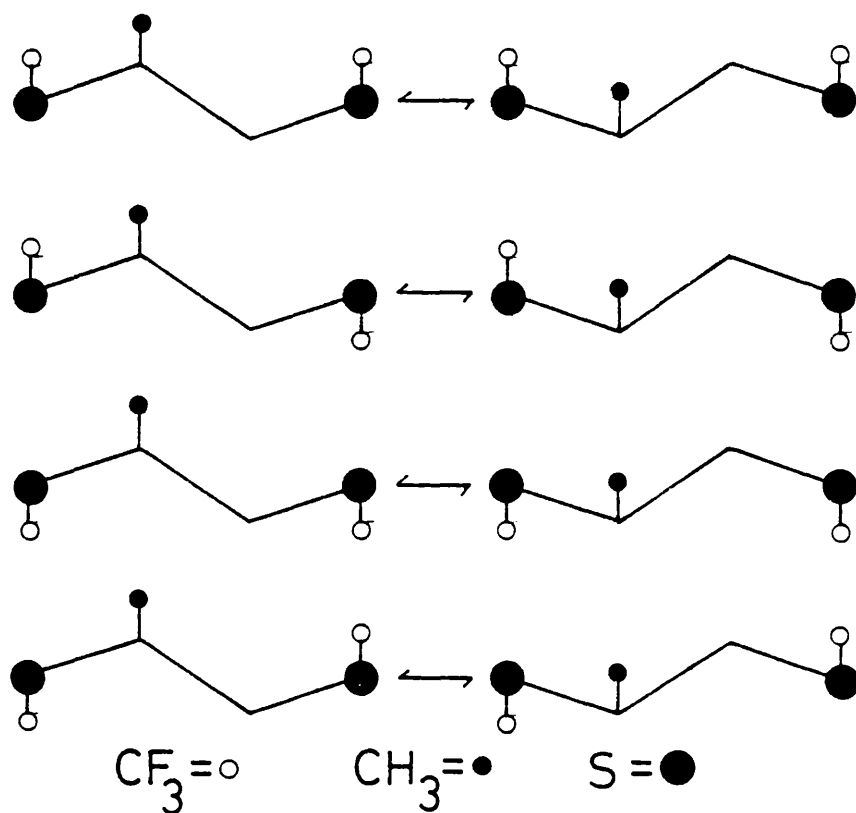


Figure 30. Four pairs of diastereoisomers of $(CF_3SCH(CH_3)CH_2SCF_3)PtCl_2$

In order to identify each arrangement with a simple nomenclature, the relative orientation of the bridge substituent and the adjacent

sulphur substituent will be referred to as syn or anti, followed by the reference to the relative orientation between both sulphur substituents, also as syn or anti, as illustrated in figure 31.

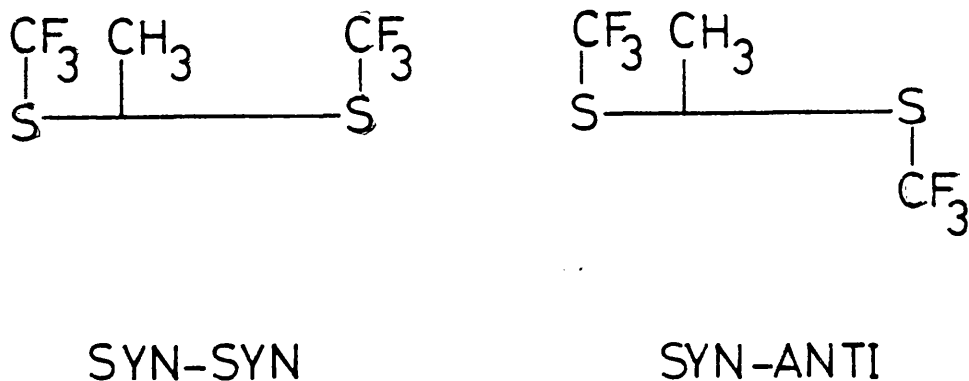
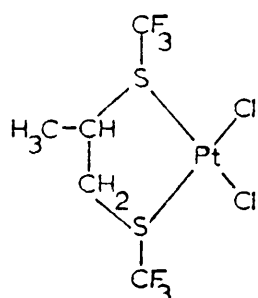


Figure 31. Nomenclature for complexes containing a bridge substituent.

N.m.r. spectra on acetone solution of $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ showed the presence of four isomers as expected from the above discussion; thus the 94.1 MHz, proton decoupled, ^{19}F n.m.r. spectrum, shown in figure 32 has four pairs of resonances with platinum satellites. Components of each pair have the same relative intensity but it is different from pair to pair. Two of the pairs are singlets whereas the other two are quartets due to ^{19}F - ^{19}F coupling between fluorine atoms in non-equivalent trifluoromethyl groups.

The presence of the methyl substituent in the bridge causes the CF_3 groups in $\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3$ to be chemically distinct and, as in the case of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtClBr}$, their resonances occur at well separated frequencies. In agreement with the data from the symmetric $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$, through space coupling between trifluoromethyl groups is observed for two isomers as expected for the syn-syn and anti-syn configurations. $J(\text{F-F})$ is however, only useful in determining

which pair of resonances originates from a syn or from an anti structure, but it is not possible to decide which syn (or anti) resonance arises from which syn (or anti) structure.



^{19}F NMR

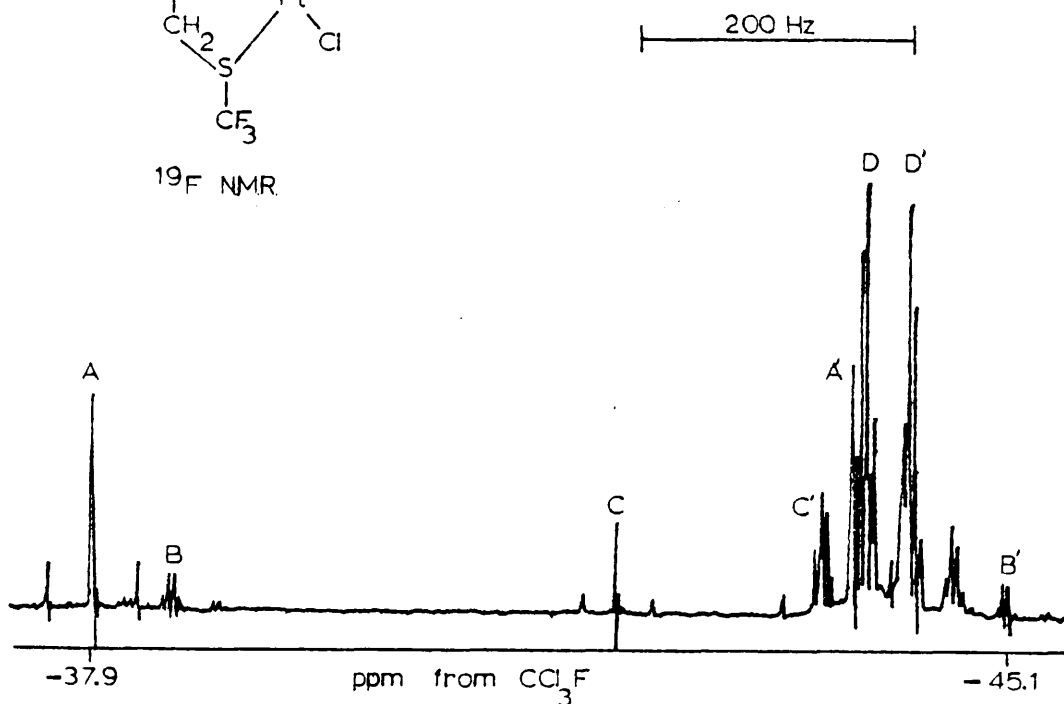


Figure 32. ^{19}F n.m.r. spectrum of $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$.

If molecular models are constructed using the bond lengths from table 9, it is found that the non bonded distances between the methyl group and trifluoromethyl substituents is less than the sum of the van der Waals radii (SVWR) in several orientations. Examining the extreme axial and pseudo-equatorial positions allowed for the methyl group and according to the next diagram, for an axial orientation of the methyl group all but the anti-syn isomers show $\text{CF}_3\text{-CH}_3$ distances shorter than SVWR. Similarly, when the distances between the equatorial methyl group and sulphur substituents are compared to their SVWR, they

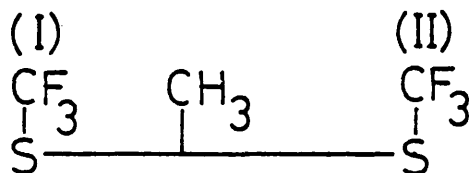


Diagram I

are found to be shorter for both syn-syn and anti-syn isomers whereas in the case of anti-syn and anti-anti structures these distances are larger. Table 12 gives the distances found to be less than the SWR.

Table 12

Non-bonded distances less than the sum of van der Waals radii in $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2^*$

Isomer	CH_3 -axial	CH_3 -equatorial	Interactions
syn-syn	$\text{CH}_3\text{-CF}_3(\text{I})$	$\text{CH}_3\text{-CF}_3(\text{I})$	3
	$\text{CH}_3\text{-CF}_3(\text{II})$		
syn-anti	$\text{CH}_3\text{-CF}_3(\text{I})$	$\text{CH}_3\text{-CF}_3(\text{I})$	2
anti-anti	$\text{CH}_3\text{-CF}_3(\text{II})$	none	1
anti-syn	none	none	0

* Roman numeral refer to Diagram I.

The information summarized in table 12 must be approached with caution because of the manner in which it has been obtained. It is interesting to note, however, that in contrast with the results found for symmetric compounds, e.g. $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$, for which the anti form predominates, the n.m.r. results for $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ show that an isomer with both CF_3 groups syn relative to each other is by far - 78% vs. 12%, 6% and 4% - the more abundant isomer. In the

solid state the compound studied has the anti-syn structure described and from table 12, as an indication of the sort of steric interactions that can be expected, the anti-syn configuration minimizes all interactions between bridge and sulphur substituents. On these bases, it seems likely that the predominant form in solution is the anti-syn structure found in the solid state. N.m.r. parameters are consistent with this assignment.

According to the data on table 12 no $\text{CH}_3\text{---CF}_3$ interaction is predicted for the anti-syn isomer; one non-bonded distance is shorter than the SWR in the anti-anti structure, two for the syn-anti case and three in the syn-syn isomer. Therefore after the anti-syn isomer, - highly populated as predicted - the next favoured structure would correspond to the anti-anti orientation and from the n.m.r. data, the next most intense resonance - 12% - should indeed arise from an anti arrangement, since $^{19}\text{F}\text{---}^{19}\text{F}$ coupling is absent.

Similarly, in terms of inter-substituent interactions a syn-anti structure should be present in larger proportion than the syn-syn form, the last isomer having maximum steric interactions. The n.m.r. intensities are in this order, with the lowest population - 4% - for a syn isomer, followed by 6% corresponding to an anti structure.

The structural assignment described is summarized in table 13.

The next compound to be considered is $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$ which also was found by n.m.r. spectroscopy, to form an equilibrium mixture of four isomers in acetone solution at room temperature. The 94.1 MHz proton decoupled, ^{19}F n.m.r., figure 33, shows four singlets with platinum satellites. The relevant n.m.r. parameters are given in table 14.

Table 13

Structure and corresponding n.m.r. parameters of $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$

Structure	relative %	$\delta^{19}\text{F}^a$	$J(\text{F-F})^b$	$J(\text{F-Pt})^b$
syn-syn	4	-38.5 -45.1	+4.6	+65.5 +54.0
syn-anti	6	-37.9 -43.9	0	68.7 54.0
anti-syn	78	-44.0 -44.4	+4.6	+59.0 +59.0
anti-anti	12	-42.1 -43.7	0	58.0 62.0

a) p.p.m. positive to low field of external CCl_3F

b) Hz.

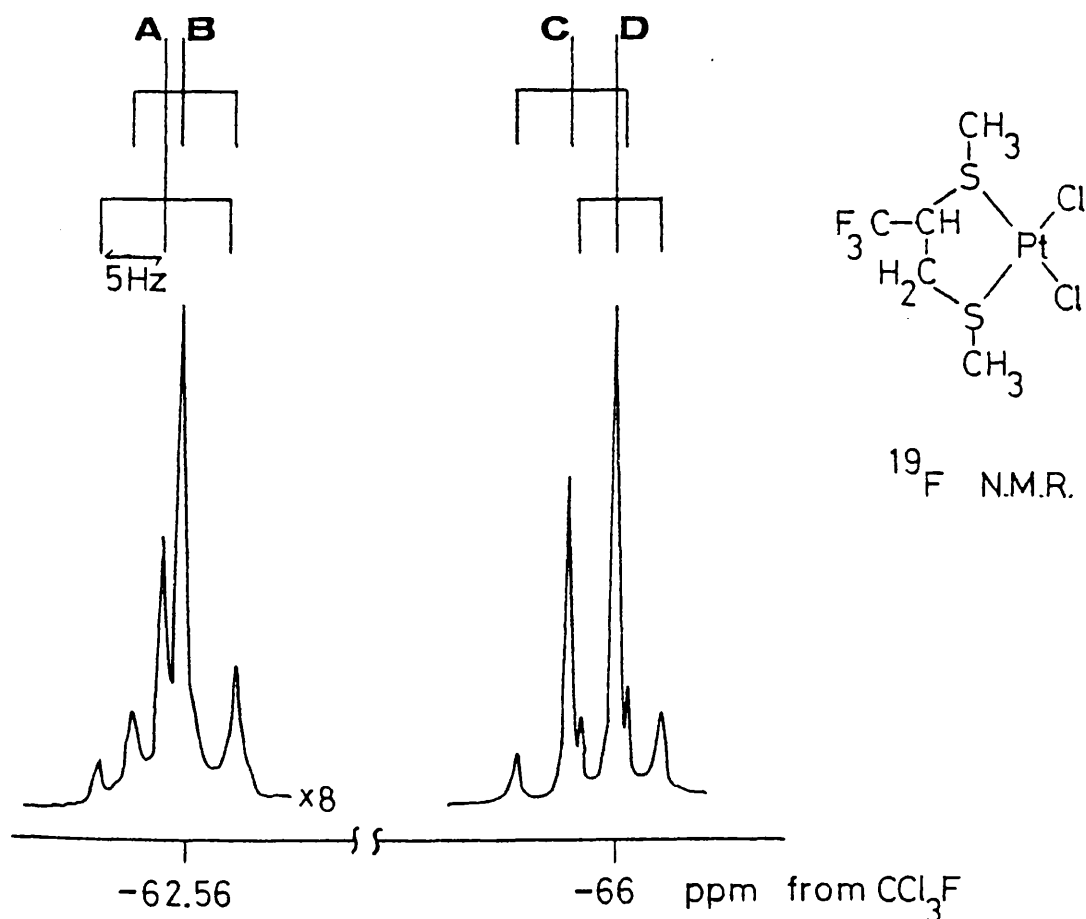
Figure 33. ^{19}F n.m.r. spectrum of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$

Table 14

N.m.r. parameters of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtX}_2$
 $\text{X} = \text{Cl}, \text{Br}, \text{I}.$

Compound	relative %	$\delta_{\text{F}}^{19\text{a}}$	$J(\text{Pt-F})^b$
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$			
Isomer A	4	-62.56	10.0
Isomer B	57	-66.00	6.2
Isomer C	8	-62.56	8.0
Isomer D	31	-65.96	8.4
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}_2$			
Isomer A	6	-62.24	9.1
Isomer B	53	-65.75	5.7
Isomer C	13	-62.19	6.9
Isomer D	28	-65.67	7.4
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtI}_2$			
Isomer A	5	-62.02	6.1
Isomer B	52	-65.55	3.6
Isomer C	19	-61.74	4.4
Isomer D	24	-65.49	5.1

a) p.p.m. positive to low field of external CCl_3
 b) Hz.

Unlike $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$, no direct evidence for the structure corresponding to each resonance is available for any of the compounds formed by $\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3$. The correlation between each isomeric form and the n.m.r. parameters must therefore be made by comparisons with pre-assigned structures. Substitution of methyl by trifluoromethyl groups gives small changes to parameters affected only

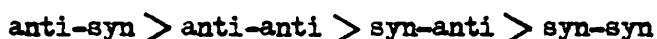
Table 15

Structural assignment for $(\text{RSCH(R)CH}_2\text{SR})\text{PtX}_2$

S T R U C T U R E

Compounds	syn-syn	syn-anti	anti-syn	anti-anti
<hr/>				
$(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$				
relative %	4	6	78	12
$\delta^{195}\text{Pt}$	-100.5	-154.7	-98.3	-202.3
<hr/>				
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$				
relative %	4	8	57	31
$\delta^{195}\text{Pt}$	-195.3	-165.6	-192.8	-219.4
<hr/>				
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}_2$				
relative %	6	13	53	28
$\delta^{195}\text{Pt}$	-580.8	-554	-580.4	-618.9
<hr/>				
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtI}_2$				
relative %	5	13	52	24
$\delta^{195}\text{Pt}$	-1399.3	-1371.4	-1397.9	-1427.3
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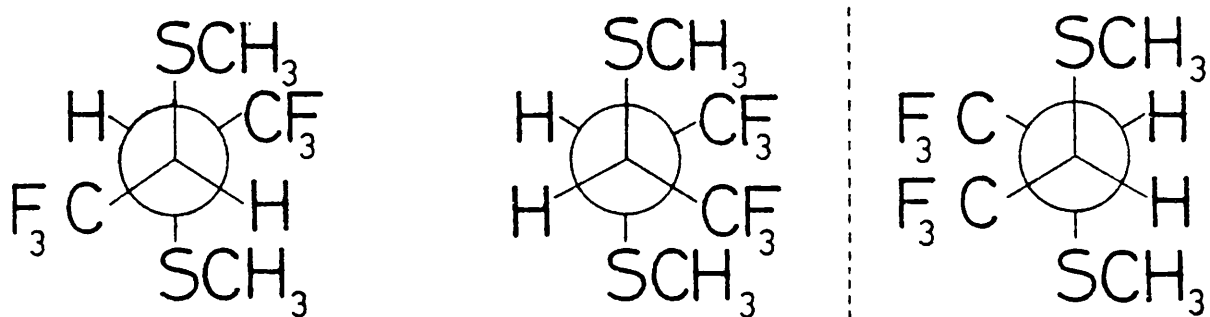
by atomic dimensions; thus models of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$ using bond distances from similar compounds^{15,220} produce a similar set of results to those given in table 12. Interatomic distances and van der Waals radii variations and therefore changes in the relative intensities of non-bonded interaction could be expected. The relative population for isomers of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$, (table 14) are 57, 31, 8 and 4%. For $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$, the order of increasing population is:



Assigning this order to $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$, gives the results shown in table 15.

It should be noticed that although the structural assignments of table 15 are based on the assumption that the relative isomeric distribution is dominated by the repulsive effects, it has led to the correlation of the largest value of $\delta^{195}\text{Pt}$ to the same anti isomer in all asymmetric compounds, and has related to a pair of syn isomers (syn-syn and anti-syn) the only pair of platinum chemical shifts found to occur within 3 ppm of each other. This trend of platinum chemical shifts, consistent within a series of different compounds is considered as indirect evidence in support of the original assignment.

Finally, the possible structures of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtX}_2$ X= Cl, Br or I will be discussed. As described in chapter I $\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$ having two chiral carbon atoms in the bridge has two possible isomeric forms, meso and (\pm) shown in figure 34.



MESO

(±)

Figure 34. Isomers of $\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$

Rotation about the central carbon-carbon bond will produce two additional spatial arrangements of both isomers. These conformational isomeric-structures IA, IB, IIA and IIB in figures 35 and 36, represent three pairs of mirror images. IA is identical to the mirror image of IB and vice versa, therefore the pair IA and IB are equivalent to IA and its mirror image. IIA and IIB as a pair of enantiomers are however

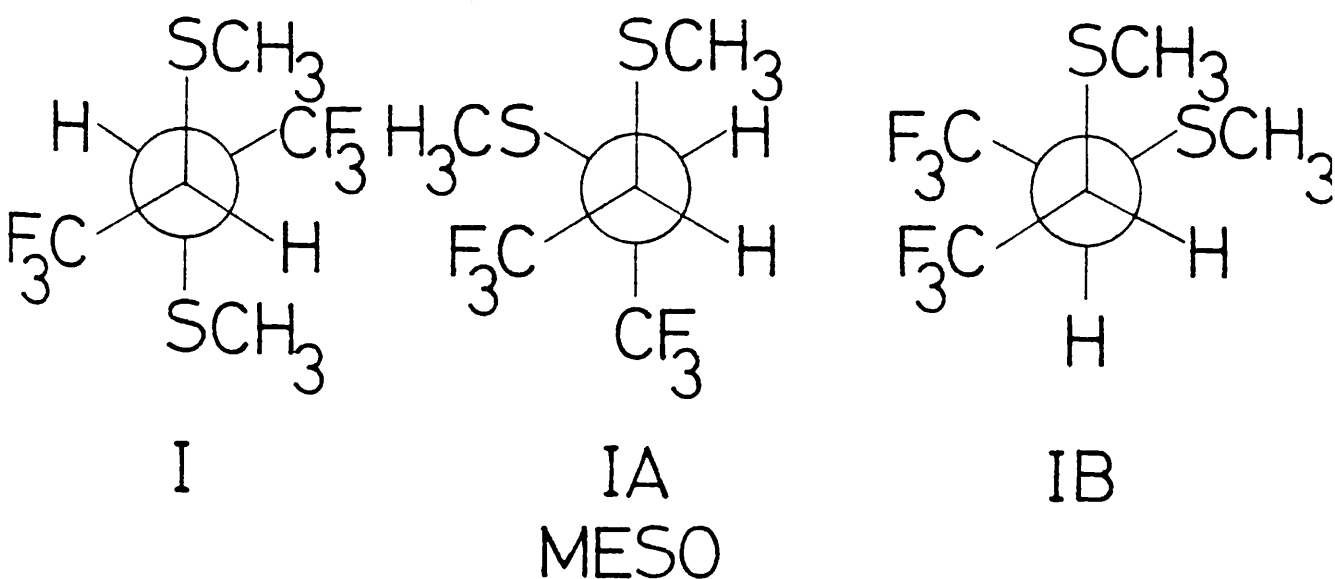


Figure 35. Enantiomers of the meso form.

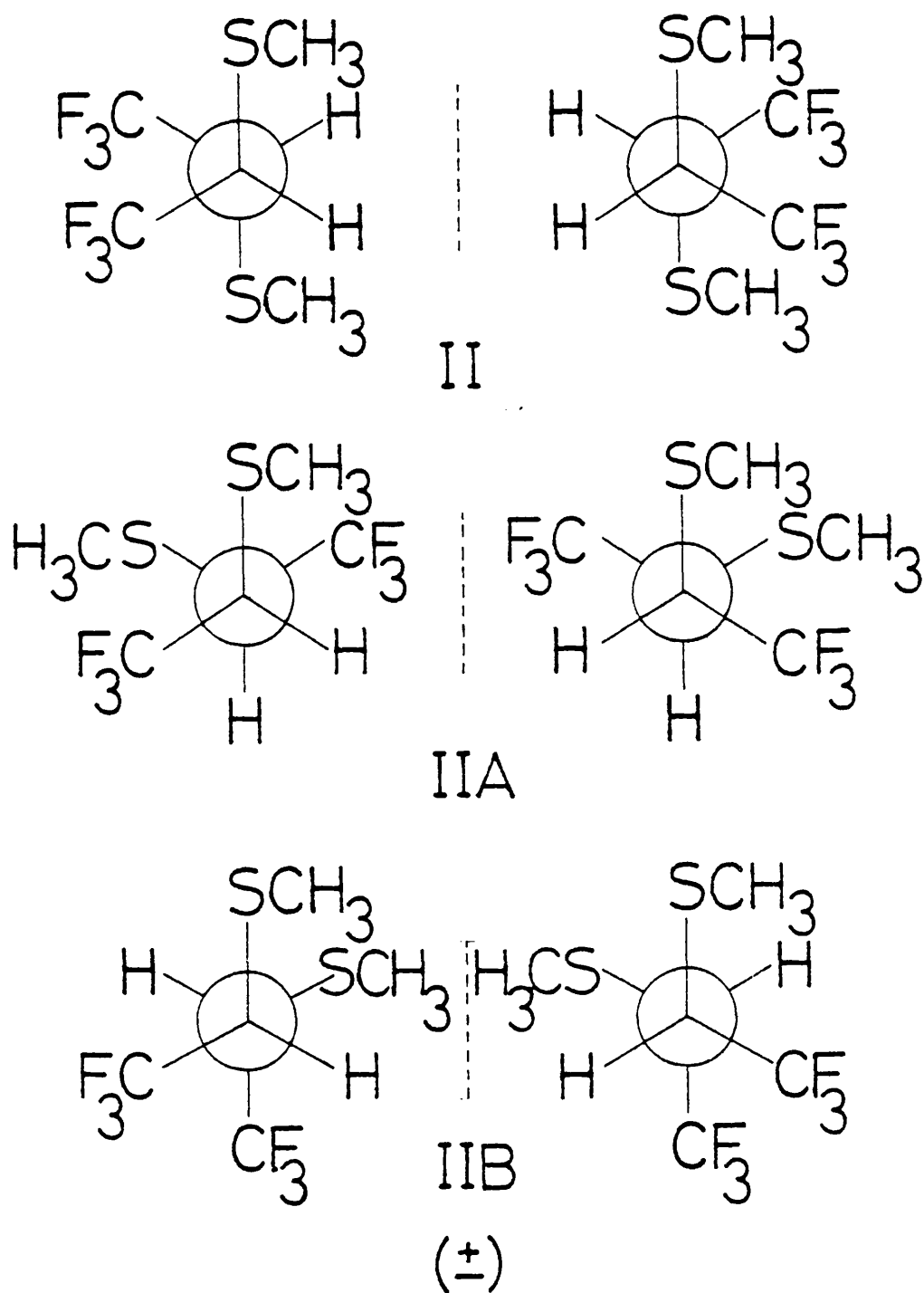
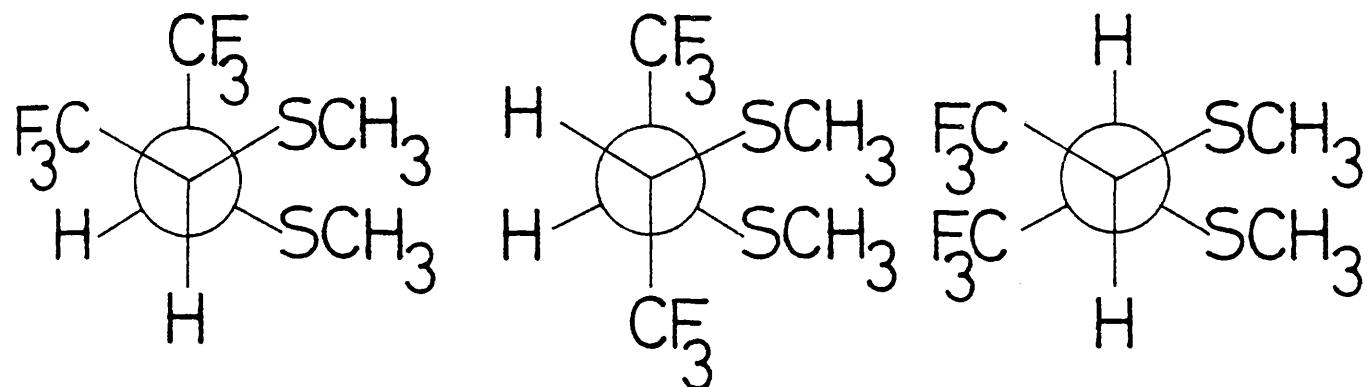


Figure 36. Enantiomers of the (\pm) form.

chemically different. In order to discuss the possible isomers of the complexed ligand, it will be sufficient to consider the gauche forms of both meso and (\pm) isomers, since these are the only forms capable

of forming complexes. These structures are shown in figure 37. Clearly,



MESO

(\pm)

Figure 37. Gauche form of meso and (\pm) isomers.

the fact that we can eliminate other ligand structures to clarify this analysis, does not imply that conformers can exist as isolated species at room temperature.

Since individual enantiomers are indistinguishable by n.m.r. spectroscopy, the same results would be achieved by considering both or only one conformer of each pair of mirror images IA, IIA and IIB. Furthermore, if rapid rotation about the carbon-carbon bond, as found for the free ligand, is maintained after formation of metal complexes, the interchange between axial and pseudo-equatorial positions of proton and trifluoromethyl group would result in an averaged signal. The distinction between structures IIA and IIB will no longer be possible and, as a result, only two structures, described in figure 38, could be detected by n.m.r. techniques.

An important difference between the magnetic properties of these structures is that, although averaging of the meso form will make indistinguishable each static orientation of the trifluoromethyl groups,

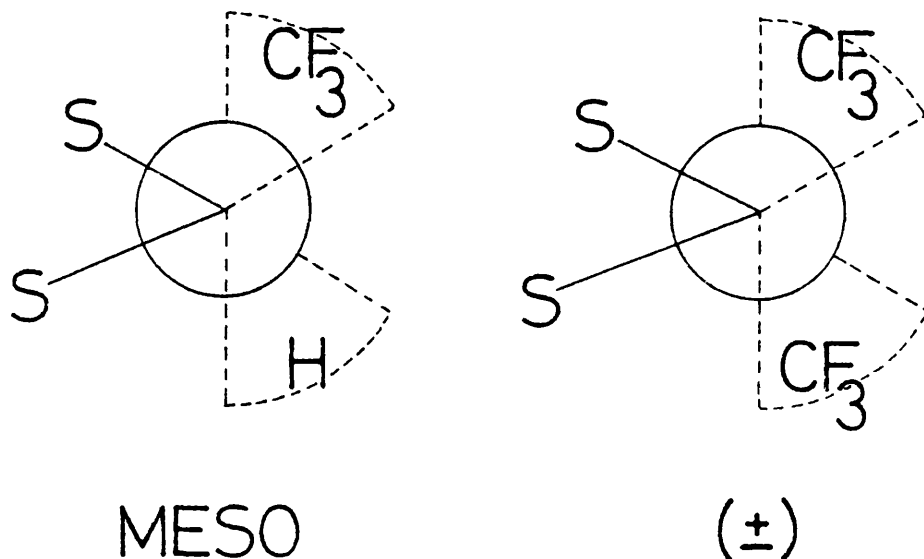


Figure 38. Averaged meso and (\pm) isomers

these groups will nevertheless remain chemically non-identical one to each other, since they are trans to a different carbon substituent. However, CF_3 groups in the (\pm) isomer are equivalent regardless their relative orientation. Rapid rotation about the carbon-carbon bond will therefore, produce similar n.m.r. resonances for both isomers.

Complexation imposes a restriction on the rotation of the $\text{CH}_3\text{S}-\text{C}$ bond, fixing two possible orientations of the methyl substituents in the same way found for other dithioether complexes. The relative position of the sulphur substituents and the meso and (\pm) orientations of the bridge substituents, involves geometrical possibilities leading to isomerism and gives rise to three meso isomeric structures A, B and C in figure 39 and three (\pm) isomeric structures D, E and F. In the diagrams used in figure 39, the S-Pt-S plane is perpendicular to the paper plane with the platinum atom behind the diagram. The figures represent averaged structures and therefore, in structure A for example, trifluoromethyl groups will be rapidly changing between axial and pseudo-equatorial positions.

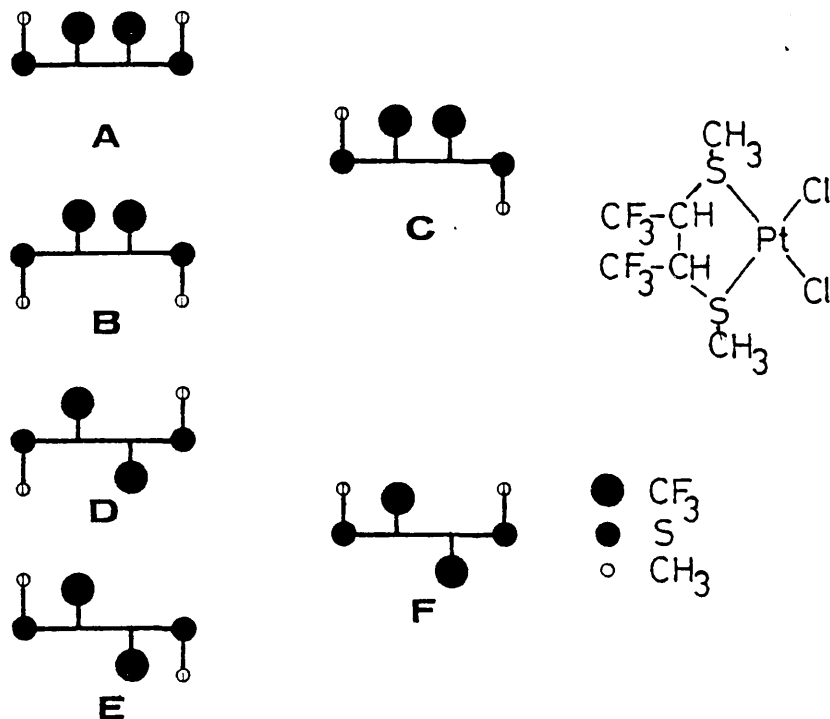
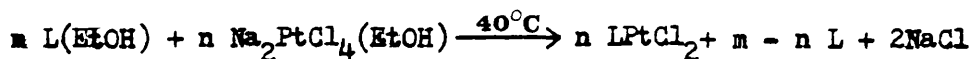


Figure 39. Possible isomers of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtCl}_2$.

Each set of meso - A, B and C - and (+) - D, E and F - isomers represent a non interconvertable group of isomers. Within each set, however, each structure can undergo a change of configuration only by inverting the orientation of the methyl substituents. This fact gives some indication of the relative proportion of meso and (+) isomers expected, since their ratio will depend on the relative proportion of meso and (+) isomers in the ligand mixture originally used.

To ensure that both isomers of the ligand had similar opportunities for complexation, the formation of the Pt(II) complex was followed by n.m.r. spectroscopy. The reaction studied was:



where $\text{L} = \text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$ and $m > n$

The experiment showed that the relative proportion of meso and (+) isomers in the pure ligand was maintained throughout the reaction

of complex formation. The composition of the excess ligand remaining after the reaction was complete, showed the same proportion of meso to (\pm) isomers found initially for the pure ligand.

Since the ratio was approximately 2:1 (meso:(\pm)), a larger population of meso than (\pm) complexes is expected.

It should be noticed, from the structures in figure 39, that two different types of n.m.r. resonances will be produced, depending on the relative positions of the sulphur and bridge substituents.

Trifluoromethyl groups are equivalent in isomers A, B, D and E and therefore, their resonances will be distinct from those arising from isomers C or F in which both trifluoromethyl groups are non-equivalent.

^{19}F n.m.r. spectra were recorded, as for previous complexes, at 94.1 MHz with heteronuclear proton decoupling and are shown in figures 40, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtX}_2$, X=Cl; 41, X=Br and 42, X=I.

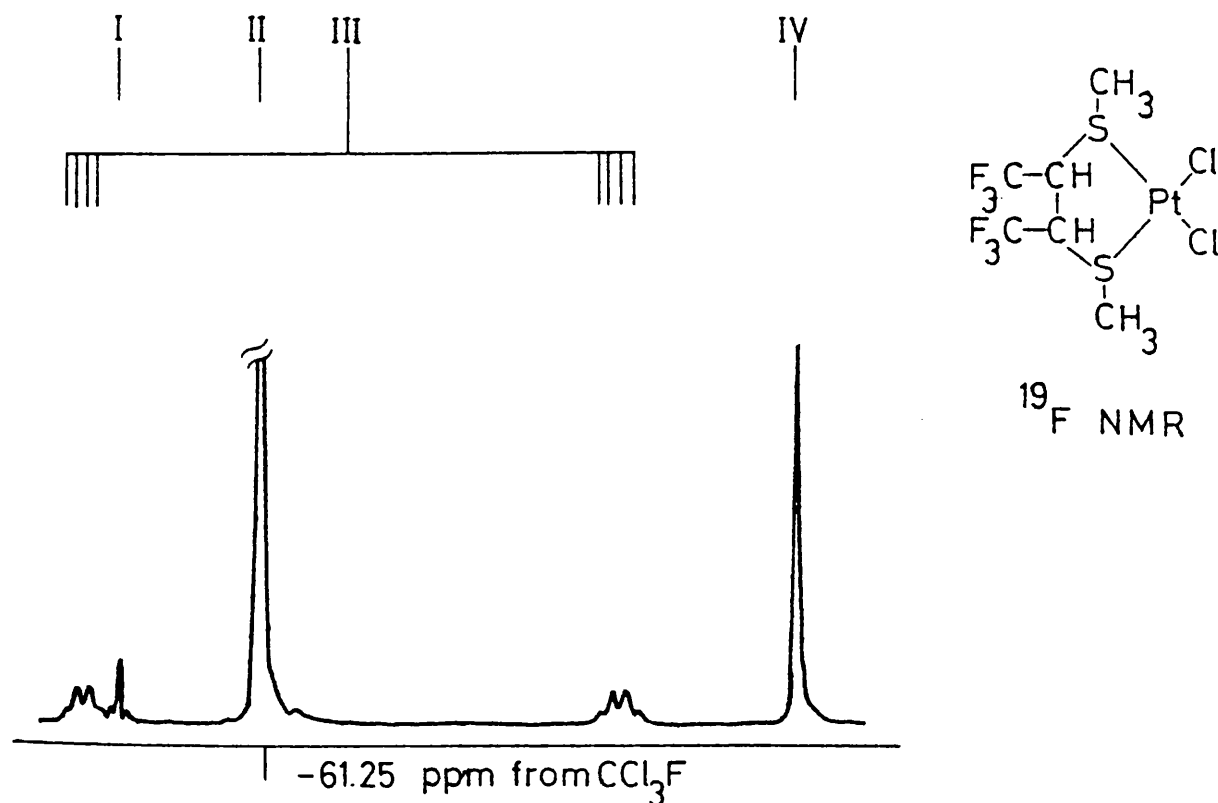
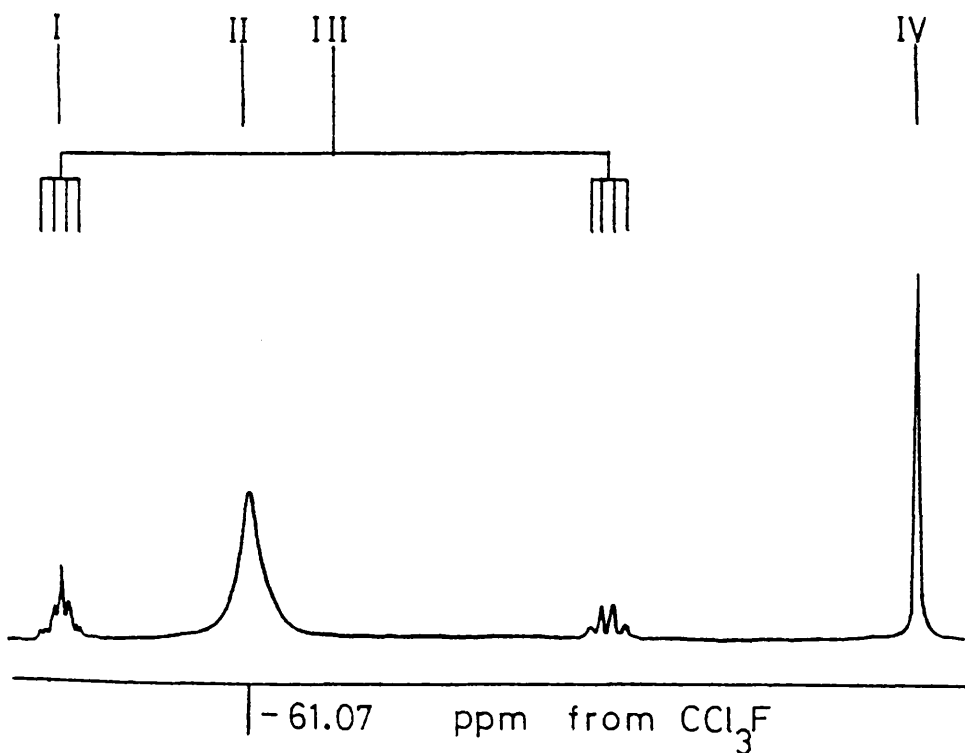
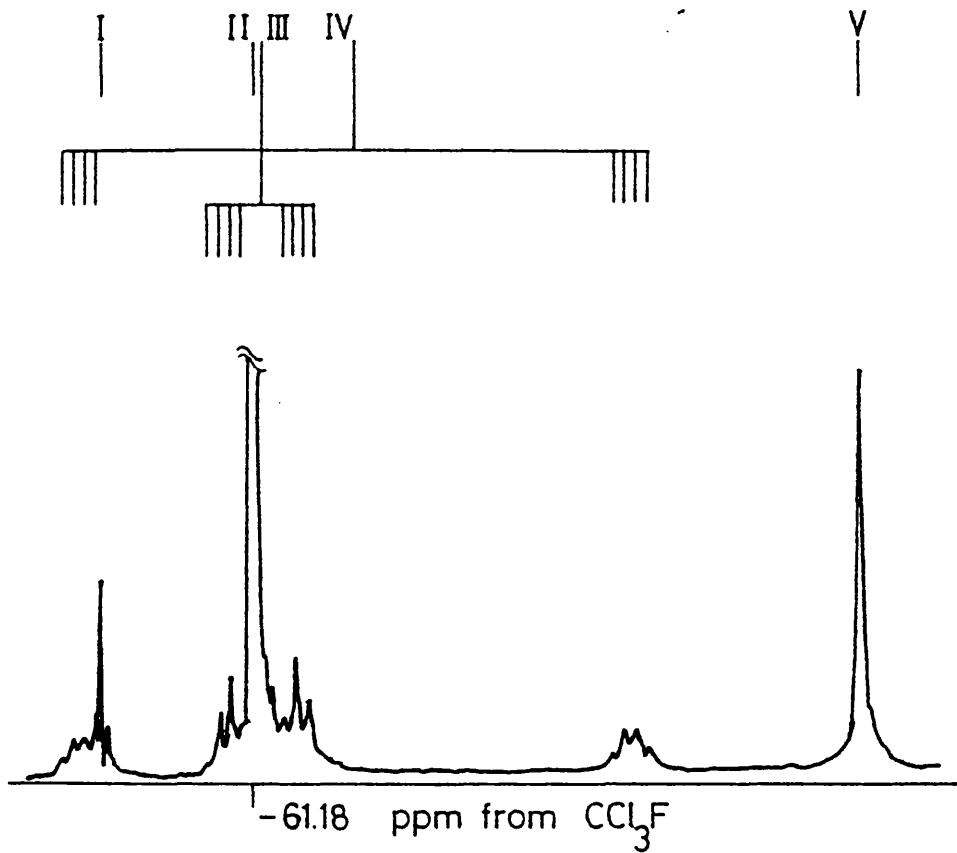


Figure 40. ^{19}F n.m.r. spectrum of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtCl}_2$



Figures 41 and 42. ^{19}F n.m.r. spectra of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtX}_2$
 $\text{X}=\text{Br}$ and I .

The relevant n.m.r. parameters of the complexes discussed are given in table 16.

Table 16

N.m.r. parameters of $(CH_3SCH(CF_3)CH(CF_3)SCH_3)PtX_2$						
X	Isomer	%	$\delta^{19}F^a$	$\delta^{195}Pt$	$J(F-F)^b$	$J(Pt-F)^b$
Cl	IV	18	-65.5	-231.2	0	6.1
	III ^c	13	-64.09 -59.82	-200.8	9.5	5.0 13.0
	II	62	-61.25	-204.1	0	5.3
	I	3	-60.11	-201.2	0	10.6
Br	V	18	-65.97	-628.4	0	<u>ca</u> 7
	IV ^c	11	-64.13 -59.76		<u>ca</u> 9	
	III ^c	18	-61.51 -60.90		<u>ca</u> 9	
	II	51	-61.18	-596.4	0	4.3
	I	2	-59.94	-594.1	0	9.6
I	IV	13	-66.26	-1469.8	0	3.5
	III ^c	9	-63.9 -59.5	-1424.0	9	
	II	73	-61.07	-1425.9	0	
	I	5	-59.54	-1415.7	0	7.0

a) p.p.m. positive to low field of external CCl_3F

b) Hz.

c) Values of δCF_3 for two chemically distinct CF_3 groups.

The number of isomers that can be detected at room temperature is not constant. For both chloride and iodide complexes, 4 isomers were observed, whereas the n.m.r. spectrum of the bromide complex showed the presence of 5 different structures. There are two alternative reasons to explain why the number of detected isomers would be

different from the six structures predicted. One is that the analysis of possible isomers failed to consider some factor forbidding a given structure or structures. It seems extremely unlikely however, that the possibilities of spatial arrangements for the bromide complex would be different from those possible for chloride or iodide compounds. On the other hand, it seems more reasonable to assume that although all six structures expected are feasible, the levels of population can be vanishingly small for some isomers and, in consequence, undetectable by the instrumentation used in this work.

Each ^{19}F n.m.r. spectrum shows three singlets and a doublet of quartets except for that corresponding to the bromide complex, in which an additional pair of quartets is present. The presence of three singlets confirms the assumption that rotation about the carbon-carbon bond is faster than the n.m.r. time scale at room temperature, for if that were not the case, trifluoromethyl groups in structures A and B would no longer be equivalent and only two - instead of three - singlets, arising from isomers C and D, would have been observed (see figure 39).

As expected for resonances of the asymmetric CF_3 groups of isomers C or F, the intensities of each quartet are equal. Therefore, for all compounds three symmetric isomers are present in a measurable proportion. Although it is likely that the structures of these isomers are the same for all three chloride, bromide and iodide complexes, there is no experimental evidence supporting this suggestion. Only one asymmetric isomer was found for both, chloride and iodide compounds, whereas two were present for the bromide complex. The origin of this difference is not clear.

At this point, the information on individual structures is still ambiguous. A more precise identification of each structure was possible by studying the variation of n.m.r. parameters with temperature. The

results obtained are discussed in chapter III with other dynamic
n.m.r. results.

CHAPTER III

DYNAMIC N.M.R.

CHAPTER III

DYNAMIC N.M.R.

Introduction.

Most studies of dithioether and related complexes have been based on dynamic n.m.r. spectroscopy, in which the effects of variable temperature or concentration are analysed^{22,23,26}. In particular, the study concerning the interconversion of isomers in solution, which is a temperature dependent phenomenon, is producing an increasing amount of information on the mechanism and energies involved in this process^{24,26}. This chapter presents the results of variable concentration n.m.r. for the reaction of $(\text{CH}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ with KBr and those of variable temperature for $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ and $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtI}_2$.

Variable concentration.

The preparation of hydrocarbon dithioether complexes of platinum(II) and palladium(II) invariably occurs in two steps^{23,244-246} as shown in figure 43.

Intermediate A is, in general, a stable species, easy to isolate and has been characterized before for several different ligands. The second reaction to produce the covalent 1:1 complex B, require relatively high temperature^{23,244}. In contrast, fluorinated dithioethers, where $\text{R}=\text{CF}_3$ or C_6F_5 , react in a different way, apparently without formation of intermediate A as an isolable species. Thus the presence of electron withdrawing substituents at the ligands, seems to favour the formation of compound B rather than the production of compound A.

To obtain more information on the influence of fluorinated sulphur substituents, the halide substitution reaction involving the asymmetric chelate complex $(\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ was studied. This

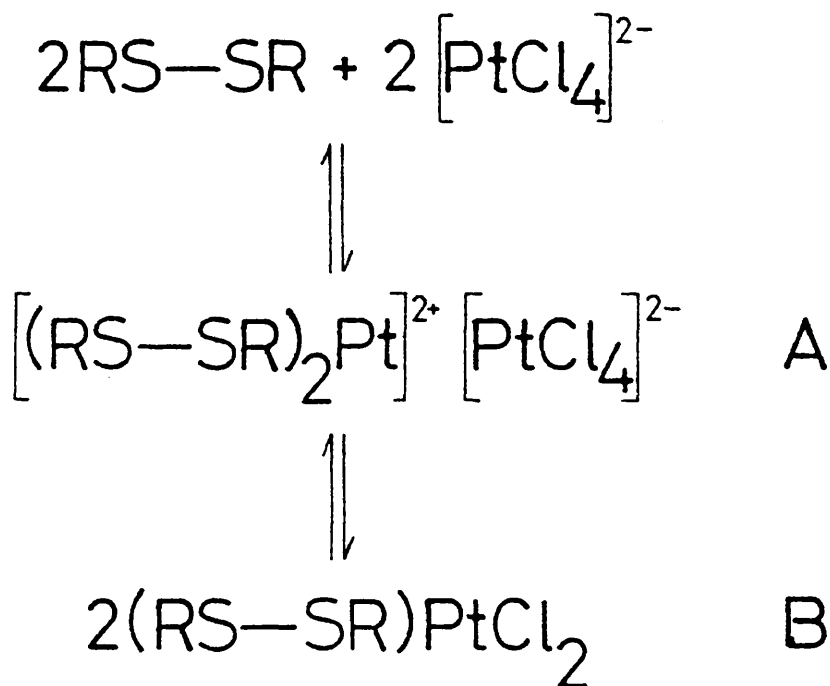


Figure 43. Obtention of complexes $(\text{SR-SR})\text{PtCl}_2$

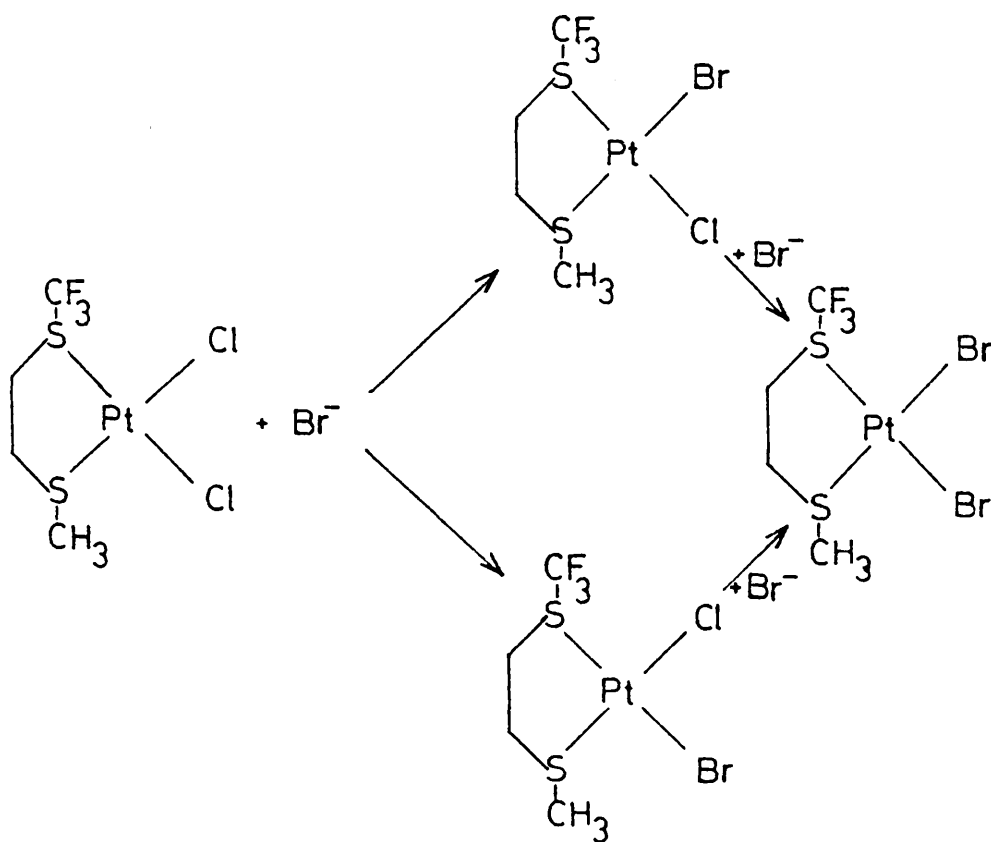


Figure 44. Possible products from the substitution reaction.

reaction, described in the experimental part, is especially suitable for this experiment because three different situations can arise: halide substitution taking place A) preferentially trans to a $\text{CH}_3\text{S-}$ group, B) without any preferred orientation and C) preferentially trans to a $\text{CF}_3\text{S-}$ group. The possible stereospecific reactions are shown in figure 44.

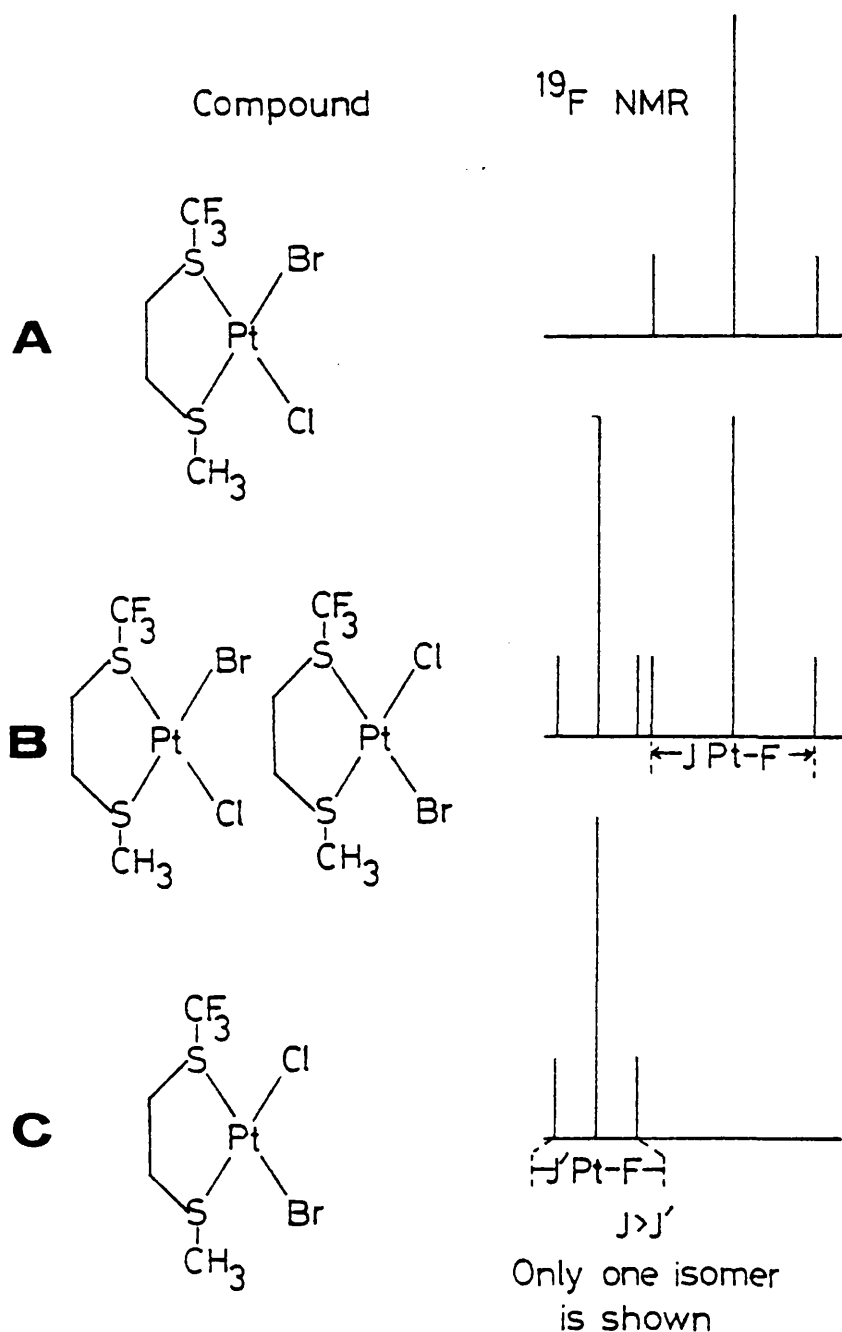


Figure 45. Predicted ^{19}F n.m.r. resonances. Letters denote substitution taking place preferentially A) trans to $\text{CH}_3\text{S-}$, C) trans to $\text{CF}_3\text{S-}$ and B) without preference.

Each case, A), B) or C) would, in principle, give rise to completely characteristic sets of n.m.r. parameters as shown in figure 45.

The n.m.r. patterns expected for the cases A) and C), i.e. substitution trans to a CH_3S or to a CF_3S group respectively, are similar and the distinction between these cases would have to rely on differences in $J(\text{Pt}-\text{F})$ since, as discussed earlier, the bromide substitution trans to the CF_3S group gives a decrease in $J(\text{Pt}-\text{F})$, whereas the reaction giving rise to a cis-Br substitution, relative to the CF_3S group, should have no effect on the Pt-F coupling constant on the assumption that no cis effects are present.

Unexpectedly, the experiment produced a completely different set of more definite results.

A selected set of experimental n.m.r. spectra, over the whole range of concentration ratios used, are shown in figure 46.

The 56.4 MHz, ^{19}F n.m.r. spectrum of the pure complex, shown at the top of figure 44, shows two single resonances with platinum satellites corresponding to the syn and anti isomers present in solution.

The most important feature of this sequence of spectra is the single resonance appearing at -39.7 ppm as the concentration of Br^- is increased. The singlet arises from an uncoordinated CF_3S group since it shows no platinum-fluorine spin-spin coupling. The fluorine chemical shift is very similar to that found for cis-($\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$) $_2\text{PtCl}_2$ (-41.0 ppm), which has two non bonded CF_3S groups. This resonance appears at very low concentrations of KBr. Slight broadening of the signals occurs when the amount of KBr is increased, probably reflecting a site interchange process as the reaction proceeds. There is no indication however that additional, different halide species are present. The resonances arising from the chloride complex change by decrease in intensity only, without substantial change of shape.

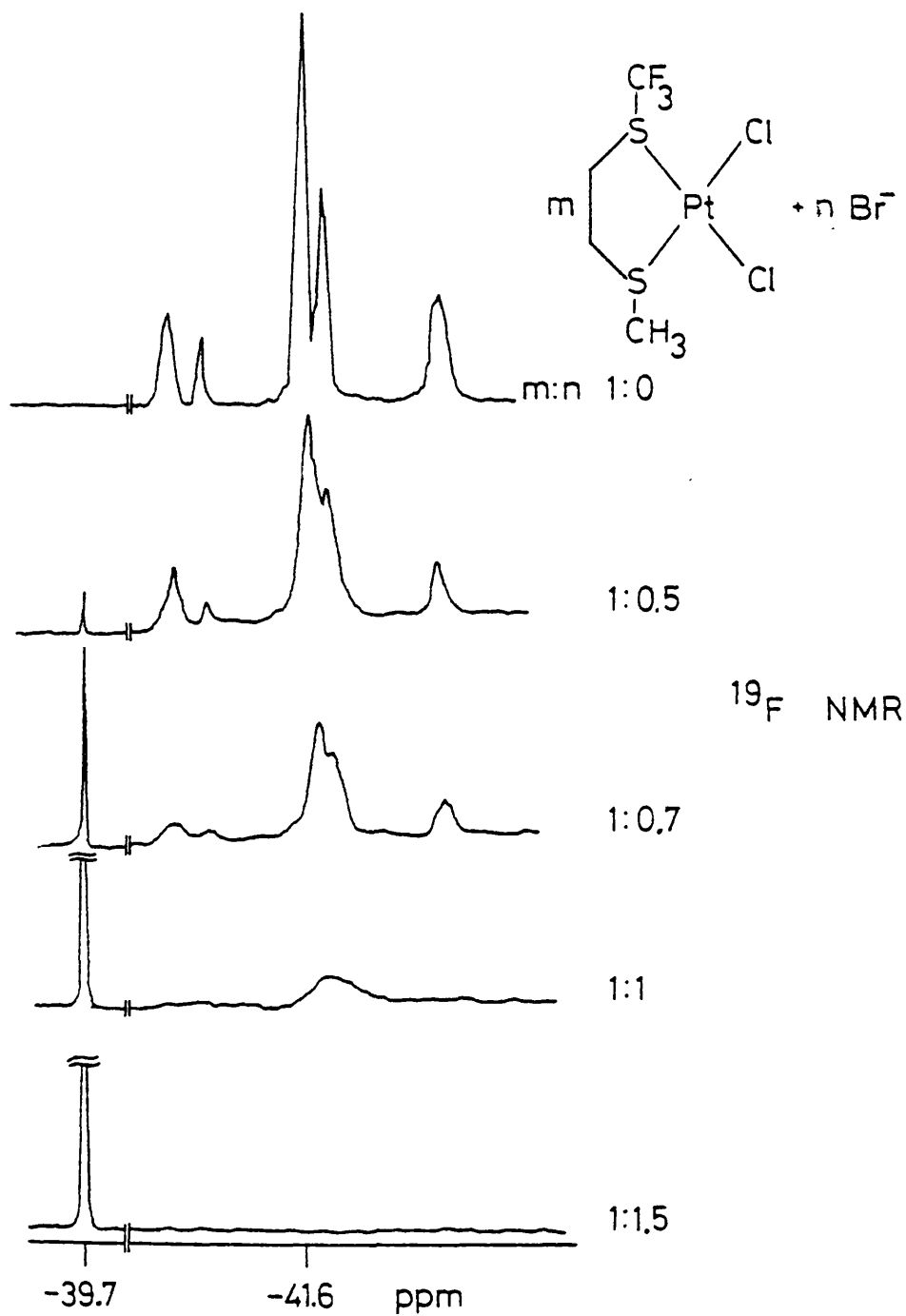
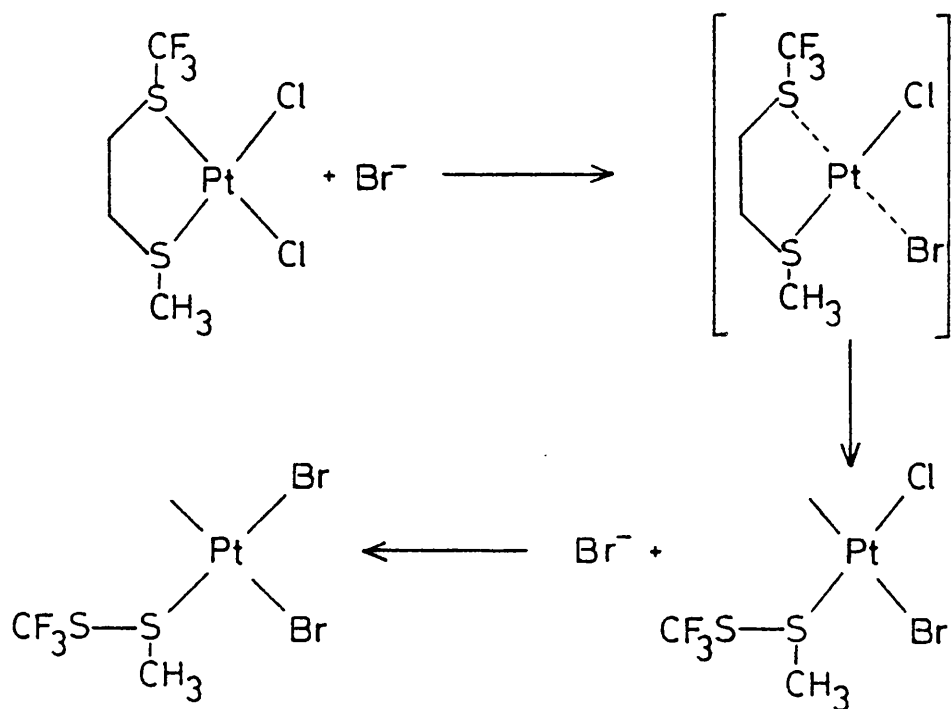


Figure 46. Variable concentration n.m.r.

Interestingly, the relative intensities of both isomers and therefore their concentrations, show no appreciable variation either. The results described are compatible with the following reactions.



It must be emphasized that the compound in brackets is not intended to represent a transition state. It is used only to point out the rupture and formation of S-Pt and Br-Pt bonds, respectively.

The mixed chloride-bromide complex could be A or B in figure 47. The complex was not isolated, but the reaction of $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ and $[\text{PdCl}_4]^{2-}$ afforded a bridged species, similar to A, characterized by analysis and molecular weight measurements and it is probable that a similar structure is formed in the present reaction.

In any case, the results show that the concentration of the chelate complex is undetectable by n.m.r. spectroscopy when the concentration of KBr reaches a 1:1 ratio, clearly indicating that preferential bromide substitution takes place trans to the CF_3S group.

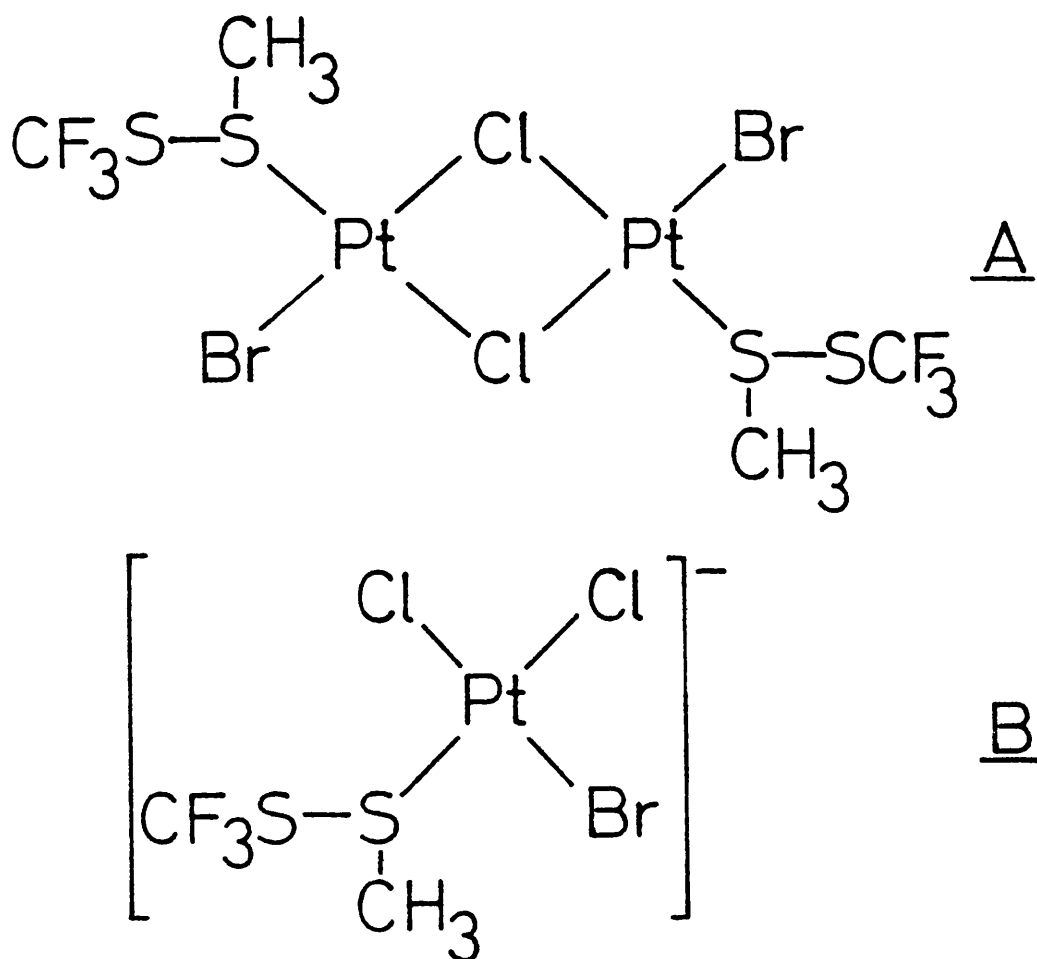


Figure 47. Possible products from bromide substitution in $(\text{CH}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$.

When the concentration of KBr is larger than that of $(\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCF}_3)\text{PtCl}_2$, subsequent reactions do not appear to affect the n.m.r. parameters. This is consistent with the now remote position of the fluorine atoms in the molecule.

If these results are kinetically controlled, the course of the reaction could be explained by assuming a larger trans effect of the CF_3S group than that of the CH_3S substituent. A similar argument provide a rationale for the apparently different stability of intermediate A in page 89, since ligands in $(\text{RS-SR})_2\text{Pt}^{2+}[\text{PtCl}_4]^{2-}$ would

labilize each other, facilitating the formation of the 1:1 complex. Clearly however, the suggestion that trans effect increases from CH_3S to CF_3S , can only be tentative and more evidence is required to draw any definitive conclusion.

Variable temperature.

Because of lack of time, a full study of the dynamic n.m.r. of all compounds reported here was not possible. Instead, two representative examples were examined. The first example is that of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ chosen for comparison purposes, since its corresponding hydrocarbon analogue has already been studied^{23,28}. The second compound examined was $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtI}_2$.

The 56.4 MHz variable temperature ^{19}F n.m.r. spectra of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ in dimethyl digol $((\text{CH}_3\text{-OCH}_2\text{-CH}_2\text{-})_2\text{O})$ solution, are shown in figure 48.

As for other dithioether complexes the pair of resonances observed at room temperature, arising from the presence of syn and anti isomers, gradually became broader as the temperature was increased until, eventually both signals coalesced into a singlet. These experimental results have been explained²² in terms of the process shown in figure 49.

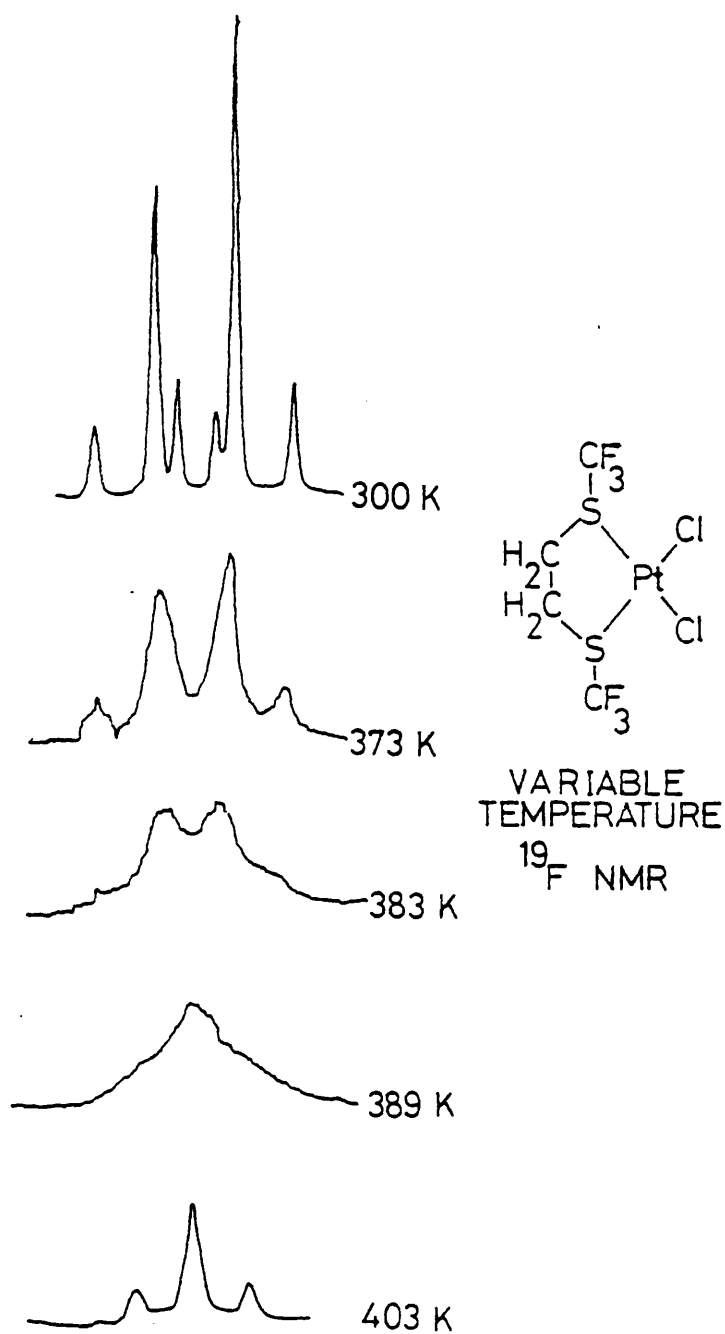


Figure 48. Variable temperature ^{19}F n.m.r. of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$.

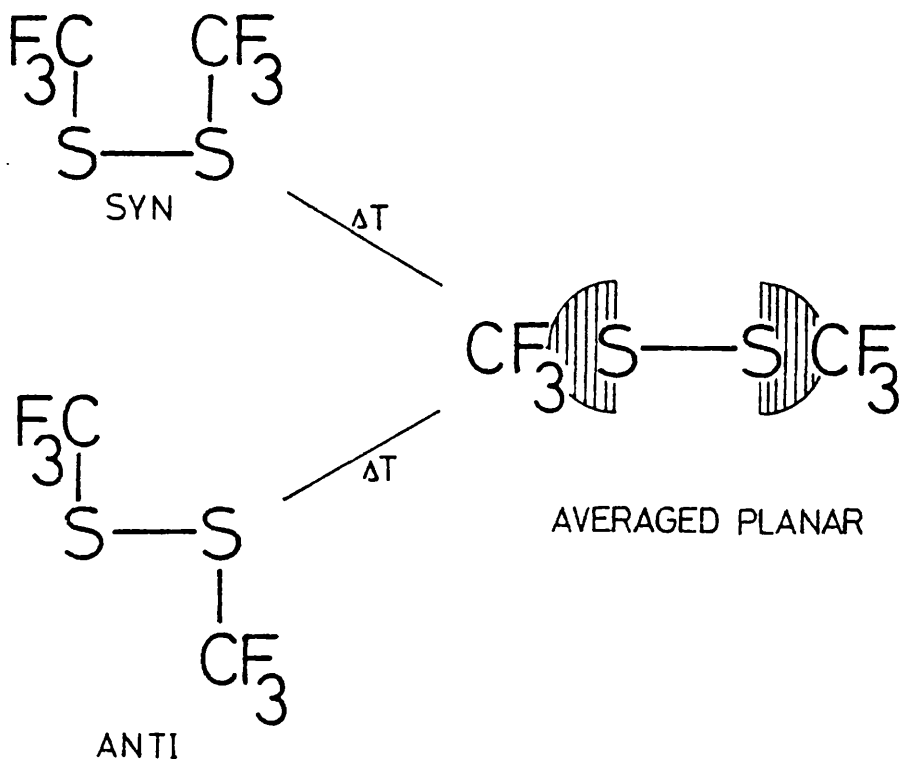


Figure 49. Averaged planar structure resulting from sulphur inversion.

This process of inversion of configuration at sulphur increases its rate with temperature until eventually it takes place very rapidly in the n.m.r. time scale and only an averaged structure is observed.

In studies of sulphur inversion or other fluxional processes for which an energy barrier between different molecular arrangements is present, the thermodynamic parameter normally used to describe this barrier is the free energy of activation ΔG^{\ddagger} ^{24,247-249}.

The simplest method to determine ΔG^{\ddagger} requires the evaluation of a rate constant K , equation I, at the coalescence temperature²⁵⁰. K is, in turn, related to ΔG^{\ddagger} according to the Eyring equation²⁵¹ II.

$$K = \pi / \sqrt{2} \Delta \nu_{AB} \quad \text{I}$$

$$\ln K = \ln K_B T / h - \Delta G^{\ddagger} / RT \quad \text{II}$$

Where $\Delta\nu_{AB}$ is the chemical shift difference between the equally intense resonances A and B in the absence of exchange, K_B and h are Boltzman's and Planck's constants respectively, R is the gas constant and T the coalescence temperature (K).

Approximate methods, like the one involving equation I incur large errors²⁵². Therefore, unless a complete line shape analysis is performed²⁵³, it seems more convenient to compare coalescence temperatures which if other factors are constant, are proportional to the energy barriers.

The coalescence temperature for the compound studied here is given in table 17, together with coalescence temperatures reported for similar compounds.

Table 17

Coalescence Temperatures. (T_c , °C)

	Compound	T_c
I	$(CF_3SC_2H_4SCF_3)PtCl_2$	119
II	$(CH_3SC_2H_4SCH_3)PtCl_2$ ²³	100
III	$(EtSC_2H_4SEt)PtCl_2$ ²³	80
IV	$(Pr^nSC_2H_4SPr^n)PtCl_2$ ²³	95

From the coalescence temperatures of the more directly comparable compounds I, and II, it is evident that the barrier of sulphur inversion is larger for the fluorinated complex I. The factors affecting this barrier are not complete understood, but the information available indicates that the rate of inversion is controlled by a) the metallic centre^{23,254}, the inversion barrier rising as the atomic number increases, b) steric factors^{255,256} and c) factors related with electronic changes at the donor atom during inversion²⁵⁷⁻²⁶⁰.

Sulphur inversion is sensitive to steric factors particularly^r when bulky groups in a molecule tend to adopt a configuration which

minimizes steric interactions; this is not the case for either compound I or II since in each complex both isomers are highly populated. On the other hand, the electronic changes at the centre of inversion depend on the substituents at the donor atom and on other ligands. Two mechanisms have been suggested to rationalize this process. In 1967, Haake and Turley²⁷ suggested the mechanism depicted below.

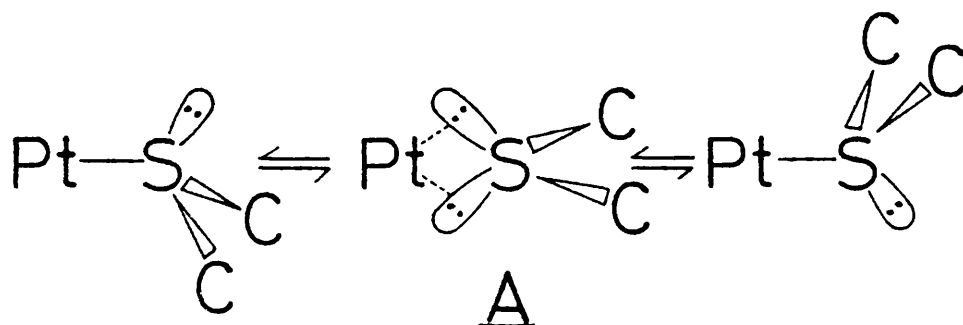


Figure 50. 'Haake - Turley' mechanism for sulphur inversion.

The inversion process is described as an internal displacement of one lone pair by another and in this sense, it is an intramolecular displacement process rather than a true inversion of configuration.

In structure A, Pt, S and both carbons are coplanar and therefore the sulphur atoms retain tetrahedral configuration during the process. Alternatively a more widely accepted mechanism^{24,28,248}, similar to that suggested for inversion at nitrogen²⁶¹, and sulfoxides²⁶² is shown in figure 51. This involves the passage through a transition state in which the lone pair has pure p-character. Inversion of configuration occurs through a coplanar, or nearly coplanar, arrangement of substituents around the central sulphur atom in which bonds of the donor atom represent a sp^2 hybridization²⁶³.

Recently Abel and Co-workers^{24,248}, have suggested that the distinction between a) both sulphur lone pairs bonding simultaneously

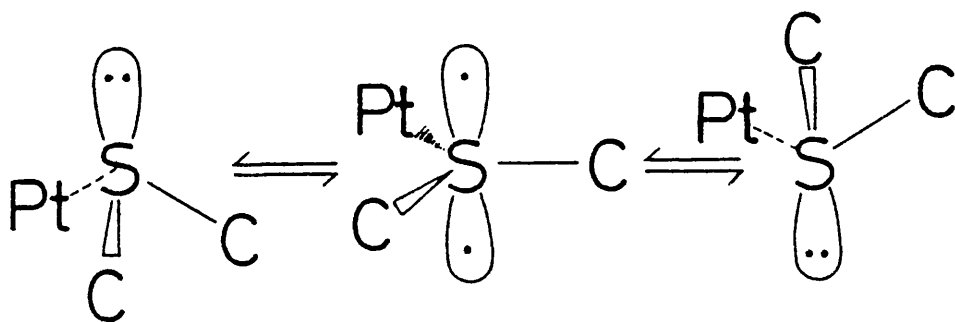


Figure 51. Classical mechanism for sulphur inversion.

to the metal (Haake-Turley mechanism) and b) a σ bond with the remaining lone pair in a pure p orbital at sulphur (classical mechanism), has no physical significance and therefore both mechanisms could be regarded as static representations of the same process. The equivalence of both mechanisms is perhaps clearer if the electronic localization in the transition state is avoided as in figure 52.

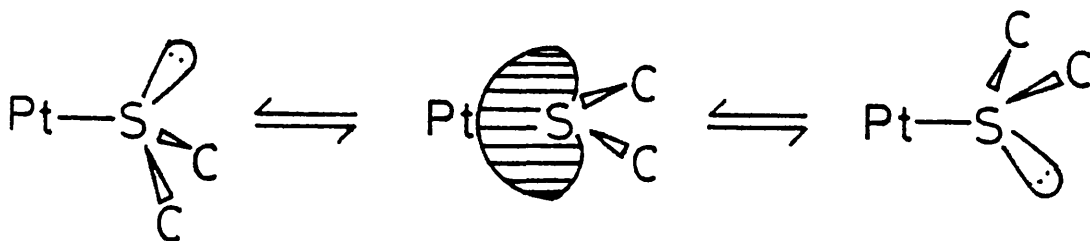


Figure 52. Mechanism for sulphur inversion.

According to this description of sulphur inversion, the larger coalescence temperature of $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ compared with that of the hydrocarbon compound, can be explained by the increased electronegativity of the sulphur substituents, which will increase the s character of the lone pair. This situation would hinder the process

of inversion risen the energy barrier and the coalescence temperature.

Additionally¹ and probably operating simultaneously, the vibrational mode involved during inversion would be affected by the increased mass of the sulphur substituents from which an increase in coalescence temperature is also expected.

As discussed in chapter II, ^{19}F n.m.r. spectra of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtX}_2$, $\text{X} = \text{Cl}, \text{Br}$ or I , are compatible with the presence of four ($\text{X} = \text{Cl}$ and I) or five ($\text{X} = \text{Br}$) isomers. The data obtained at room temperature is, however insufficient for a precise identification of the structures present in solution. To obtain additional information about the origin of each signal, spectra of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtI}_2$ were obtained at different temperatures. The iodide complex was chosen because coalescence temperatures in other dithioether complexes of Pt(II) are known²³ to decrease, after halide substitution, in the order $\text{Cl} > \text{Br} > \text{I}$, and a process taking place at relatively low temperature was desirable if it had to be measured in an acetone solution of the complex. Unexpectedly two different processes were detected. Figure 53 shows the effect of increasing the temperature from 253K in which three singlets, I, II and III and a pair of quartets, IV, are present. At 293K the changes of singlets II and III show an opposite trend since signal III has broadened and has almost disappeared, whereas resonance II has narrowed becoming a sharp signal. Simultaneously, quartet IV and singlet I have followed a similar process and are almost undetectable at this temperature. Further increase in temperature produces broadening of singlet II and, at the same time, a more defined coalescence of signals III and IV takes place until, at the temperature limit of the experiment the coalescence is almost complete and has produced a symmetric, though

VARIABLE
TEMPERATURE
 ^{19}F NMR

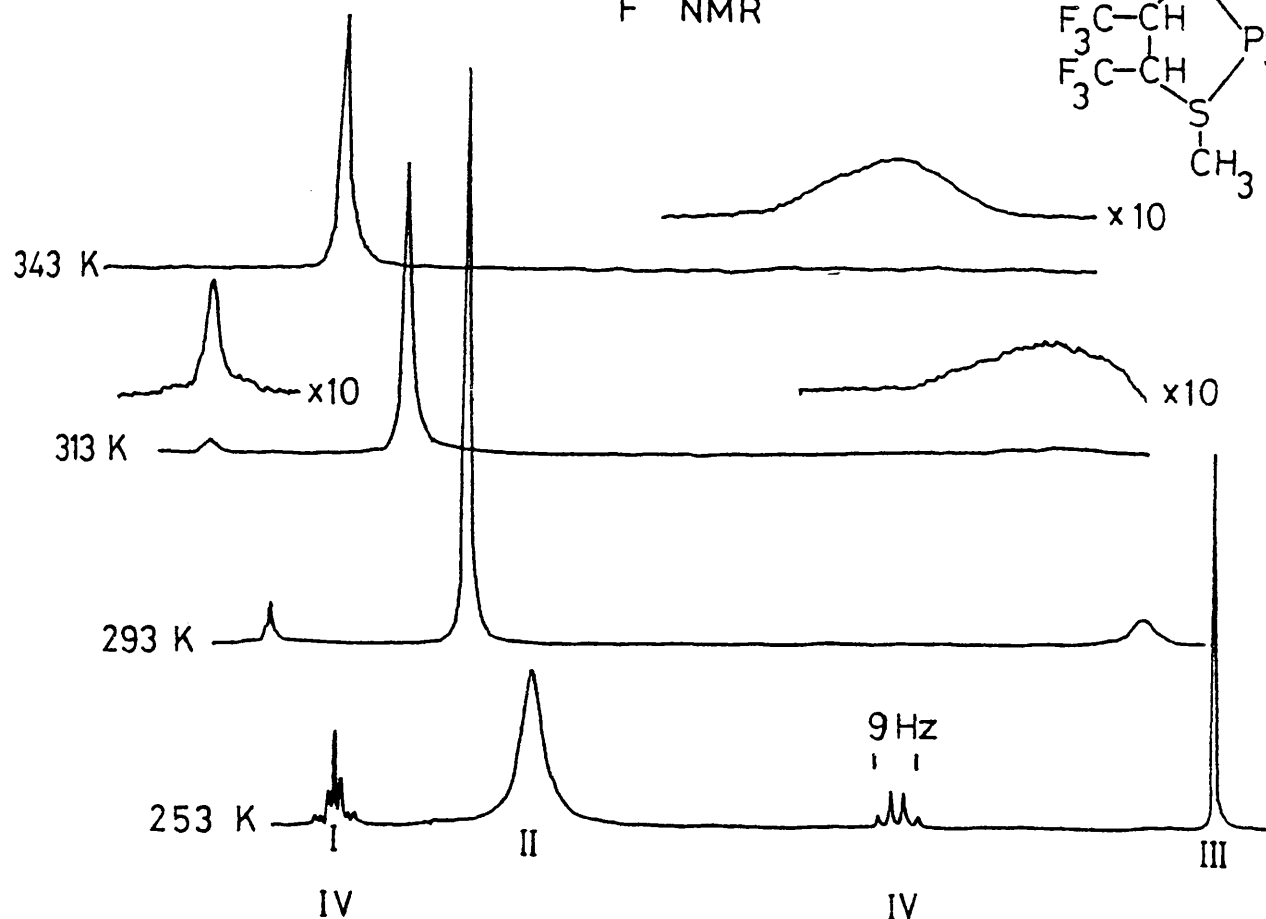
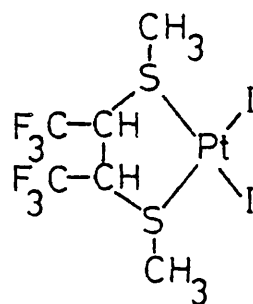


Figure 53. High temperature ^{19}F n.m.r. spectra.

very broad, peak. The behaviour of the spectral changes just described, is very similar to those observed for closely related dithioether complexes of Pt(II) ^{22,23,28}, for which the dynamic process has been established to occur because the rate of inversion of configuration at sulphur is directly proportional to the increment in temperature. This similarity suggests that a comparable process takes place for $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtI}_2$. The coalescence temperatures found for resonances III and IV is of the same order of magnitude as those

measured for similar compounds, shown in table 18, for which the dynamic n.m.r. reflects the interconversion of isomers described above, further

Table 18

Coalescence Temperatures for Iodide Complexes

Compound	Coalescence Temperature °C
(MeSCH ₂ CH ₂ SMe)PtI ₂	87 ^a
(EtSCH ₂ CH ₂ SEt)PtI ₂	50 ^a
(Pr ⁿ SCH ₂ CH ₂ SPr ⁿ)PtI ₂	50 ^a
(Pr ⁱ SCH ₂ CH ₂ SPr ⁱ)PtI ₂	47 ^a
(Bu ⁿ SCH ₂ CH ₂ SBu ⁿ)PtI ₂	67 ^a
(MeSCH(CF ₃)CH(CF ₃)SMe)PtI ₂	70
a) Reference 23	

suggesting a similar origin for the spectral changes observed.

For both, meso and (±) isomers, sulphur inversion can occur either simultaneously at both sulphur atoms or at single sulphur atoms.

Coalescence of resonances III (syn) and IV (anti) suggests that the predominant process is inversion at single sulphur atoms, since it involves the interconversion syn ↔ anti.

The second process, (figure 54) appearing when the temperature is decreased also produces broadening of signal II until eventually the resonance, below its 'low coalescence temperature', LTC, splits apart forming two quartets at 183 K. These changes also suggest that exchange between two sites in the molecule is producing an averaged signal above coalescence temperature whereas both sites are distinct below it. Since the changes have their origin in a molecule in which the orientation of sulphur substituents is fixed, the dynamic part of the molecule undergoing such site exchange must be the five-membered ring, particularly the bridge, since this contains the nuclei under observation. The

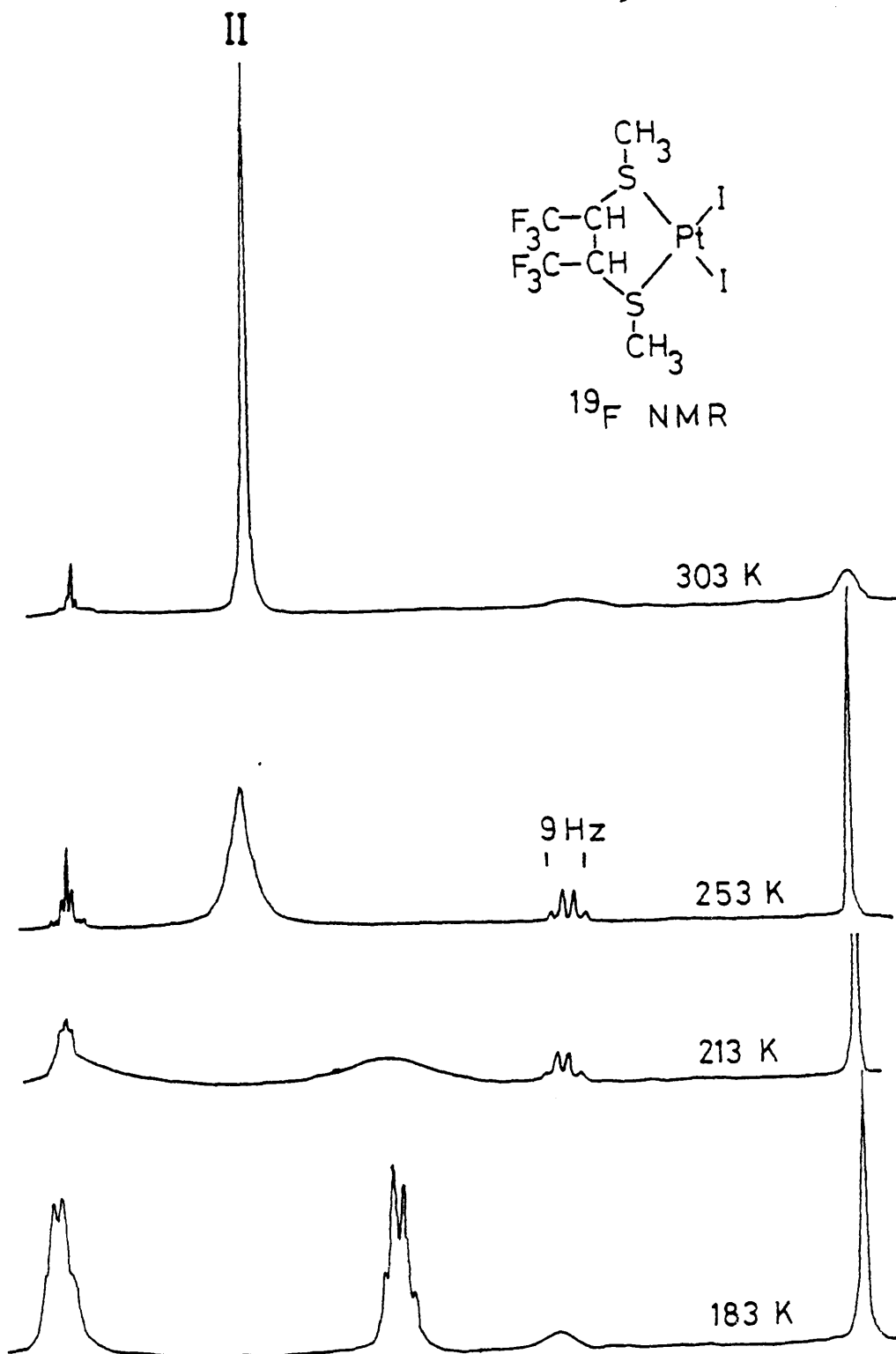


Figure 54. Low temperature ^{19}F n.m.r. spectra.

experimental results are in agreement with a slow interchange between axial and pseudo-equatorial positions of the bridge substituents as discussed below.

If rapid rotation about the carbon-carbon bond no longer occurs, several changes in the original assumptions regarding the isomeric structures of these compounds have to be made. It can still be considered that mirror images will be indistinguishable by n.m.r. measurements. Considering each diastereoisomer, the number of possible static rotamers is four and therefore, 24 structures can be drawn. However, there are a number of structures that are equivalent.

For meso isomers, both orientations in which methyl groups are mutually syn to each other give rise to a pair of identical diastereoisomers - structures I, II, III and IV in figure 55.

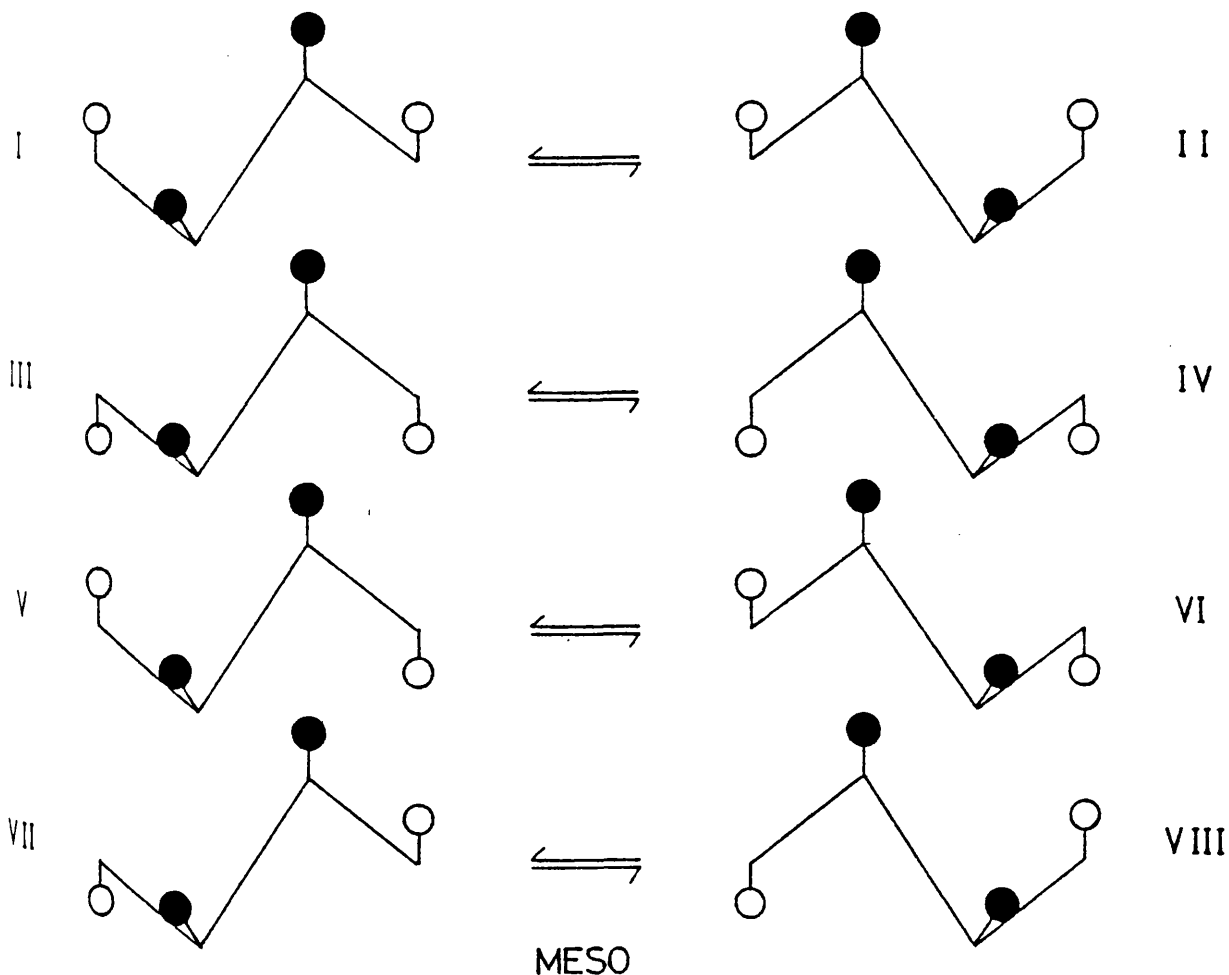


Figure 55. Rotamers of the meso form.

It is important to notice that substituents in axial and pseudo-equatorial positions are chemically non-equivalent and therefore, that the effect of a rigid carbon-carbon bond will be the adoption of a pair of mirror-image structures bearing distinct bridge substituents. If both methyl groups are mutually anti, structures V, VI and VII in figure 55 are possible.

Two pairs of mirror images are found for isomers V and VII as well as VI and VIII and in terms of n.m.r. spectroscopy, the compounds in each pair are identical. As before, bridge substituents are distinct in each structure.

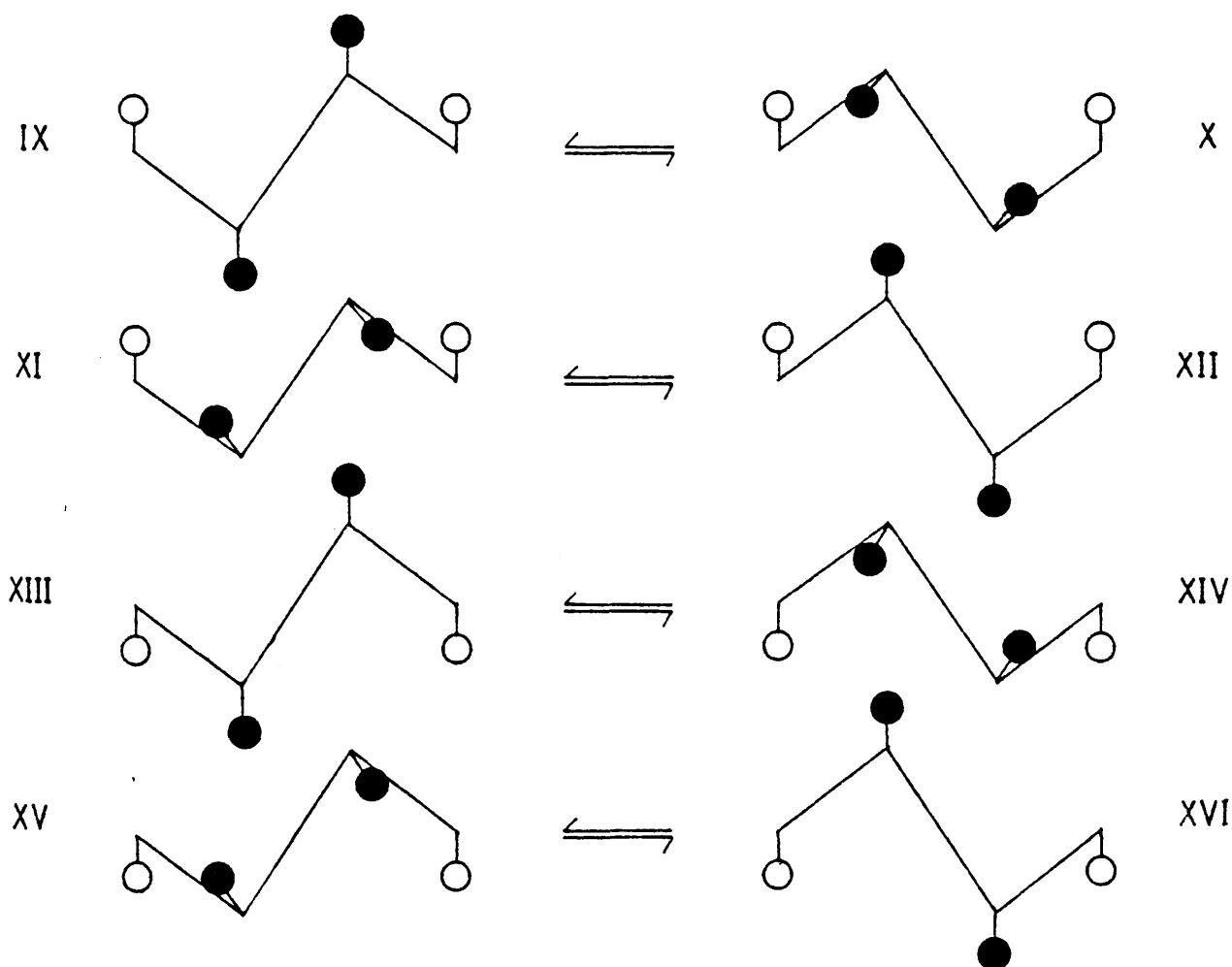


Figure 56. Rotamers of the (+) form.

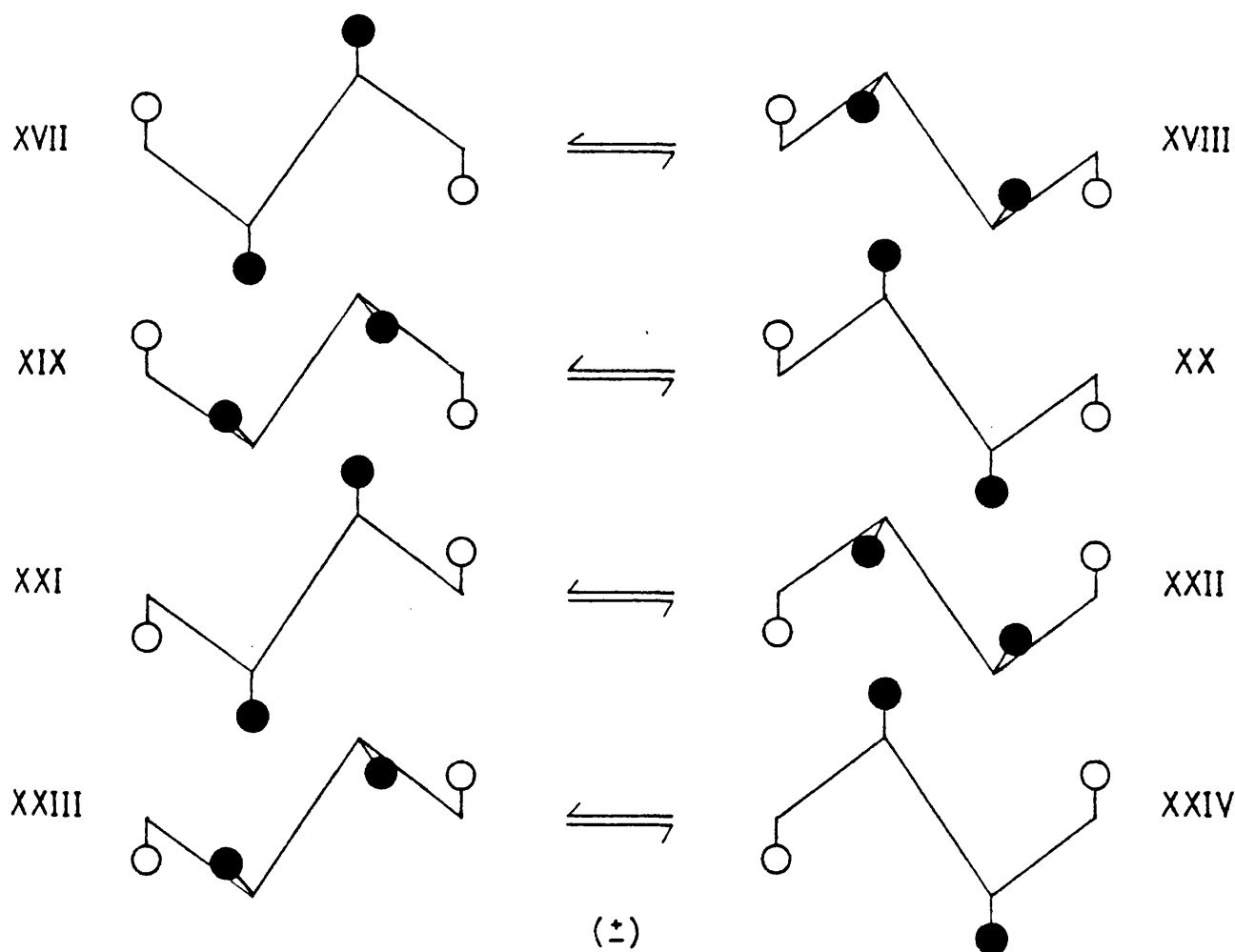


Figure 56. Continued.

Following the same order for the (±) isomeric form figure 56, syn methyl substituents can adopt two orientations relative to the rest of the molecule but, because the bridge is symmetric both orientations are identical and produce structures IX, X, XI, and XII from which, as before, two pair of mirror image structures are obtained; the overall effect of decreasing the rate of carbon-carbon bond rotation in this case will be the adoption of two different rotamers where, although bridge substitution are inherently equivalent, the environment of each

one makes them distinct.

Each of the possible orientations of mutually anti methyl substituents, give rise to a pair of mirror-image structures represented in figure 56 by rotamers XVII, XVIII, XIX and XX in one isomer and XXI, XXII, XXIII and XXIV, in the other. The effect detectable by n.m.r. spectroscopy, is the formation of a non-equivalent pair of structures for each orientation. In each pair of rotamers, bridge substituents are in identical environments and are therefore equivalent.

In summary, the n.m.r. detectable effects of a slow rotation about the carbon-carbon bond are shown in figures 57, 58 and 59. Equivalence or non-equivalence, in terms of n.m.r. spectroscopy, for pairs of static diastereoisomers and bridge substituents is indicated by equality symbols respectively.

In all, three different effects can be expected. Isomers A and B will transform a single resonance into a doublet of the same intensity. Since the original equivalence of bridge substituents in A or B is no longer present in their rotamers, spin-spin coupling is possible. Isomers

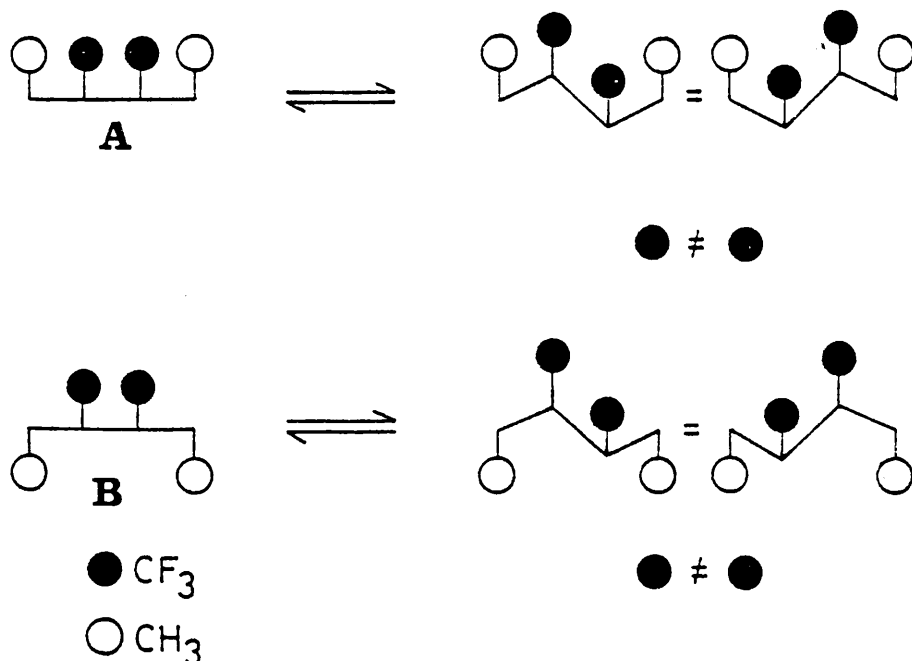


Figure 57. Rotamers with equivalent structures but distinct substituents.

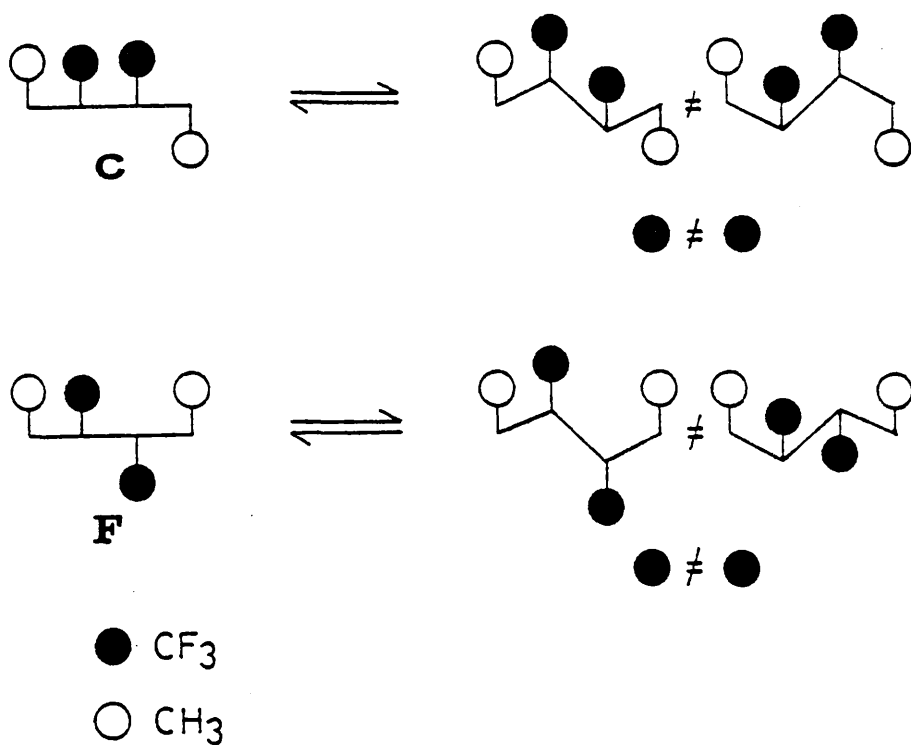


Figure 58. Rotamers with non-equivalent structures and substituents.

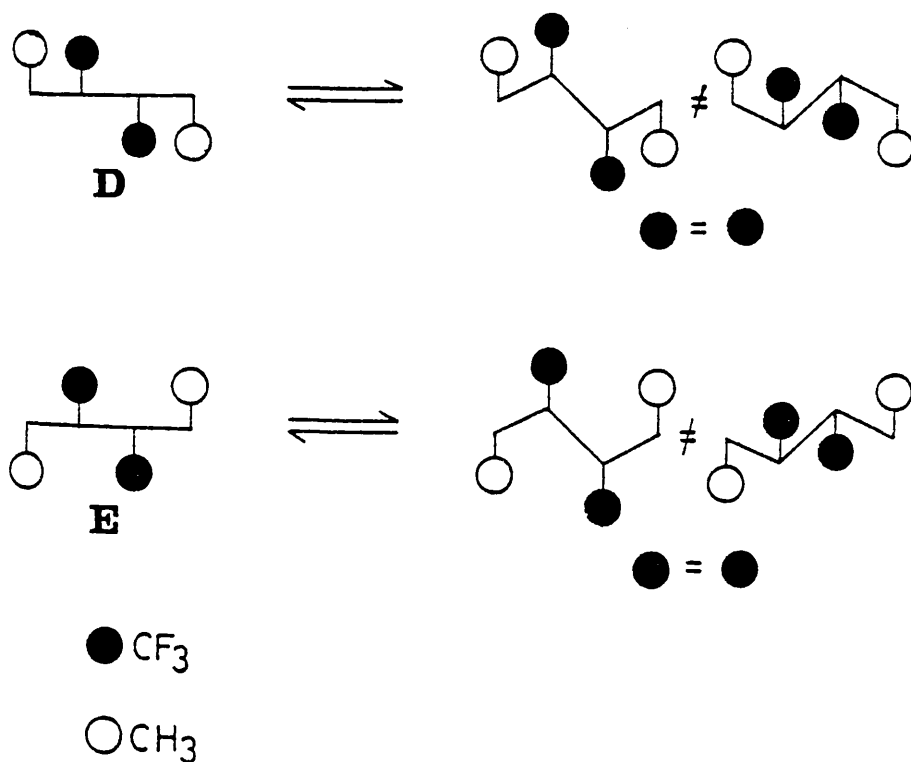


Figure 59. Rotamers ^{with} equivalent substituents but distinct structures.

D and E will also change their singlet resonance into a doublet. In this case each signal in the resulting doublet arises from a different rotamer and therefore, their relative intensity can adopt any ratio depending on the relative population of the rotamers. Bridge substituents are equivalent and no coupling between them will be detected. Finally isomers C and F, which originally gave a doublet with additional multiplicity due to spin-spin coupling between bridge substituents, will generate a doublet arising from two distinct rotamers; in which as before, intensities will reflect relative populations. Each resonance will be further split into two signals of the same intensity arising from distinct bridge substituents and can, therefore, show additional multiplicity due to magnetic spin-spin coupling.

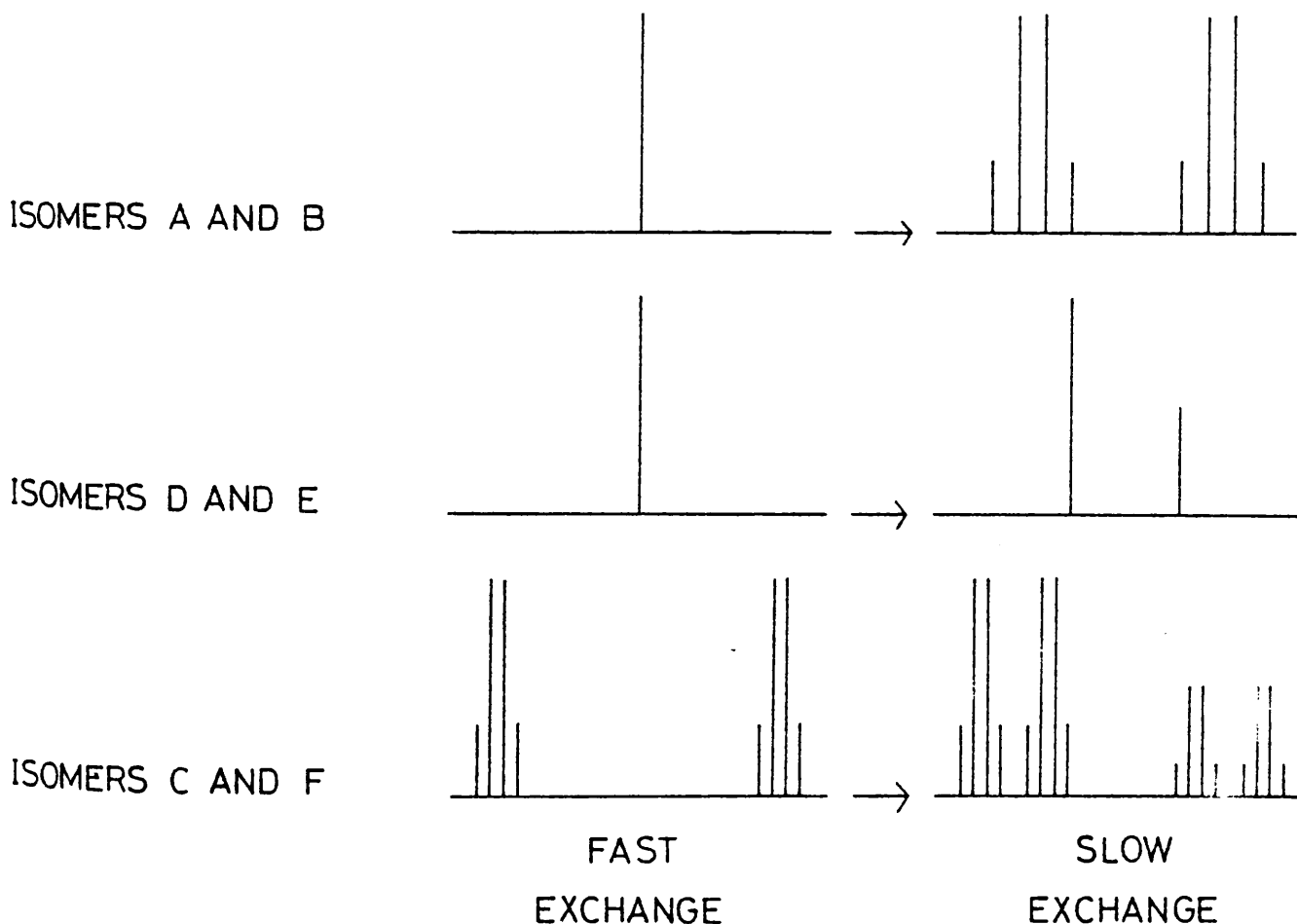


Figure 60. Expected appearance of the ^{19}F n.m.r. spectrum of each isomer with fast and slow central carbon-carbon bond rotation.

A schematic representation of the expected results is shown in figure 60. Spin-spin coupling between trifluoromethyl groups in the bridge is shown and to emphasize the possibility of different isomeric populations a 2:1 ratio of rotamers has been assumed.

The experimental results are in excellent agreement with the predicted changes expected for isomers A or B and indicate that the original interpretation of the phenomenon observed, as a dynamic process hindering rotation about the carbon-carbon bond, is essentially correct. Several studies indicate that the energy differences between conformers of five membered chelate rings are small²⁶⁴⁻²⁶⁶. Energy barriers to conformational inversion are also small^{191,267,268}. N.m.r. conformational studies of these systems are based on the observation of coupling constants which are indicative of a preferred ring conformation. Site exchange is nevertheless rapid and averaged n.m.r. parameters are always obtained. In contrast, the experimental results described here, represent the observation of a static conformer. This appears to be the first report of a five-membered chelate compound with a barrier to ring inversion high enough to allow n.m.r. detection of a rigid rotamer. The influence of steric factors in determining the barrier to carbon-carbon bond rotation was first recognized by Bailar et al.²⁶⁹; following their arguments, larger barriers are to be expected for carbon-carbon rotations which produce more or larger steric interactions than those present on the conformer before bond rotation.

In this sense it is important to notice that although the changes of resonance II, in figure 54, indicate a relatively high barrier to ring fluxion, the remaining signals undergo a similar process and presumably they will show a similar behaviour at temperatures below the limit of the experimental conditions used, suggesting the presence of lower energy barriers. Based on molecular models, increased steric interaction resulting from the relative orientation of the sulphur substituents

would be found in the following order:

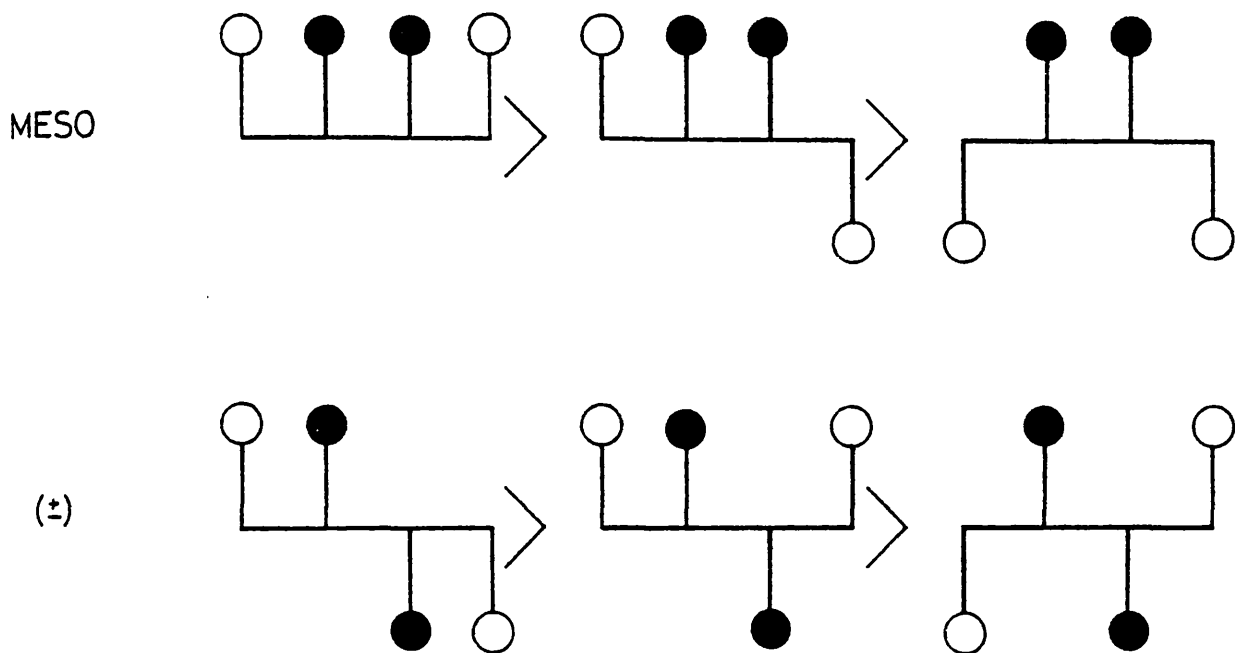


Figure 61. Order of steric interactions.

It must be noticed that in terms of steric factors, meso isomers seem to have greater interactions between bridge substituents than those found in (\pm) forms. In addition if, as expected, the ratio of meso to (\pm) isomers of the complex reflects the ratio of meso to (\pm) isomers of the ligand, the experimental results could be interpreted by a large preponderance of the meso isomer B in figure 39 which shows the larger barrier to ring inversion and also a relatively high coalescence temperature. The remaining n.m.r. resonances will then be originated by the (\pm) isomers, in which n.m.r. intensities probably reflect the order shown in figure 61.

The equilibria established could therefore be schematically represented as in figure 62, in agreement with the relative populations expected, given in parenthesis.

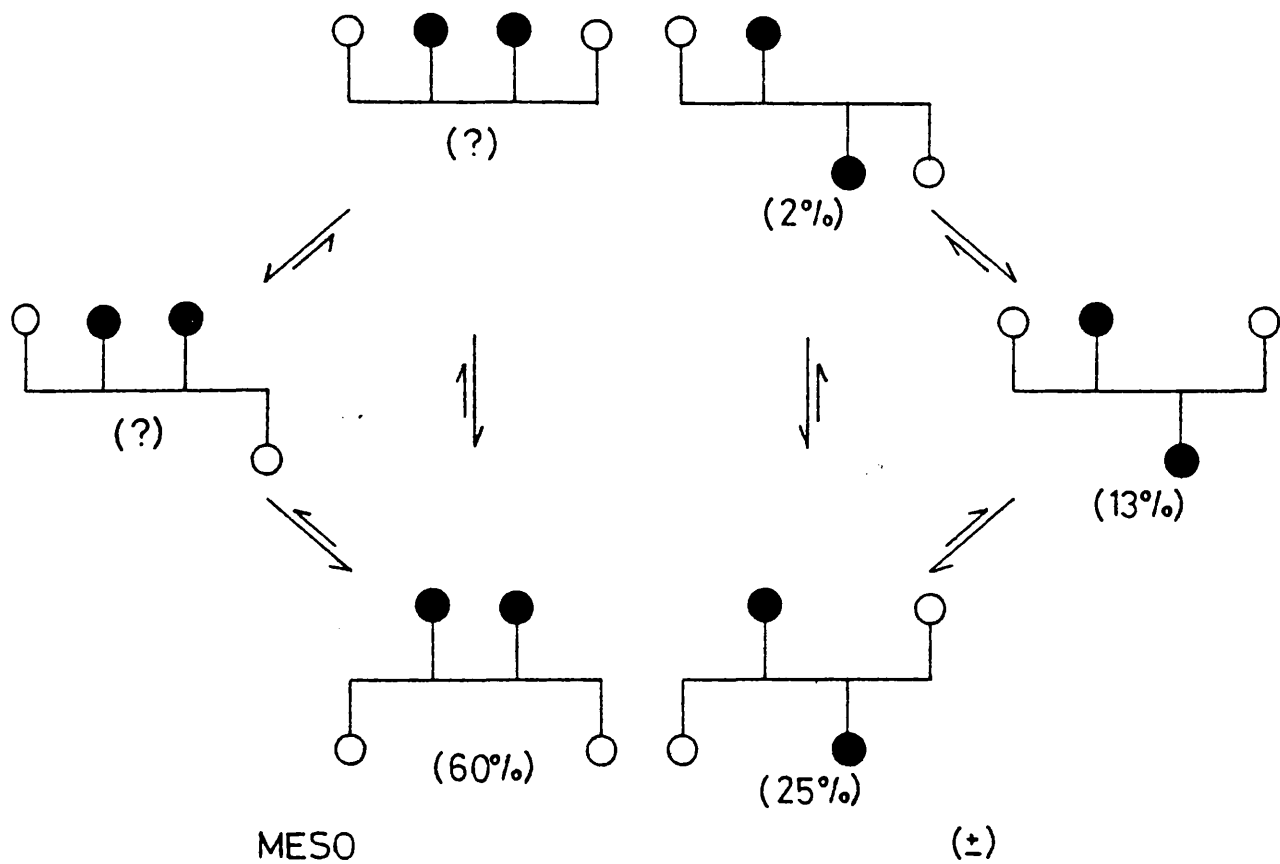


Figure 62. Structural assignment for $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtI}_2$.

CHAPTER IV

PLATINUM CHEMICAL SHIFTS

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PLATINUM CHEMICAL SHIFTS

Although the direct observation of ^{195}Pt resonance was first reported by Proctor and Yu²⁷¹, in 1958, the potential of platinum chemical shifts as an investigative tool in the study of both structural and electronic bonding features was not demonstrated until 1968 when McFarlane²⁷², Pidcock et al.¹⁷⁴ and Von Zelewsky²⁷³ showed that ^{195}Pt chemical shifts cover a wide range of values, being sensitive not only to the ligands present around the metal atom but also to their arrangement.

The relative low sensitivity of platinum, (9.94×10^{-3} for an equal number of protons at constant field) originally restricted direct measurements to spectrometers not commonly available but Fourier transform n.m.r. techniques²⁷⁴ and heteronuclear multiple resonance methods²⁷⁵ made it possible to obtain ^{195}Pt measurements with readily accessible equipment and by October 1977 around 400 platinum chemical shifts had been reported^{127,174,271-273,276-281,283,285,287-290}. This information, although extremely small by comparison with ^1H or ^{19}F data, has already been successfully applied to practical problems; there are systematic trends that can be used to predict chemical shifts for compounds which have not previously been studied²⁸⁴ and erroneous structural assignments have been discovered from the position of their platinum resonances²⁷⁷.

The explanation of these results however, has encountered enormous difficulties. Chemical shifts are influenced by several interrelated parameters; the factors which affect nuclear shielding are still poorly understood and despite the efforts in the last decade, theoretical interpretations have been of very limited success^{174,279}.

In view of this situation, the following discussion makes no attempt to quantify the effects observed; instead, its purpose is to compare the results obtained with data previously reported, emphasizing the dependence of platinum chemical shifts on the nature as well as on the structure of the compounds considered.

Following a simplified picture, it is useful to consider the shielding constant σ , as arising from well-defined groups of electrons in a molecule. This approach was first suggested by Saika and Slichter²⁸² and was later extended by several workers^{284,286}. The shielding constant for a nucleus is written as

$$\sigma = \sigma_D + \sigma_P \quad 1$$

where σ_D represents the diamagnetic screening for the circulation of electrons on the same atom as the nucleus in question²⁹¹ and σ_P represents the paramagnetic contribution to the screening constant²⁹².

For some relatively simple cases in which screening constants have been calculated²⁹³⁻²⁹⁶, the theoretical and experimental results shown discrepancies not attributable to the theoretical calculations of σ_D or σ_P . Such differences arise from factors which are not considered by the diamagnetic (σ_D) or the paramagnetic (σ_P) terms.

The most obvious of such effects are the contributions arising from solvents, which are basically dependent on intermolecular interactions between solvent and solute²⁹⁷. On the other hand, intramolecular contributions to the screening constant can also be important. although very little is known about such effects involved in polyatomic molecules.

In order to include this type of contribution to the screening constant, an additional term $\sum \sigma_N$ is included in the definition of σ (equation 1) so that

$$\sigma = \sigma_D + \sigma_P + \Sigma \sigma_N$$

2

it has been suggested that

$$\Sigma \sigma_N = \sigma_S + \sigma_{RC} + \sigma_E + \sigma_M$$

3

where σ_S represents solvent effects which, in turn, have been studied as the result of several different contributions²⁹⁸; σ_{RC} is associated with electric currents present in cyclic molecules²⁹⁹; σ_E arises from electric fields centered on neighbouring atoms³⁰⁰ and σ_M can be defined as

$$\sigma_M = \Sigma \sigma_N - (\sigma_S + \sigma_{RC} + \sigma_E)$$

4

including all effects not previously considered.

With the exception of σ_M all terms involved in σ_N are basically contributions which have not been included on considering the relevant molecular wave functions. As the complexity of molecules grows, knowledge of exact atomic and molecular wave functions becomes more difficult to obtain and approximations fail to consider large effects which are ultimately grouped together within σ_M . It is not surprising therefore, that rigorous descriptions of contributions to σ_M are very scarce and instead, terms as 'ring contribution'³⁰¹ or 'bulky atom effect'²⁷⁸ are used to explain experimental trends which are not clearly understood.

Before discussing the experimental results in detail, it is convenient to consider, in general, the possible variations of σ with regard to the compounds studied here. For atoms others than hydrogen, and particularly for transition metals, the non-bonding electronic distributions are normally assumed to remain practically unaffected within a series of closely similar compounds.

Flygare and Goodisman³⁰², developed a simple but accurate method to calculate σ_D with which good results have been obtained for nitrogen³⁰³ and carbon³⁰⁴. Similar corrections for platinum chemical shifts however

have demonstrated that the magnitude of σ_D represents only a small contribution compared with the total variation of $\delta^{195}\text{Pt}$.

For the compounds reported here, the neighbouring-atom diamagnetic correction would only apply when considering different halides in, which case the values, as approximated by McFarlane²⁷⁸, are Cl, 68; Br, 129; and I, 181 ppm.

Changes in the diamagnetic term are therefore considered negligible ($\Delta\sigma_D \simeq 0$) and the screening constant for compound i can be written as

$$\sigma_i = \sigma_D + \sigma_{PI} + \sum \sigma_{MI} \quad 5$$

Jameson and Gutowsky³⁰⁵ have demonstrated that in heavy metal systems, the chemical shielding is dominated by the paramagnetic term σ_P .

An expression for σ_P in diamagnetic $5d^8$ square-planar (D_{4h}) Pt(II) complexes has been formulated by Pidcock et al.¹⁷⁴ as

$$\sigma_P(D_{4h}) = AB \langle r^{-3} \rangle \left[2C_{b2g}^2 / \Delta E_{A_{2g}}^1 + 2C_e^2 / \Delta E_{E_g}^1 \right] \quad 6$$

where $\Delta EK = EK - E(A_{1g})$, $\langle r^{-3} \rangle$ represents a radial average over the $5d$ orbitals and $C(K)$ are coefficients of the metal d orbitals in the molecular orbitals.

Similar expressions of σ_P for other metals, also predict a correlation between chemical shifts and ligand field transition energies that is linear if the terms $\langle r^{-3} \rangle$ and the coefficients of molecular orbitals remain constant from one compound to another. Such a correlation has been successful in a number of ^{59}Co complexes containing nitrogen and oxygen as donor atoms although the correlation is less satisfactory when chlorine is attached to Co^{306,307}. Similar attempts to correlate ΔE_i with $\delta^{195}\text{Pt}$ have been largely unsuccessful¹⁷⁴,

presumably because none of the variables in equation 6 can be considered as a constant within the series of compounds studied. It is therefore necessary to consider that

$$\sigma_P = f(\langle r^{-3} \rangle, C(K), \Delta E_i^{-1}) \quad 7$$

and only under very special circumstances can the variables involved in this expression be considered as fixed parameters.

One additional point that will be used later is the effect of the temperature on σ_P . Linear correlation between chemical shifts and temperature have been found for Co³⁰⁶, Rh³⁰⁸ and Pt²⁷⁸. Although there is some disagreement on the interpretation of this effect³¹¹, it is accepted that it involves a temperature dependence of the term ΔE_i . Its variation has been attributed to the change in population of low lying excited levels with temperature³⁰⁹. On the other hand, it has been suggested that increasing the temperature changes the population of higher vibrational energy levels, which results in a lowering of excited states involved in mixing with the ground state, leading to an increased nuclear resonance frequency³¹⁰. It will be sufficient for our purpose to consider the linear variation of $\delta^{195}\text{Pt}$ with the temperature as arising from changes of ΔE_i .

Finally, since the last term in equation 5 involves the summation of contributions which frequently are dependent on specific compounds, it will be discussed together with the experimental results below.

Table 19 gives the platinum chemical shifts for each compound studied and the quantity $\Delta \delta_{mn}$ defined as

$$\Delta \delta_{mn} = |\delta_m - \delta_n| \quad 8$$

where δ_m and δ_n are the platinum chemical shifts associated with isomers m and n of compound i.

The reference system used throughout this work takes as origin (0 ppm) the resonance of cis - $(\text{Me}_2\text{S})_2\text{PtCl}_2$ which is taken as having

Table 19
¹⁹⁵Pt Chemical Shifts

Compound	$\delta^{195}\text{Pt}^b$	$\Delta \delta_{mn}$
<hr/>		
$(\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3)\text{PtCl}_2$		
Isomer A anti	- 232.8	AB = 55.3
Isomer B syn	- 177.5	
<hr/>		
$(\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3)\text{PtClBr}$		
Isomer A anti	- 440.8	AB = 38
Isomer B syn	- 402.8	
<hr/>		
$(\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3)\text{PtBr}_2$		
Isomer A anti	- 666.9	AB = 29.4
Isomer B syn	- 637.5	
<hr/>		
$(\text{CF}_3\text{SCH}_2(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$		
Isomer A syn-anti	- 154.7	AB = 54.2
Isomer B syn-syn	- 100.5	BC = 101.8
Isomer C anti-anti	- 202.3	CD = 104.0
Isomer D anti-syn	- 98.3	DA = 56.4
		AC = 47.6
		BD = 2.2
<hr/>		
$(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtBr}_2$		
Isomer A syn-anti	- 599.7	AD = 29.4
Isomer B syn-syn	ND ^c	
Isomer C anti-anti	ND ^c	
Isomer D anti-syn	- 570.3	
<hr/>		
$(\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$		
Isomer A anti	- 239.1	AB = 3.7
Isomer B syn	- 235.8	
<hr/>		
$(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$		
Isomer A anti	- 122.1	AB = 7.4
Isomer B syn	- 114.7	

Table 19, continued.

Compound	$\delta^{195}\text{Pt}$	$\Delta\delta_{\text{mm}}$
<hr/>		
$(\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$ ²⁷⁸		
Isomer A	- 248.0	AB = 15
Isomer B	- 233.0	
<hr/>		
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtCl}_2$		
Isomer A	- 231.2	AB = 30.4
Isomer B	- 200.8	BC = 3.3
Isomer C	- 204.1	CD = 2.9
Isomer D	- 201.2	AD = 30
		AC = 27.1
		BD = 0.4
<hr/>		
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtBr}_2$		
Isomer A	- 628.4	AD = 32
Isomer B	ND ^c	DE = 2.3
Isomer C	ND ^c	AE = 34.3
Isomer D	- 596.4	
Isomer E	- 594.1	
<hr/>		
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtI}_2$		
Isomer A	-1469.8	AB = 45.8
Isomer B	-1424.0	BC = 1.9
Isomer C	-1425.9	CD = 10.2
Isomer D	-1415.7	DA = 54.1
		AC = 43.9
		BD = 8.3
<hr/>		
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$		
Isomer A syn-syn	- 195.3	AB = 2.5
Isomer B anti-syn	- 192.8	BC = 27.3
Isomer C syn-anti	- 165.5	CD = 53.9
Isomer D anti-anti	- 219.4	DA = 24.1
		AC = 29.8
		BD = 26.6
<hr/>		

Table 19, continued.

Compound	$\delta^{195}\text{Pt}$	$\Delta\delta_{\text{mn}}$
<hr/>		
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}_2$		
Isomer A syn-syn	- 580.8	AB = 0.4
Isomer B anti-syn	- 580.43	BC = 26.4
Isomer C syn-anti	- 554.0	CD = 64.9
Isomer D anti-anti	- 618.9	DA = 38.1
		AC = 26.8
		BD = 38.5
<hr/>		
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtI}_2$		
Isomer A syn-syn	-1399.3	AB = 1.4
Isomer B anti-syn	-1397.9	BC = 26.5
Isomer C syn-anti	-1371.4	CD = 55.9
Isomer D anti-anti	-1427.3	DA = 28
		AC = 27.9
		BD = 29.4
<hr/>		
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$		
Isomer A	- 215.5	AB = 54.9
Isomer B	- 160.6	BC = 18.6
Isomer C	- 179.2	AC = 36.3
Isomer D	ND ^c	
<hr/>		
$(\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$		
<u>cis</u>	- 25.1	CT = 143.2
<u>trans</u>	118.1	
<hr/>		
$(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{SCH}_3)_2\text{PtCl}_2$		
<u>cis</u>	- 36.5	CT = 152.6
<u>trans</u>	116.1	

a) structural assignment as discussed in chapter II

b) p.p.m. positive to low field cis-(Me₂S)₂PtCl₂, for which
 $\delta^{195}\text{Pt} = 21\,420\,980\text{ Hz}^{278}$.

c) insufficiently resolved to be determined.

$\Xi(^{195}\text{Pt}) = 21\,420\,980 \pm 10\text{ Hz}^{278}$. Conversion between scales used in the literature is in most cases trivial and for other scales, Goodfellow et al.²⁷⁷ have given adequate correction factors. $\delta^{195}\text{Pt}$ are taken as positive at high frequencies.

In order to discuss the results, 3 different cases have been distinguished. A) changes of $\delta^{195}\text{Pt}$ on substitution of the neutral ligands B) changes of $\delta^{195}\text{Pt}$ on halide substitution and C) changes of $\delta^{195}\text{Pt}$ for different isomers of each compound.

A) Changes of $\delta^{195}\text{Pt}$ on substitution of the neutral ligands.

The presence of different isomers and therefore different platinum chemical shifts for each compound, makes the direct comparison between single values very difficult since the number of isomers is not the same for each compound. Alternatively, it is possible to contrast ranges of values rather than single values or compare averaged values defined as

$$\delta_{av} = \frac{\sum X_n \delta_n}{n} \quad 9$$

where X_n is the population of isomer n as determined by integration of their n.m.r. resonances. δ_{av} may or may not have a definite physical meaning. Its relation with the single value of platinum chemical shift above the coalescence temperature may change from compound to compound but it is probably a valid indicator of the variation of $\delta^{195}\text{Pt}$ for closely related compounds. δ_{av} are listed in the following table.

Table 20

Values of Averaged Platinum Chemical Shifts

Compound	δ_{av}
$(CF_3SCH_2CH_2SCF_3)PtCl_2$	- 212.44
$PtBr_2$	- 658.66
$CF_3SCH_2CH_2SCH_3)PtCl_2$	- 236.91
$(CH_3SCF_2CH_2SCH_3)PtCl_2$	- 117.80
$(CF_3SCH(CH_3)CH_2SCF_3)PtCl_2$	- 114.44
$(CH_3SCH(CF_3)CH(CF_3)SCH_3)PtCl_2^a$	- 194.25
PtI_2	-1430.75
$(CH_3SCH(CF_3)CH_2SCH_3)PtCl_2$	- 198.96
$PtBr_2$	- 587.76
PtI_2	-1399.97

a) average only over interconvertable isomers.

The only values of $\delta^{195}Pt$ in a dithioether complex that have been reported previously correspond to the anti and syn isomers of $(MeSCH_2CH_2SMe)PtCl_2$, determined by McFarlane²⁷⁸. Including this value, platinum chemical shifts in complexes with the general formula $(RSR'SR)PtCl_2$ extend over 150 ppm, from -98.3 in isomer D of $(CF_3SCH(CH_3)CH_2SCF_3)PtCl_2$ to -248 ppm for isomer A of $(MeSCH_2CH_2SMe)PtCl_2$. In comparison with the total range of platinum chemical shifts - over 6000 ppm - this set of values is narrow enough to be characteristic if used with caution. It is interesting to note that neither the values reported for the similar compounds

cis-trans(RR'S)₂PtCl₂ nor those for cis-trans (R_fSCH₂CH₂SCH₃)₂PtCl₂ where R_f=CF₃ or C₆F₅ (monodentate ligands), are found within this set. On the other hand some mixed halide platinum complexes of sulphides and selenides have been found to display $\delta^{195}\text{Pt}$ in the region considered. Some examples are given in the following table..

Table 21

Selected values of $\delta^{195}\text{Pt}$ in the region
-100 to -250 ppm.

Compound	$\delta^{195}\text{Pt}^{279}$
trans - (Me ₂ S) ₂ PtBrCl	- 106
cis - (Me ₂ S) ₂ PtBrCl	- 152
cis - (MePhS) ₂ PtBrCl	- 114
cis - (Me ₂ Se) ₂ PtCl ₂	- 198
cis - (Me ₂ Se) ₂ PtBrCl	- 182
trans - (Me ₂ Se) ₂ PtBrCl ²⁷⁷	-218

The amount of data available for bromide and iodide complexes is smaller than that for chloride compounds and therefore probably less significant. Nevertheless, from table 19, comparative ranges of values are found. Platinum chemical shifts for bromide complexes span 112 ppm and for iodide compounds over 98 ppm.

Comparison with cis-trans(RR'S₂)PtX₂ where X= Br or I, shows a similar specificity to that found for the series of chloride complexes.

On the other hand, although 150 ppm is small set of values in relation with the total range known, in itself, it is large enough to reflect small differences between closely related compounds. According to expression 5, the differences in $\delta^{195}\text{Pt}$ arise from σ_p and the terms involved in $\sum \sigma_R$ and thus is virtually impossible to

compare values of $\delta^{195}\text{Pt}$ when both variables can change independently. Considering exclusively the effects of electronegativity on the S-Pt bond in complexes LPtCl_2 containing the ligands $\text{MeSCH}_2\text{CH}_2\text{SMe}$, $\text{MeSCF}_2\text{CH}_2\text{SMe}$, $\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$ and $\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$, the successive substitution of hydrocarbon by fluorocarbon groups would be expected to produce successive displacement of their platinum resonances, resulting in a distribution in which $\text{MeSCH}_2\text{CH}_2\text{SMe}$ and $\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ would occupy both extremes; $\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3$ is expected to be closer to the hydrocarbon ligand than $\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$. Figure 63 includes the values of $\delta^{195}\text{Pt}$ for both isomers of each compound.

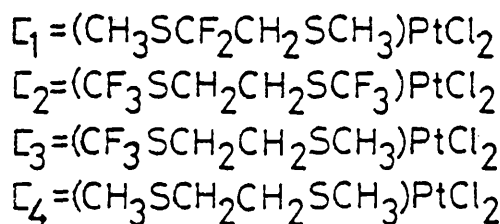
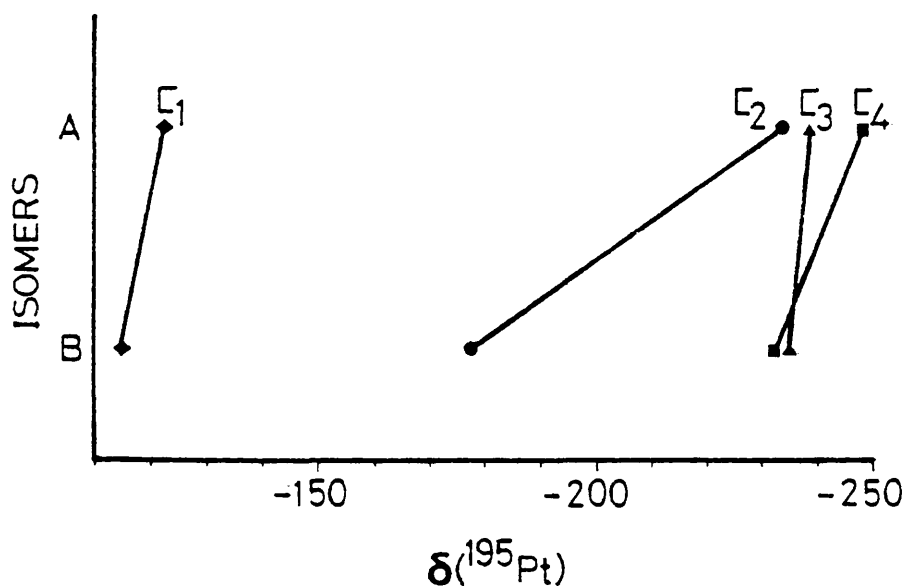


Figure 63. Values of platinum chemical shift.

It is evident that not only is the ordering of $\delta^{195}\text{Pt}$ different from that expected but also that other parameters like the large difference between the complexes containing $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$ and

$\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3$ and the variable slope, related with $\Delta\delta_{AB}$, show tendencies which cannot be explained exclusively in terms of the variables $\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3$ or expression 5 for σ_p .

The effect of fluorine substitution in the bridge is particularly intriguing. The difference in $\delta^{195}\text{Pt}$ for both isomers of $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$ with respect to those of $(\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$, represents a substantial proportion of the complete range observed for dithioether complexes and yet, the effect that the fluorine substituents on the bridge can produce on the electronic distribution of the sulphur-platinum bond, cannot be assumed to be greater than that produced by the far more electron-withdrawing CF_3 substituent.

The effect of variations of the sulphur-platinum bond on the parameters of equation 6 and the corresponding changes in chemical shift are grouped in table 22.

Table 22

Variation of $\delta^{195}\text{Pt}$ with changes of S-Pt bond.

<u>Increase σ-bonding</u>	Change in $\delta^{195}\text{Pt}$
Increase electron density	
Decrease $\langle r^{-3} \rangle$	Shielding
Increase ΔE	Shielding
Decrease molecular-orbital	
Coefficients	Shielding
<u>Increase π-bonding</u>	
Decrease electron density	Deshielding
Increase $\langle r^{-3} \rangle$	
Increase ΔE	Shielding
Decrease molecular-orbital	
Coefficients	Shielding

Both ΔE and the molecular orbital coefficients are explicitly¹ considered in approximations of Ramsey's equation of shielding constant. The radial average $\langle r^{-3} \rangle$ term is, generally, not considered as an independent variable and variations of radial distances are reflected by changes in the molecular orbital coefficients. Table 22 therefore includes all variables normally involved in shielding constant calculation; it should be noticed that the effect of the radial term in the expected change of platinum chemical shift is to increase the shielding when σ bonding increases but has the opposite effect, when π bonding is increased. Both effects cancel each other and therefore there is no net effect on $\delta^{195}\text{Pt}$. This is an expected result since table 22 has been written following the model proposed by Chatt-Duncanson-Venanzi¹⁴⁵ in which Pauling's electroneutrality principle has been considered and therefore, the variations of electron density arising from σ and π bonding cancel each other in the same way as $\langle r^{-3} \rangle$ does.

Since we have chosen to examine the effects of 'increasing' π and σ bonding on $\delta^{195}\text{Pt}$, we need to refer such increments to a standard, for the table to be operative. If compound $(\text{MeSCH}_2\text{CH}_2\text{SMe})\text{PtCl}_2$ is taken as reference in table 19, all other complexes exhibit platinum chemical shifts to low field relative to those of the reference. From table 19 it seems that the increase of the $(\sigma+\pi)$ bonding follows the order $\text{MeSCF}_2\text{CH}_2\text{SMe} < \text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3 < \text{CF}_3\text{SC}_2\text{H}_4\text{SMe} < \text{MeSC}_2\text{H}_4\text{SMe}$. This order is inconsistent with the observed chemical behaviour towards halide substitution of the complexes, which suggests that sulphur-platinum bond strength probably decreases in the series $\text{CH}_3\text{SC}_2\text{H}_4\text{SCH}_3 \approx \text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3 > \text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ similar to the order intuitively predicted considering the electron withdrawing character of the sulphur substituents.

We have considered only changes that ideally would be attributed to the paramagnetic contribution but, in the limited region considered,

other terms can become as important as σ_P . Differences of chemical shift between isomers can be as large as 100 ppm -see following section c- and only a fraction of such a shift would reverse the whole order of the series. It must be added however, that, at this point, it is not possible to predict the magnitude of the effect of $\Sigma \sigma_N$ nor its direction.

Similarly, figure 64, represents the results for compounds containing ligands with different substituents in the bridge, indicating that the effective shielding increases in the series

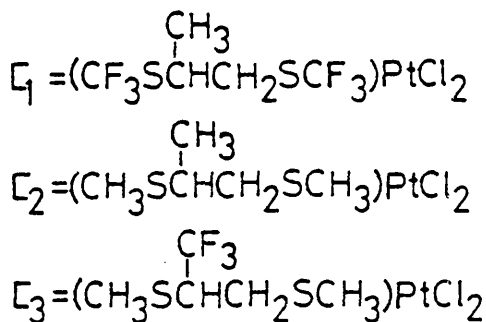
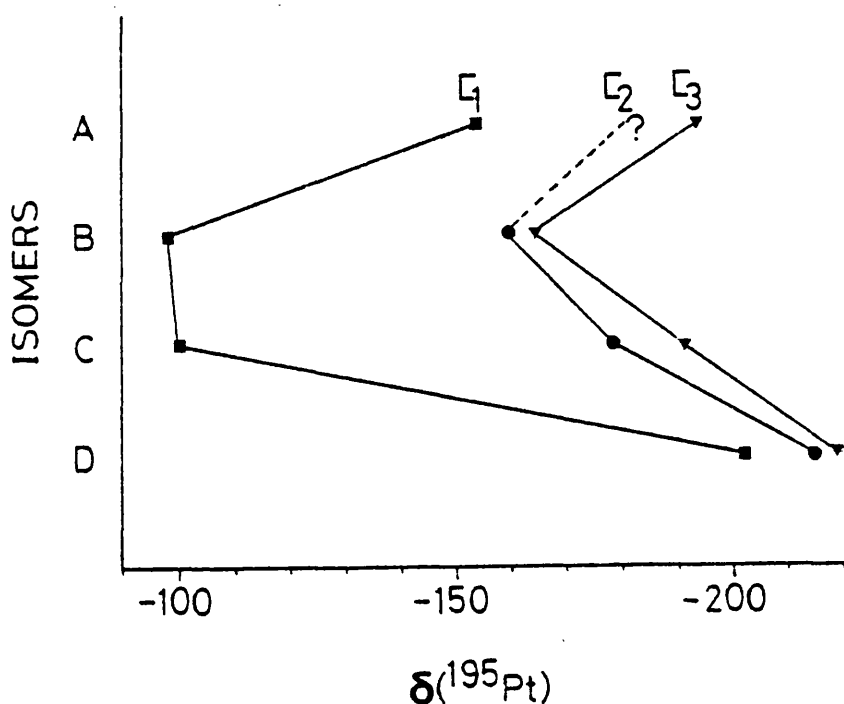
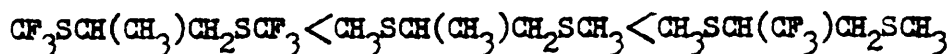


Figure 64. Values of platinum chemical shift.

Again, the values of $\delta^{195}\text{Pt}$ found in complexes containing fluorinated ligands are largely displaced to high frequencies relative to hydrocarbon compounds. The order between complexes containing a fluorinated bridge substituent and their hydrocarbon analogues would appear to be reversed, purely in terms of the variables of the paramagnetic term, but the effects on this parameter are expected to be relatively small since CF_3 group here far from the donor atom, and therefore its influence on the S-Pt bond would be substantially decreased. Accordingly, it is interesting to note the close similarity of values found for both complexes.

B) Changes of $\delta^{195}\text{Pt}$ on halide substitution. Previous studies have been relatively successful in proposing empirical relationships accounting for the successive changes of chemical shift for replacement of one halide by another. Von Zelewsky²⁷³ studied the changes in $\delta^{195}\text{Pt}$ of the compounds resulting after mixing solutions of K_2PtCl_6 and K_2PtBr_6 . Goodfellow et al.²⁷⁷ have proposed a detailed procedure to calculate $\delta^{195}\text{Pt}$ in species with the general formulation $[\text{LPtXYZ}]^-$, where L is a neutral ligand and X, Y and Z are halogen atoms.

The large differences between the range of values found for $\delta^{195}\text{Pt}$ corresponding to each halide, makes platinum chemical shifts a much more definite probe of the nature of the compound than any other n.m.r. parameter. This fact is illustrated in figure 65. Fluorine chemical shifts for complexes $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtX}_2$ X=Cl, Br or I, span a narrow band of ca 7 ppm. The set of values for each compound overlap and the origin of each signal is ambiguous. On the other hand, the range of platinum chemical shifts are distributed so far apart one from another that the recognition of different halide complexes is relatively simple.

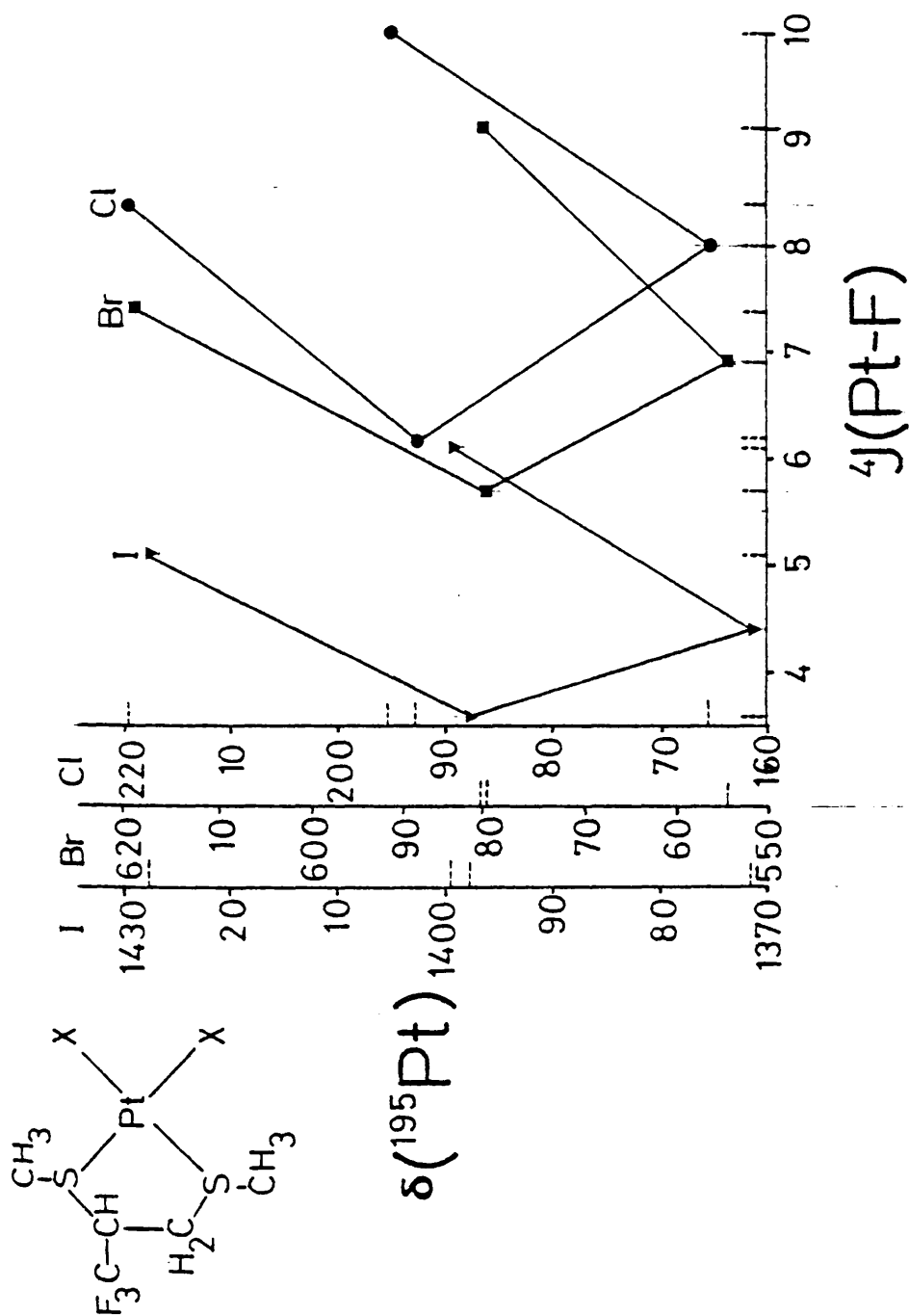


Figure 65. Correlation between platinum chemical shifts and platinum-fluorine coupling constants for different halide complexes.

Table 23 gives the difference of $\delta^{195}\text{Pt}$ for each compound when the halogen atoms are replaced, according to

$$\Delta X_2 - Z_2 = \delta^{195}\text{Pt}(\text{LPt}Z_2) - \delta^{195}\text{Pt}(\text{LPt}X_2) \quad 10$$

Table 23

$\Delta X_2 - Z_2$ for $\text{LPt}X_2$ Complexes

L = ligands listed; X = Cl, Br or I.

Ligand			
$\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$	$\Delta \text{Cl}_2 - \text{ClBr}$	$\Delta \text{ClBr} - \text{Br}_2$	$\Delta \text{Cl}_2 - \text{Br}_2$
Isomer A	208.0	226.1	484.1
Isomer B	225.3	234.7	460.0
$\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3$	$\Delta \text{Cl}_2 - \text{Br}_2$		
Isomer A	445.0		
Isomer D	472.0		
$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$	$\Delta \text{Cl}_2 - \text{Br}_2$	$\Delta \text{Br}_2 - \text{I}_2$	$\Delta \text{Cl}_2 - \text{I}_2$
Isomer A	397.2	841.4	1238.6
Isomer B	-	-	1223.2
Isomer C	3014.1	829.5	1223.6
Isomer D	392.9	821.6	1214.5
$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3$	$\Delta \text{Cl}_2 - \text{Br}_2$	$\Delta \text{Br}_2 - \text{I}_2$	$\Delta \text{Cl}_2 - \text{I}_2$
Isomer A	385.5	818.5	1204.0
Isomer B	387.6	817.4	1205.1
Isomer C	388.5	817.4	1205.9
Isomer D	399.5	808.4	1207.9

In this case also, only the two final terms in equation 5 would be relevant and, if comparisons are carried out between structurally similar isomers, the effect produced by the different exchanged halides can be followed. $\Delta \text{Cl}_2 - \text{Br}_2$, for example, will correspond to

$$\begin{aligned}\sigma_{\text{Br}_2} - \sigma_{\text{Cl}_2} &= (\sigma_D + \sigma_{\text{PBr}} + \sum \sigma_{\text{NBr}}) - (\sigma_D + \sigma_{\text{PCl}} + \sum \sigma_{\text{NCl}}) \\ &= \sigma_{\text{PBr}} - \sigma_{\text{PCl}} + (\sum \sigma_{\text{NBr}} - \sum \sigma_{\text{NCl}}) \quad 11\end{aligned}$$

and because ligand factors are assumed to remain unchanged regardless of the halide, $\sum \sigma_{\text{NBr}} = \sum \sigma_{\text{NCl}}$ giving

$$\sigma_{\text{Br}_2} - \sigma_{\text{Cl}_2} = \sigma_{\text{PBr}} - \sigma_{\text{PCl}} \quad 12$$

We might expect the changes in $\delta^{195}\text{Pt}$ on replacing one halide by another to be affected by the trans influence of the ligand trans to it. Strictly speaking, platinum chemical shifts do not constitute an experimental observation of the trans influence³¹². However, it does indicate the effect of ligands on platinum itself and some information can be gained from its measurement. If X forms a covalent bond with platinum or if the extent of π -bonding is appreciable, all coefficients in equation 6 are reduced and platinum chemical shifts move upfield. The substantial upfield shifts in the series



are indicative of the increased covalent bond character on substitution of chlorine by bromine and iodine.

To correlate $\delta^{195}\text{Pt}$ with the trans influence of the ligand, it should be noticed that $\Delta \text{Cl}_2\text{-Br}_2$ are substantially higher for compounds with electronegative substituents at the sulphur atom than those found for hydrocarbon ligands, which suggest that the trans influence decreases in the order



where R and Rf are hydrocarbon and fluorocarbon substituents respectively.

From the values in table 23 two relations for each type of ligand are found to describe the change in $\delta^{195}\text{Pt}$ on halide substitution. The platinum chemical shifts of LPtX_2 ; X=Br and I, $\delta_{\text{Pt}}^{\text{X}}$, can be calculated from the values observed for LPtCl_2 , $\delta_{\text{Pt}}^{\text{Cl}}$, with

$$\delta_{\text{Pt}}^{\text{Br}} = \delta_{\text{Pt}}^{\text{Cl}} + (453 \pm 19) \quad -1 \leq n \leq 1 \quad 13$$

when $L = \text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ or $\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3$ or

$$\delta_{\text{Pt}}^{\text{Br}} = \delta_{\text{Pt}}^{\text{Cl}} + (393 \pm n55) \quad 14$$

$$\text{and } \delta_{\text{Pt}}^{\text{I}} = \delta_{\text{Pt}}^{\text{Cl}} + (1221 \pm n17) \quad 15$$

when $L = \text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$ or $\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3$

It should be noticed that correction factors are all smaller than 5% of the total $\delta^{195}\text{Pt}$. For the single value of platinum chemical shift in $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtClBr}$, expression 13 is valid simply by assuming that each entering bromine atom contributes half the total shift and therefore

$$\delta_{\text{Pt}}^{\text{Br}} = \delta_{\text{Pt}}^{\text{Cl}} + B(226.5 \pm n9.5) \quad 16$$

where B is number of bromine atoms.

C) Changes of $\delta^{195}\text{Pt}$ for different isomers. In 1974, McFarlane²⁷⁸ determined the platinum chemical shifts for the syn and anti isomers of $(\text{MeSC}_2\text{H}_4\text{SMe})\text{PtCl}_2$. The difference of 15 ppm was too small to be considered in his analysis, instead, he found it necessary to study a greater number of compounds to assess the importance of what he called conformational effects. A similar effect has been observed for $\delta^{103}\text{Rh}$ in $[(\text{MeSC}_2\text{H}_4\text{SMe})_2\text{RhCl}_2]^+$, producing larger differences of up to 81 ppm^{398,36}. The wider range is attributed to a larger sensitivity to changes in ΔE in the case of rhodium since the temperature dependence of the chemical shift is also larger³⁰⁸.

No other examples of compounds showing different platinum chemical shifts corresponding to different spatial arrangements of the ligand only have been reported. Several examples of $\delta^{195}\text{Pt}$ from cis and trans complexes of monodentate ligands are known^{272,277,278}.

Table 19 gives the values of $\Delta\delta_{nm}$ which effectively corresponds to the difference of platinum chemical shifts of different isomers.

From equation 5

$$\Delta\delta_{mn} = (\sigma_{Dm} - \sigma_{Dn}) + (\sigma_{Pm} - \sigma_{Pn}) + (\sum\sigma_{Nm} - \sum\sigma_{Nn}) \quad 17$$

As has already been said, the diamagnetic contribution is similar for related compounds. When considering isomeric forms of a single complex the similarities are expected to increase. Corrections for neighbouring diamagnetic contributions are needed when ligands are substituted in a complex but for isomers such correction needs not to be considered. It follows that

$$\sigma_{Dm} = \sigma_{Dn}$$

and the first term in expression 17 is therefore vanishingly small or zero.

The second term involving the individual paramagnetic contributions depend basically on differences in bonding. There is no evidence suggesting that different isomers possess different bonding features. The interconversion of isomers involves the modification of the electronic distribution when changing from one form to another through an intermediate but the n.m.r. experiment can only detect the more highly populated extreme forms. The energy barriers involved in such interconversions preclude the separation of isomers and therefore spectral information cannot be obtained for each conformer. We can assume however, that if the positions of the d orbital energy levels are unchanged for similar compounds, it is very likely that for isomeric forms they would have greater similarity. Figure 66 shows the visible-uv. spectra of complex $LPtCl_2$, $L = CF_3SC_2H_4SCF_3$, $CF_3SCH(CH_3)CH_2SCF_3$ and $CH_3SCH(CH_3)CH_2SCH_3$. The spectra of compounds containing the fluorinated ligands are practically identical, whereas the spectrum for the hydro-

carbon compound shows clear differences. It therefore appears reasonable

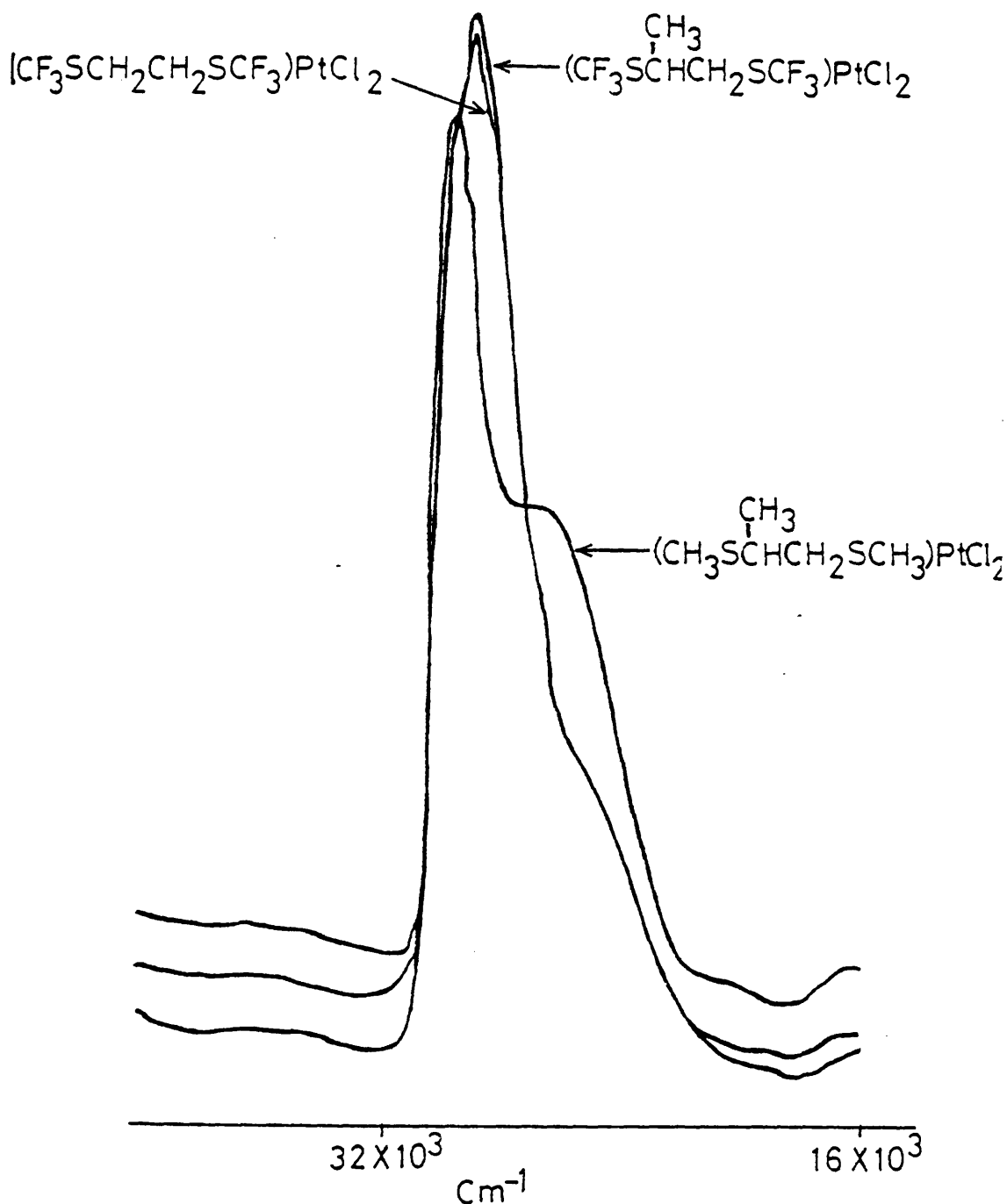


Figure 66. Ultraviolet spectra of $(\text{RSCHR}'\text{CH}_2\text{SR})\text{PtCl}_2$
 $\text{R} = \text{CF}_3$; $\text{R}' = \text{H}, \text{CH}_3$; $\text{R} = \text{R}' = \text{CH}_3$.

to suggest that ΔE would remain unchanged regardless of the conformer considered. Thus the suggestion that the larger sensitivity of energy

levels in Rh produces a large difference between isomeric metal frequencies seems unlikely. The variables in expression 7, defining the paramagnetic term are not independent and by extension, other parameters are expected to remain unaffected particularly by changes from isomer to isomer. The suggestion involved in what McFarlane called conformational effect²⁷⁸ is a dependence on the geometric arrangement of the ligand. The paramagnetic term is, by definition, independent of changing spatial arrangements as long as the bonding mode is not affected.

Additional evidence that platinum chemical shifts of different isomers are influenced by factors independent of the paramagnetic term comes from the thermal changes of $\delta^{195}\text{Pt}$. It has been shown that metal^{271,313,306} frequencies have a linear variation with the temperature and the same variation is expected to be found in each isomer according to their common ΔE . Experimentally however the $\delta^{195}\text{Pt}$ in isomers of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtI}_2$ display a distinct, individual relation with temperature. The variations are shown in figure 67.

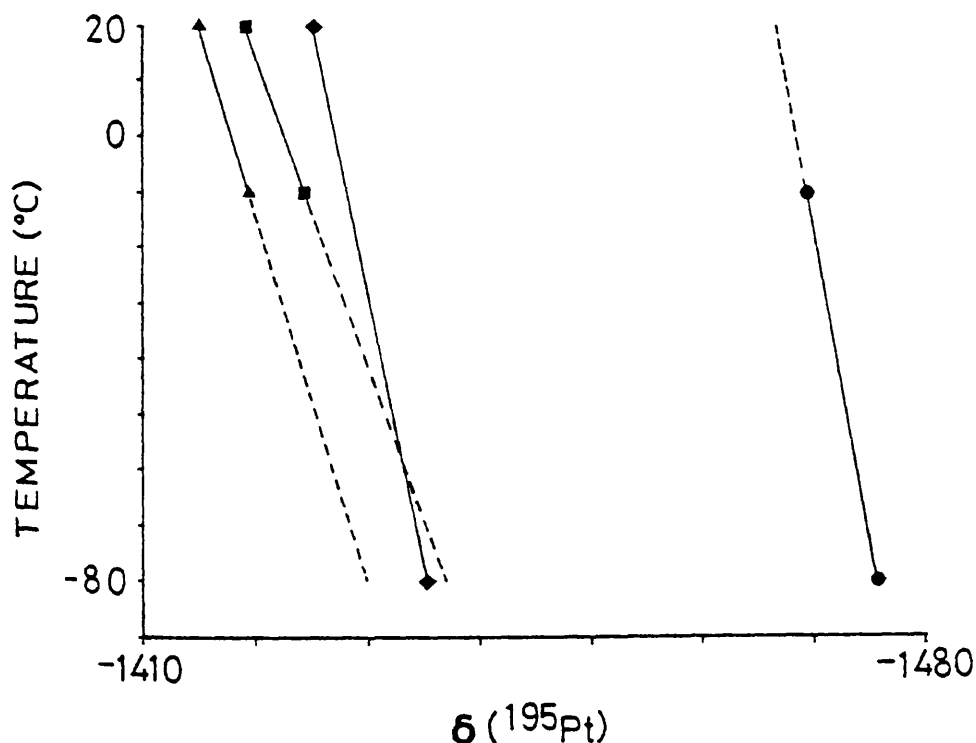


Figure 67. Variation of $\delta^{195}\text{Pt}$ with temperature for isomers of $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtI}_2$

Such differences are indicative of the fact that, whatever the factors determining $\delta^{195}\text{Pt}$, they have to be not merely dependent on structural considerations but also temperature dependent. Variations of temperature can affect platinum chemical shifts directly, since there is an inherent temperature dependence of $\delta^{195}\text{Pt}$ which gives rise to changes of about 1 ppm/ $^{\circ}\text{C}^{278}$, or indirectly, since the instantaneous averaged structure of dithioether complexes can be related to the temperature and in turn to the $\delta^{195}\text{Pt}$.

Following the description of the screening constant, we assume that

$$\sigma_{\text{Pm}} = \sigma_{\text{Pn}} \quad 18$$

and therefore

$$\sigma_{\text{m}} - \sigma_{\text{n}} = \sum \sigma_{\text{Nm}} - \sum \sigma_{\text{Nn}} \quad 19$$

For our purposes, expression 19 means that $\Delta\delta_{\text{mn}}$ in table 19 is dependent only on the terms of $\sum \sigma_{\text{N}}$. This is not a great simplification since by definition $\sum \sigma_{\text{N}}$ includes contributions insufficiently understood to be considered elsewhere.

From the definition of σ_{N} equation 3, the solvent effects can be cancelled in expression 19, since their influence is likely to be similar for all isomers. Other effects frequently included are ring current effect and the neighbouring anisotropy contribution, which have been proved to be nearly constant for all nuclear magnetically active nuclei studied³¹¹ and known to be responsible for small variations in chemical shifts of the order of ± 2 ppm³¹⁴.

As given in table 19, $\Delta\delta_{\text{mn}}$ indicates the difference in platinum chemical shifts between structurally defined isomers. This information is shown in figures 68 and 69.

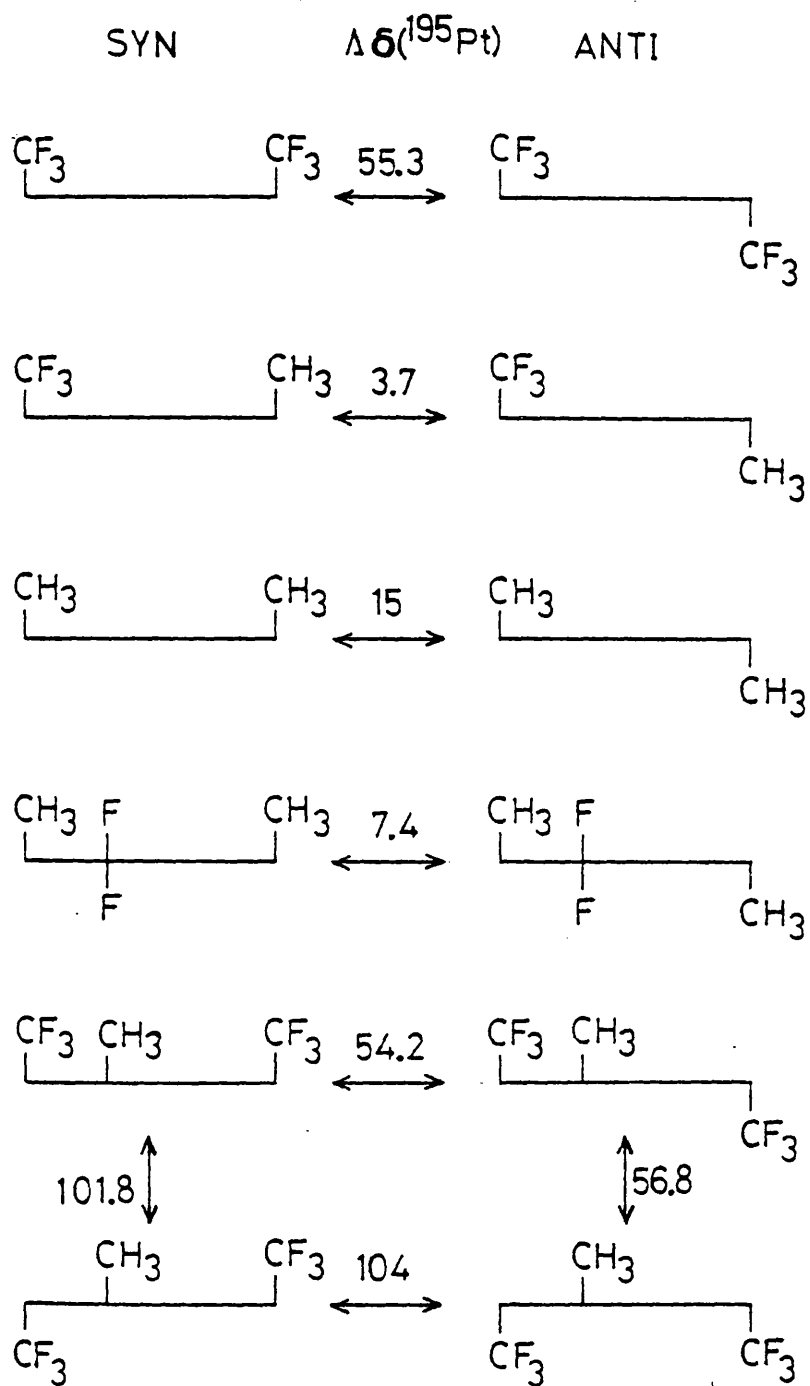


Figure 68. Differences in $\delta^{195}\text{Pt}$ between isomers.

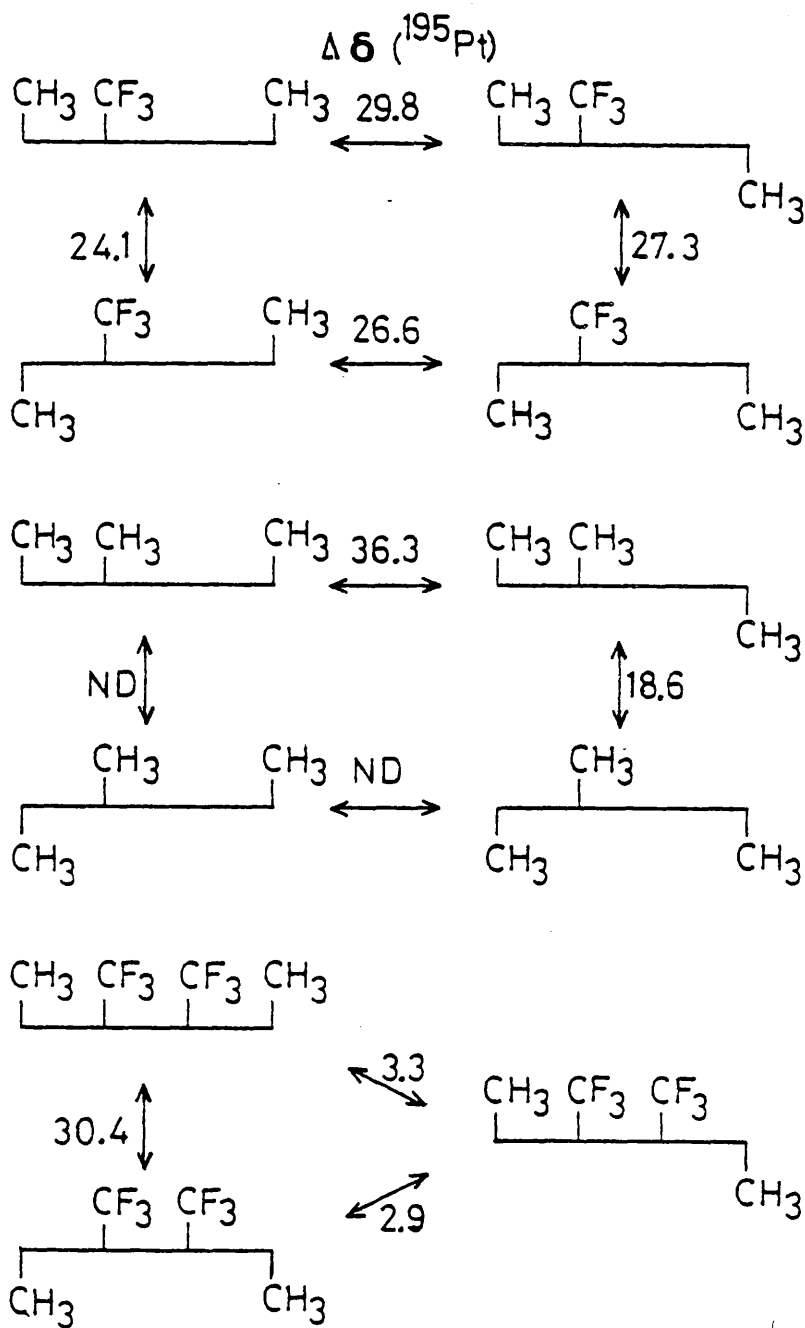


Figure 69. Differences in $\delta ^{195}\text{Pt}$ between isomers.

To account for the changes illustrated, a suitable explanation would have to include the following characteristics of $\delta ^{195}\text{Pt}$.

a) Dependence on geometry, involving the orientation of different groups in the bridge and of the sulphur substituents, hence of the sulphur lone pair.

b) Ligand dependence, since pairs of equivalent conformers in

different compounds show different $\Delta \delta_{mn}$.

c) Temperature dependence. The interconversion of isomers is a dynamic temperature dependent process and therefore geometry and temperature dependence are, as discussed before, interrelated.

In addition, it has to account for differences of platinum chemical shifts as large as 100 ppm but since above the coalescence temperature there is only one, averaged, value of $\delta^{195}\text{Pt}$, the differences between $\delta^{195}\text{Pt}$ of different isomers have to tend to zero when the temperature tend to the coalescence temperature.

These requirements are met - not exclusively - by the behaviour of electric currents generated by the movement of electrons^{315,316}. Such a contribution from interatomic currents has been proposed before by Pople and others^{286,317,319,330}, to account for contributions to proton chemical shifts, particularly in systems in which it is possible for electrons to flow round a ring of bonded atoms³¹⁸ or for molecules like acetylene¹¹⁰. There is a great difficulty in trying to incorporate the concepts involved in the general term 'current contributions' to a complex molecule of the type discussed here. Therefore the following ideas are only an attempt to rationalize intuitively the results obtained and make no claim to rigour.

As shown in figure 70, we assume the applied magnetic field H_0 to be parallel to the x axis in the sense indicated.

Diagrammatically, the sulphur substituents are indicated by circles above - for a syn isomer - the S-Pt-S plane coincident with the x-y plane. The local electronic circulations would give rise to a secondary magnetic field opposite in direction to H_0 . Dashed lines are used to indicate magnetic lines of force and H' represent the vectors symbolizing the resultant magnetic fields.

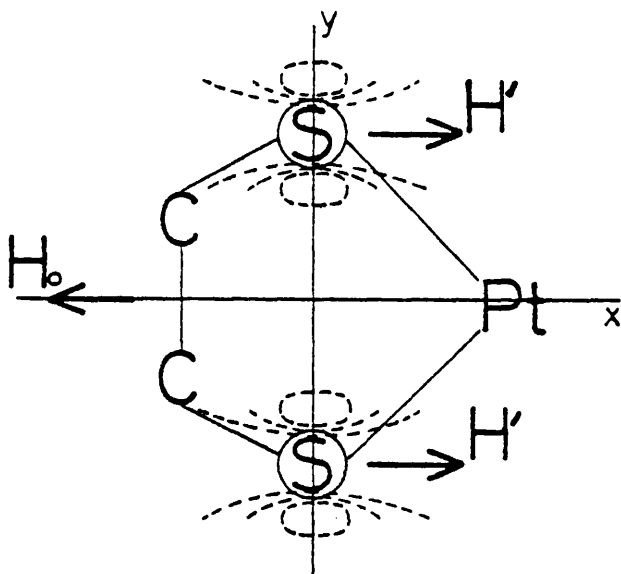


Figure 70. Secondary magnetic fields, H' , induced by a primary field H_0 .

If we have the z - y plane in the plane of the paper, the opposing magnetic fields would appear as the black dots in the following diagram.

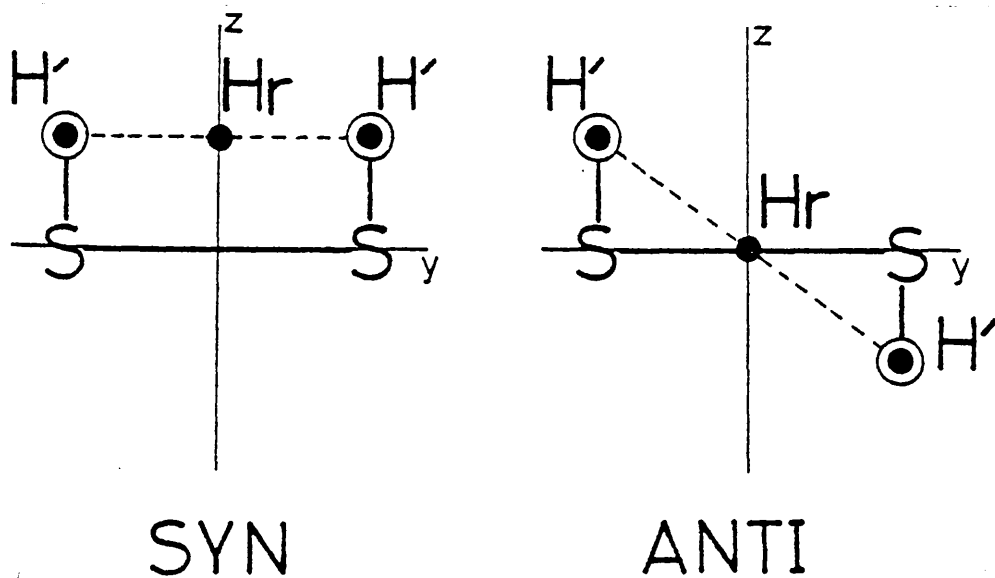


Figure 71. Secondary and resultant magnetic fields in a symmetric compound.

Treated as vectorial quantities, the resultant effect of both secondary magnetic fields is a new vector, H_r , with intensity equal to the sum of the intensities of the components and with the same direction, but with a different position. Diagram 71 illustrates the syn and anti isomers of a symmetrically substituted compound such as $(CH_3SC_2H_4SCH_3)PtCl_2$ or $(CF_3SC_2H_4SCF_3)PtCl_2$. The position of the resultant vector changes with the orientation of the substituents from a position above the S-Pt-S plane to a position on the plane which therefore points directly to the metal centre. If both compounds adopt similar conformations the mechanism would be operative in both cases and the difference of $\Delta\delta_{AB} = 15$ ppm for the hydrocarbon ligand to $\Delta\delta_{AB} = 55$ ppm for the fluorocarbon ligand would reflect the different intensities of H' .

The difference $\Delta\delta_{AB} = 3.7$ ppm for $(CF_3SC_2H_4SCH_3)PtCl_2$ is far smaller than the examples mentioned, even though, only one substituent has been replaced. A similar treatment is illustrated in the following diagram.

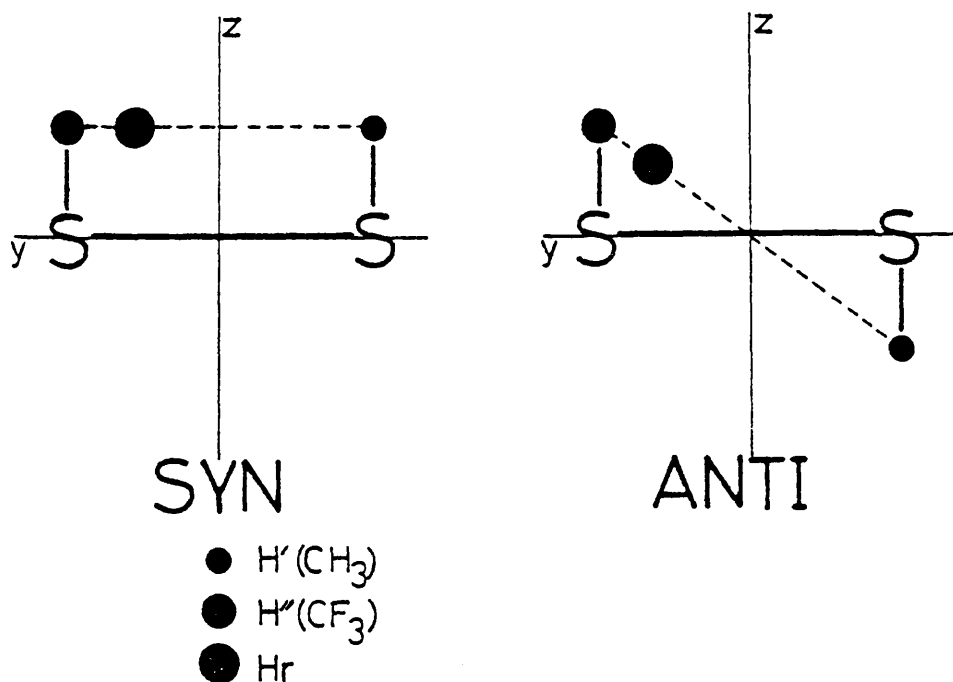


Figure 72. Secondary and resultant magnetic fields in an asymmetric compound.

The intensity of the resultant magnetic vector is also the sum of the individual intensities but since the compound is asymmetric, the resultant vector H_r has its origin not in the centre, as before, but proportionally closer to the more intense component. On changing conformation, the displacement of the resultant magnetic vector H_r will depend on its position relative to the origin of its more intense component and therefore the larger the difference between H' and H'' the smaller the displacement of H_r .

If we assume that the intensity of the secondary magnetic component which originates at the trifluoromethyl group, is very much larger than the corresponding component for the methyl substituent, a change of configuration should produce a small displacement of H_r . Therefore a small difference between platinum chemical shifts, as observed, would be predicted. The results found for $(CH_3SCF_2CH_2SCH_3)PtCl_2$ are more difficult to visualize in exactly the same way. Considering current contributions from the $-CF_2-$ group, which is assumed to have relatively large life time in specific positions above and below the S-Pt-S plane, the geometric system should include three secondary magnetic components. A schematic representation of the system in the x-y plane would place the origin of H_r always outside the z-y origin and therefore the difference $\Delta\delta_{AB}$ expected would be smaller than that for a totally symmetric case. This is in agreement with the experimental results. The last example is illustrated on figure 73. The presence of a bridge substituent changes, as before, the geometric system to be considered. The resultant vector H_r between the nearest CF_3 and CH_3 groups can be calculated previously to H_r . Note that H_r has its origin outside any specific substituent.

The results would have to be very similar to the first case described. The model predicts two sets of values as observed, but

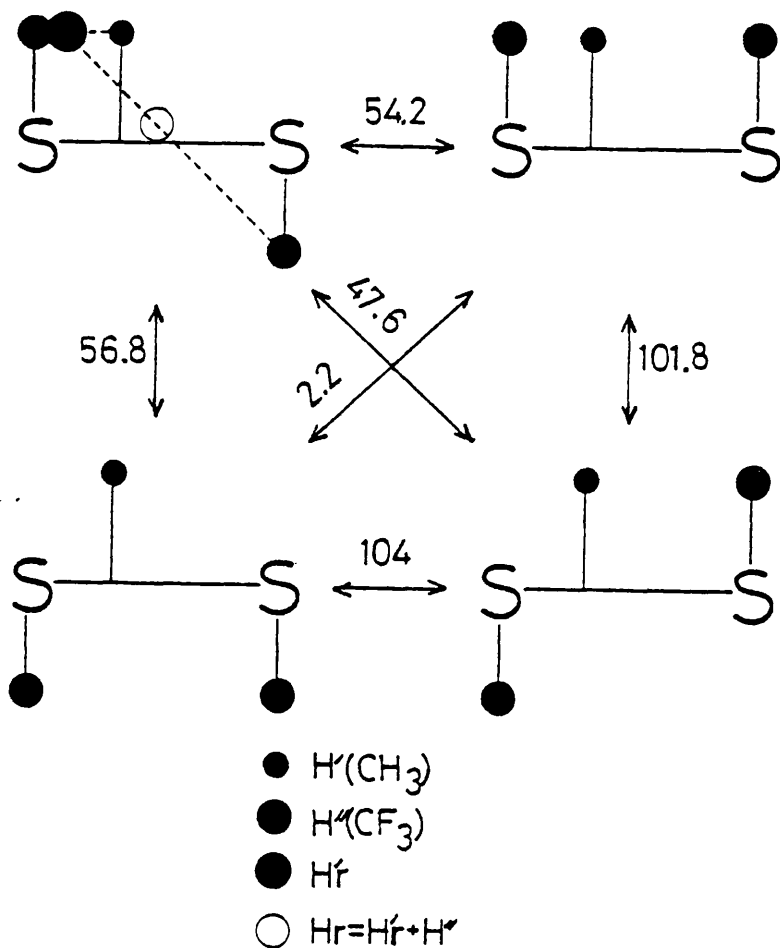


Figure 73. Changes in $\delta^{195}Pt$ for different structures of $(CF_3SCH(CH_3)CH_2SCF_3)PtX_2$.

the fact that the magnitude of one pair of values, $\Delta\delta_{BC} = 101.8$ and $\Delta\delta_{CD} = 104.0$, is almost double that of the other pair, $\Delta\delta_{AB} = 54.2$ and $\Delta\delta_{DA} = 56.4$, cannot be explained by the model. Furthermore, very small values of $\Delta\delta$ would be predicted for the changes of configuration syn \leftrightarrow syn and anti \leftrightarrow anti; yet, the experimental results are $\delta_{BC} = 2.2$ as, predicted, and $\delta_{AC} = 47.6$ which seems again too large to be accounted for by this explanation. Nevertheless, qualitatively, the model appears to appropriate to predict, in general terms, the effect of different geometrical arrangements on the Pt chemical shifts.

APPENDIX A

Analyses of the ABX type spectra of compounds with the general formula $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtX}_2$ where $\text{X}=\text{Cl}$, Br and I were based on the diagrams that follows. For each isomer the AB part of the ABX spectra were decomposed into two pseudo-quartets and treated according to the expressions^{237,311}:

$$\frac{1}{2}(\text{JAX} - \text{JBX}) = \left[(\text{D} + \frac{1}{2}\text{JAB})(\text{D} - \frac{1}{2}\text{JAB}) \right]^{\frac{1}{2}} - \left[(\text{D}' + \frac{1}{2}\text{JAB})(\text{D}' - \frac{1}{2}\text{JAB}) \right]^{\frac{1}{2}} \quad \text{I}$$

and

$$\frac{1}{4}(\text{JAX} - \text{JBX}) = (\text{D}^2 - \frac{1}{4}\text{JAB})^{\frac{1}{2}} - \frac{1}{2}\nu\delta\text{AB} \quad \text{II}$$

$\nu\delta\text{AB}$ was taken as the chemical shifts between atoms A and B as determined from the non coupled AB spectra.

Table 37 gives the corresponding n.m.r. parameters for all compounds except for isomer B of the bromide complex.

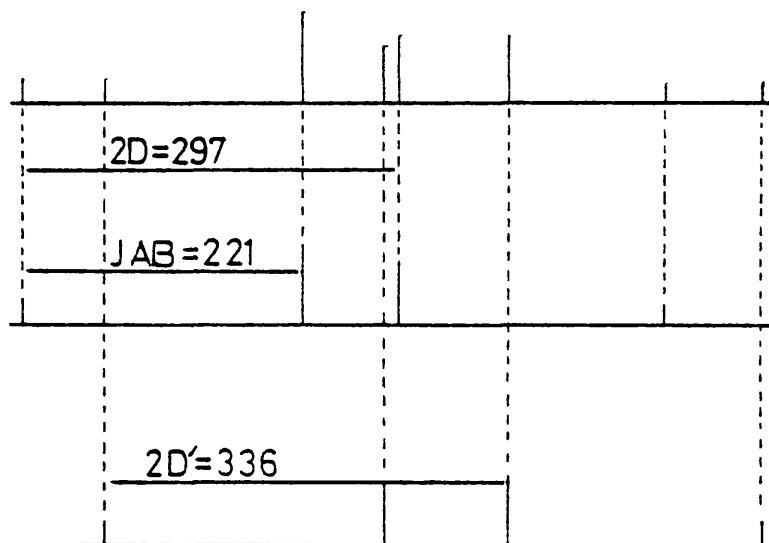
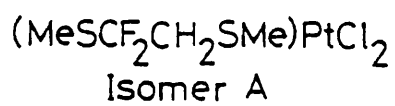
Table 37

N.m.r. Parameters for $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtX}_2$, $\text{X}=\text{Cl}$, Br , I .

Compound	AB	$\frac{1}{2}(\text{JAX}+\text{JBX})$	2D	2D'	AX	BX
$(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$						
I Isomer A	221	87.5	297	336	60.0	114.0
II Isomer B	205	107	283	209	29	184
$(\text{CH}_3\text{SF}_2\text{CH}_2\text{SCH}_3)\text{PtBr}_2$						
III Isomer A	223	80.5	381	444	43.0	118.0
IV Isomer B	205.5					
$(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtI}_2$						
V Isomer A	206	91.5	228	305	27.5	155.5
VI Isomer B	225	68	599	687	22.5	113.5

Analysis of the n.m.r. results for compound IV was not possible because the appearance of the corresponding spectrum closely resembled an AA'X spectrum. Two situations can produce this spectral form³¹¹:

a) an almost identical pair of chemical shifts, in which case the system



Isomer B

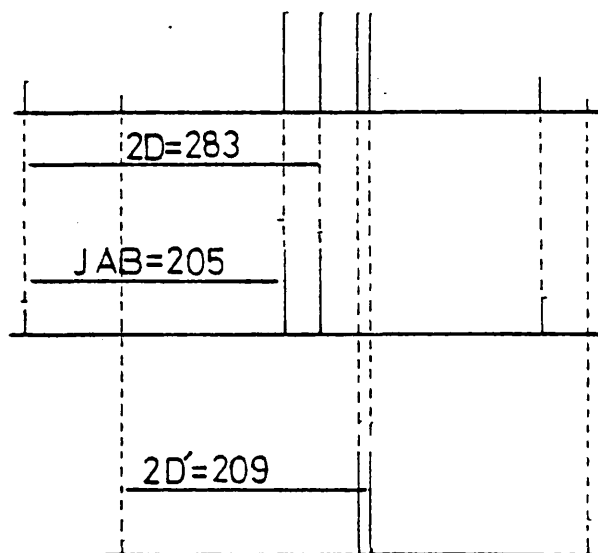


Diagram II

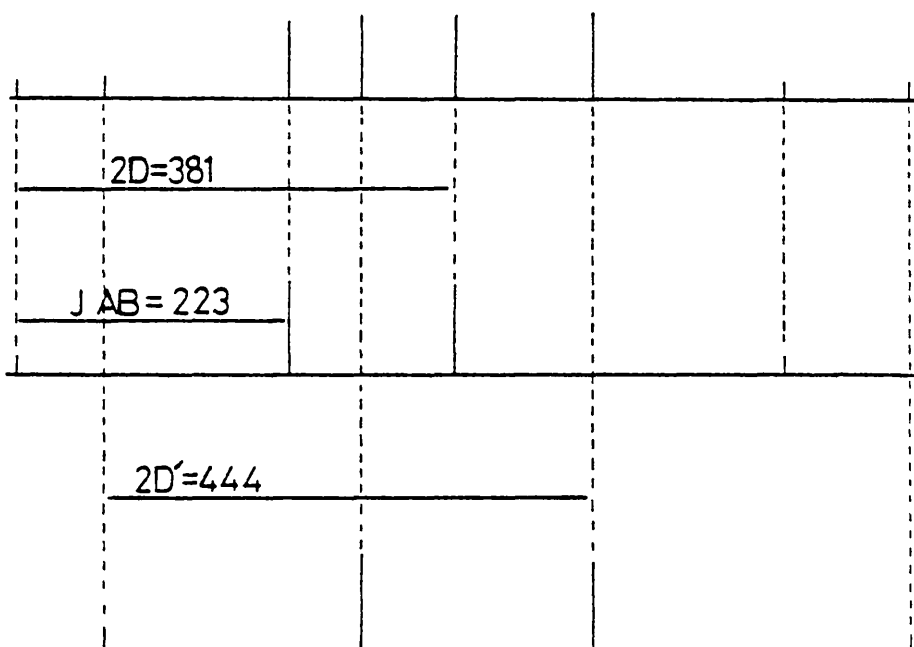
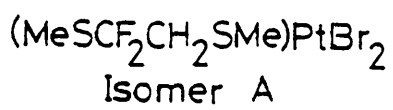


Diagram III

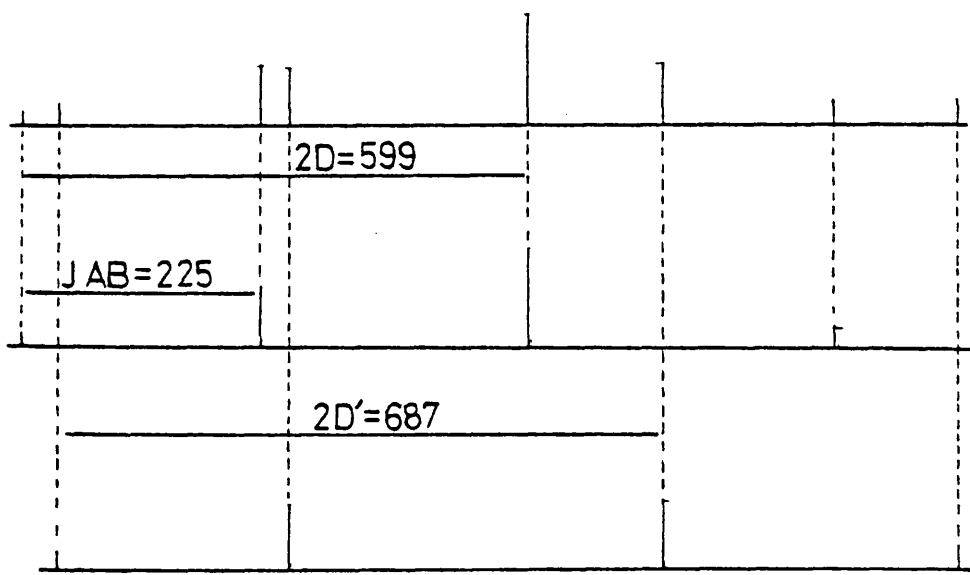
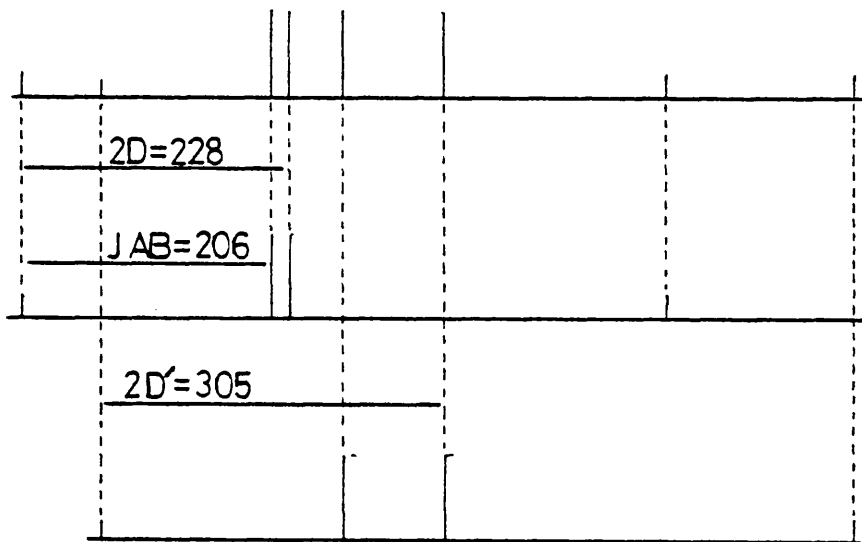
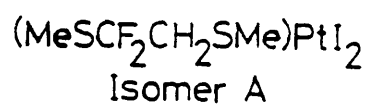


Diagram IV

is a genuine AA'X example or b) $JAX \approx JBX$ in which case the appearance of the experimental spectrum is the result of second order effects. The analysis would require the assumption that one of these situations is present but as there is no evidence to support either choice, results would be ambiguous.

APPENDIX B

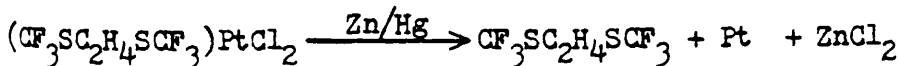
Zerovalent platinum chemistry has, so far, been mainly concerned with phosphine, mixed phosphine-carbonyl, phosphite, arsine and olefine complexes^{134,193}. Pt(0) compounds with sulphur ligand atoms are unknown to date. During the course of the present work, attempts to synthesize dithioether complexes of platinum (0) were made. Although definitive results have not yet been achieved, there are indications that zero-valent species can be prepared.

The following paragraphs describe the experimental conditions under which different reactions were carried out, and the results obtained.

Two important synthetic routes to zerovalent platinum complexes¹³⁴ are the reduction of Pt(II) compounds and the substitution of ligands in a Pt(0) species; both alternatives were utilized here. In all, four different procedures were followed:

I Reduction of a Pt(II) compound was attempted by treating

$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ with Zn/Hg amalgam. In a typical reaction, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ (0.8g, 1.6 mmol) was dissolved in the minimum amount of acetone. A four fold excess of $\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3$ (1.3g, 5.7 mmol) and Zn amalgam (1g) were added under nitrogen. The mixture was mechanically shaken and in a few minutes solid started to precipitate. After half an hour, a ^{19}F n.m.r. spectrum of the solution showed only the presence of free ligand. The reaction is probably



II. $\text{Pt}(\text{COD})_2$, COD= 1.5-cyclooctadiene, has been successfully used as starting material for the synthesis of several Pt(0) compounds by ligand substitution reactions³⁴¹. The reaction of either $\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3$ or $\text{Pr}^i\text{SC}_2\text{H}_4\text{SPr}^i$ was carried out following the procedure described by Stone and co-workers³⁴¹ for reactions with olefines and phosphines.

Typically a three-necked round bottom flask, (100cm³) containing 20 cm³ of petroleum ether (b.p. 40-60°C) was cooled to -10°C while being flushed continuously with oxygen-free nitrogen.

Bis(1,5-cyclooctadiene)platinum(0.7g, 1.7 mmol) was added in small portions, allowing each addition to dissolve. When all the complex had been added the flask was sealed with rubber stoppers and cooled to -96°C . $\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3$ (1.6g, 7 mmol) in 10 cm^3 of petroleum ether was added dropwise with a hypodermic syringe, over a period of 10 minutes. No reaction was immediately apparent and the flask was allowed to warm up slowly to room temperature.

During this last step, 3 different reactions, carried out with $\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3$, gave different products despite the precautions to maintain each experiment under similar conditions.

Analyses

Experiment	C	H	S	Cl	Colour
A	found 13.1	1.9	14.0	-	pale brown
B	found 14.0	2.0	13.9	-	pale brown
C	found 17.1	2.9	16.2	0.1	dark brown
Calculated for	14.7	1.2	19.5	-	
L_2Pt $\text{L}=\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3$					

Mass spectra for all compounds show peaks for the free ligand only.

III In a procedure similar to that used in the synthesis of $\text{Pt}(\text{COD})_2^{341}$, the reaction with $\text{Li}_2\text{C}_{10}\text{H}_8$ (dilithiumnaphthalene^h) was carried out as follows: a 100 cm^3 three-necked round-bottom flask was charged with $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$ (1g, 2 mmol) and equipped with a pressure-equalizing dropping funnel which had an external jacket to admit a coolant, a supply of dry nitrogen and a magnetic stirring bar. The apparatus was flushed with nitrogen and $\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3$ (1.9g, 8.3 mmol) in 10 cm^3 of THF added through the third neck which was then closed.

The dropping funnel was cooled to -96°C and charged with lithium (0.2g, 29 mmol) to which a solution of naphthalene (2g, 15 mmol) in THF (20 cm^3) was added and stirred for 1 hour. After this time the deep purple solution of dilithiumnaphthalene was admitted, dropwise, into

the lower flask cooled to -20°C . After the first addition, the colour disappeared immediately but it became more persistent towards the end of the reaction. The addition was stopped when the colour was no longer discharged. The flask was connected to a vacuum line and the volume of the reaction solution reduced to ca 10 cm^3 . Nitrogen was readmitted into the system and the flask cooled to -95°C when yellow crystals precipitated; the remaining solvent was transferred with a hypodermic syringe and the solid dried under vacuum at 0°C .

The yellow solid was extracted with benzene ($3 \times 10\text{ cm}^3$) and the solvent evaporated under a current of nitrogen. The final product was purified by subliming off the contaminating naphthalene under vacuum at 40°C .

Analysis

	H	C	S	Colour
Found	1.0	14.4	19.6	yellow
Calculated for L_2Pt $\text{L}=\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3$	1.2	14.7	19.5	

The yellow solid is stable to hydrolysis and is decomposed only after exposed to air for a long period.

Despite the analytical figures, ^{19}F n.m.r. spectroscopy showed the presence of at least, two species. One species produced a group of sharp singlets with platinum satellites. For the best resolved signal the platinum chemical shift was about 2500 ppm. $\text{Pt}(0)$ species are expected to have negative chemical shifts (close to -6000 ppm) and therefore the compound originating these resonances is presumably not a zerovalent complex. The second species produced a broad triplet. Measurements of platinum frequencies was not possible but on the other hand, the spectra are probably indicative of a dynamic exchange of sites presumably as a result of dissociation similar to that found in some

phosphine complexes of platinum(0).

Mass spectra showed only peaks from breakdown of the ligand. No ^Pir. absorptions were found in the 400-250 cm⁻¹ region.

IV Finally, since the compound obtained in procedure III was fairly stable, the original reduction reaction used by Venanzi¹³⁴ to prepare zerovalent compounds, was followed, thus $\text{Pr}^i\text{SC}_2\text{H}_4\text{SPr}^i$ (1.5g, 8.4 mmol) in 50 cm³ of ethanol were heated to 65°C. A solution of KOH (1g, 18 mmol) in a mixture of 15 cm³ of ethanol and 5 cm³ of H₂O was added. Then, K_2PtCl_4 (0.8g, 2 mmol) dissolved in 10 cm³ of water was added dropwise to the alkaline ligand solution, while stirring. A pale yellow compound began to separate within a few minutes of the first addition. The yellow powder was filtered, washed and dried under vacuum.

Analysis

	H	C	S
Found	6.3	34.1	23.0
Calculated for L_2Pt $\text{L} = \text{Pr}^i\text{SC}_2\text{H}_4\text{SPr}^i$	6.5	34.8	23.2

The compound is insoluble in most common solvents. It reacts with CS₂ at room temperature producing an orange compound with a composition in agreement with the formulation $(\text{Pr}^i\text{SC}_2\text{H}_4\text{SPr}^i)\text{Pt}(\text{CS}_2)$

Analysis

	H	S	C
Found	3.6	28.3	24.1
Calculated for L_2Pt $\text{L} = \text{Pr}^i\text{SC}_2\text{H}_4\text{SPr}^i$	4.0	28.5	24.0

EXPERIMENTAL

EXPERIMENTAL

Preparation of Ligands.

Reagents. The commercially available reagents used in this work and their suppliers are listed below. Purity was checked against data reported on the reference following the reagent's formula; when purification was judged to be necessary, the method employed is also listed.

<u>Reagent</u>	<u>Supplier</u>	
$\text{CF}_3\text{C}\equiv\text{CCF}_3$ ⁹⁷	Fluorochem. Ltd.	
$\text{CF}_3\text{C}\equiv\text{CH}$ ³²¹	"	
$\text{CF}_2=\text{CH}_2$ ³²²	"	
HgF_2	"	
$\text{C}_6\text{F}_5\text{SH}$ ³²³	"	
$\text{CH}_3\text{C}\equiv\text{CCH}_3$ ³²⁴	Matheson Co. Ltd.	Vacuum distillation
$\text{CH}_2=\text{CH}_2$ ³²⁵	"	
CH_3SH ³²⁶	"	
$\text{CH}_3\text{C}\equiv\text{CH}$ ³²⁴	"	
CS_2 ³²⁷	BDH Chemicals Ltd.	
$\text{Pb}(\text{CH}_3\text{COO})_2$	"	
$\text{BrCH}_2\text{CH}_2\text{Br}$ ³²⁸	"	
CCl_3SCl ³²⁹	"	Distillation
NaF	"	
CH_3SSCH_3 ³²⁶	Fluka A.G.	Distillation
Br_2	Hopkin and Williams	
$\text{ClCH}_2\text{CH}_2\text{OH}$ ^{330, 331}	Gen. Chem. and Pharm. Reagents Co. Ltd.	Distillation

Other intermediates were prepared according to published syntheses as follows:

$\text{CF}_3\text{SCH}_2\text{CH}_2\text{Cl}$ ³⁹; $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH}$ ³³⁰; $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Cl}$ ³³²; $\text{BrCF}_2\text{CH}_2\text{Br}$ ³³³; CF_2CHBr ³³⁴; CF_3SCl ⁵⁰; $\text{Pb}(\text{SCF}_3)_2$ ³³⁷; $\text{Hg}(\text{SCF}_3)_2$ ⁴⁴.

Hydrocarbon solvents were dried over sodium and distilled under nitrogen before use. Other solvents were purified and dried by standard methods³³⁵.

Experimental methods.

Volatile materials were transferred by conventional high vacuum techniques using a Pyrex glass vacuum line fitted with an 'Edwards high vacuum' two stage rotary oil pump and 'Jencons' mercury diffusion pump arranged in series. Standard glass joints were greased with 'Edwards' high vacuum silicone grease. P.T.F.E. or glass stopcocks were used when required.

Vacuum distillations were performed with continuous pumping.

Photolytic reactions were carried out in quartz reaction vessels fitted with P.T.F.E. stopcocks and irradiated by a Hanovia medium pressure mercury lamp, emitting predominantly 254 mμ, 265 mμ, 297 mμ, 313 mμ, and 366 mμ wavelengths.³²⁶

All other reactions were carried out under an atmosphere of dry, oxygen-free nitrogen.

Boiling points correspond to the purest fraction on fractional distillations carried out in semi-micro apparatus and are uncorrected. Elemental analysis were carried out by Mrs. W. Harkness, microanalyst University of Glasgow or by A. Bernhardt, Mikroanalytisches Laboratorium, West Germany.

Infra-red spectra were recorded from neat liquid films between KBr plates or as KBr discs of solid compounds. Spectra were recorded over the range 4000-200 cm^{-1} on a Perkin-Elmer PE-577 or a

Perkin-Elmer PE-225 Spectrophotometers. Spectra were calibrated against polyethylene film. The following abbreviations have been used in the text: s, strong; m, medium; w, weak; sh, shoulder; b, broad; v, very; ν , stretch.

N.m.r. spectra were recorded on a Varian Ha-100 instrument at a frequency of 100 MHz for ^1H and 94.1 MHz for ^{19}F . Double irradiation experiments were performed using the integrated spin decoupling of the instrument; triple resonance experiments were carried out with a Schomandl frequency synthesizer ND 100M. Variable temperature data were recorded directly and are assumed to be accurate to $\pm 10^\circ\text{C}$. Alternatively n.m.r. spectra were recorded on a JEOL C-60HL spectrometer operating at a frequency of 60MHz for ^1H and 56.4 MHz for ^{19}F . In the latter case, chemical shifts were measured from the smallest possible scan width with an accuracy of ± 1 ppm. The variable temperature controller unit on the JEOL instrument was calibrated by standard methanol and ethylene glycol techniques³³⁸. Samples were examined as neat liquids or for solid compounds as d_6 -acetone solutions.

$\text{Si}(\text{CH}_3)_4$, (TMS) and CCl_3F were used as external or internal references as indicated in the text.

Mass spectra were obtained using an A.E.I.M.S. 12 spectrometer. Volatile samples were admitted as gases directly into the electron beam; involatile samples were introduced into the electron beam on a ceramic probe at temperatures between 100 and 280°C . Molecular weights were determined by mass spectrometry.

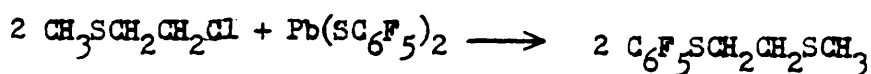
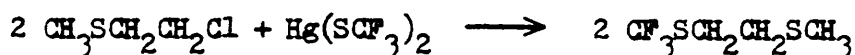
Summary of reactions

Preparation of $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SR}$ $\text{R}=\text{CF}_3$ or C_6F_5

Method A



Method B

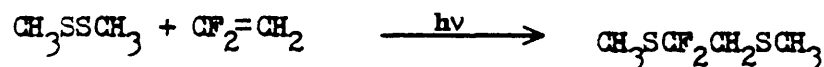


Preparation of $\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SC}_6\text{F}_5$



Preparation of $\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3$

Method A



Method B



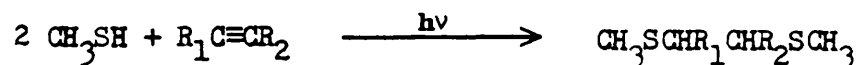
Preparation of $\text{CH}_3\text{SCHR}_1\text{CHR}_2\text{SCH}_3$

a) $\text{R}_1=\text{R}_2=\text{CF}_3$

b) $\text{R}_1=\text{R}_2=\text{CH}_3$

c) $\text{R}_1=\text{CF}_3$, $\text{R}_2=\text{H}$

d) $\text{R}_1=\text{CH}_3$, $\text{R}_2=\text{H}$



Data of the compounds prepared by the methods described below are shown in the following tables: melting or boiling points and analyses, table 25; infrared data, table 26; mass spectrometry data, table 27; ^1H chemical shifts, table 28; ^{19}F chemical shifts, table 29; spin-spin coupling constants, table 30.

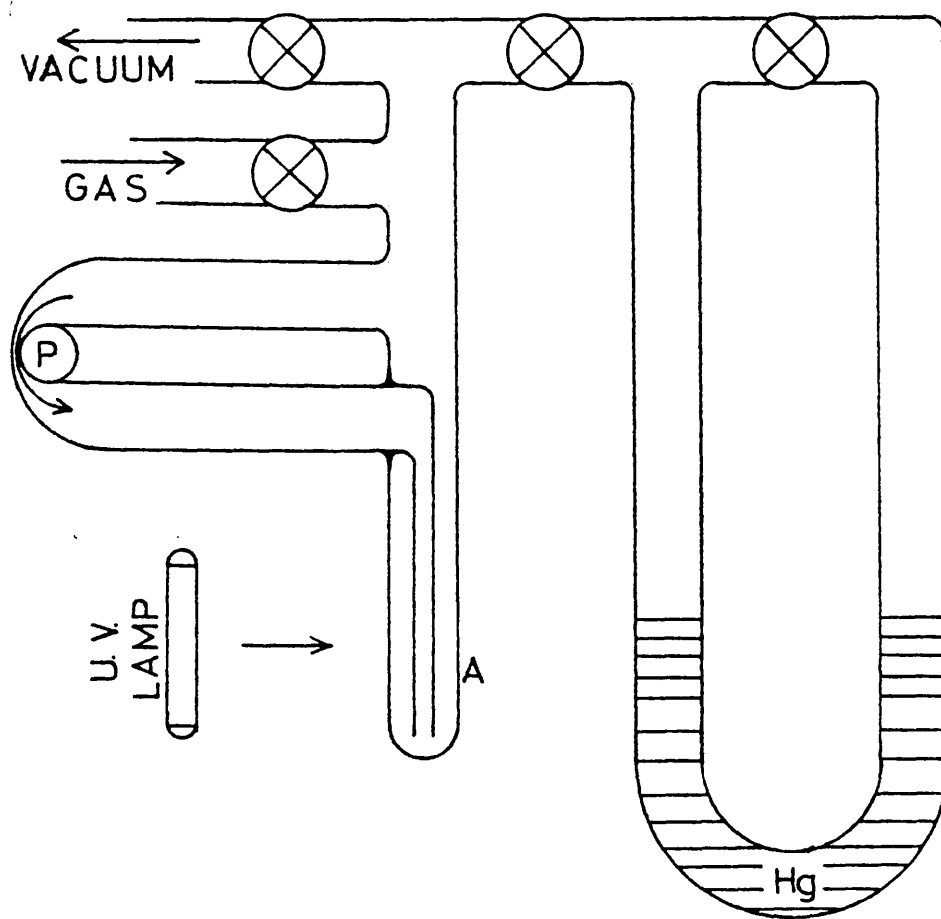
Preparation of $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$. Method A. $\text{CF}_3\text{SCH}_2\text{CH}_2\text{Cl}$ (2g, 12.2 mmol) and NaSCH_3 (1.70g, 24.3 mmol) in 20 ml. of benzene were refluxed for 16 hrs.. The excess NaSCH_3 and the precipitated NaCl were filtered off and washed with 20 ml. of benzene. The solvent was pumped off at 268°K and the remaining liquid distilled under reduced pressure producing $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ (1.13g, 12mmol) in 53% yield. Method B. $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Cl}$ (3g, 27 mmol) and $\text{Hg}(\text{SCF}_3)_2$ (5.5g, 13.6 mmol) were refluxed; white HgCl_2 slowly precipitated out of the liquid reactants. After 24 hrs. the reaction mixture was cooled and filtered, the precipitate washed with 20 ml. of diethyl ether. HCl was bubbled into the ether solution to remove any unreacted $\text{Hg}(\text{SCF}_3)_2$ (which would co-distil with the product) and the solution was refiltrated. Ether was evaporated under a current of nitrogen and the remaining liquid distilled under reduced pressure to give $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ (4g, 22.7 mmol) in 84% yield.

Preparation of $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCF}_5$. To $\text{Pb}(\text{SC}_6\text{F}_5)_2$ (5.5g, 9 mmol) suspended in 20ml. of benzene $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Cl}$ (2g, 18.2 mmol). was added. The reaction proceeds slowly at room temperature but at 353K the reaction was complete within one hour. The extent of the reaction is easily followed by the progressive disappearance^a of the bright yellow colour of $\text{Pb}(\text{SC}_6\text{F}_5)_2$. The reaction mixture was filtered, the solvent pumped off at 268 K and the liquid distilled under vacuum giving $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SC}_6\text{F}_5$ (3.5g, 13.1 mmol), 73% yield.

Preparation of $\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SC}_6\text{F}_5$. $\text{BrCH}_2\text{CH}_2\text{Br}$ (1g, 5.3 mmol) and HSC_6F_5

(2.2g, 11 mmol) in 20 ml. of ethanol were heated to ca 313 K. To this mixture, a solution of NaOH (0.5g, 10.7 mmol) in hot ethanol was added dropwise and immediately a white precipitate was formed. After the addition was completed all volatile solvents were distilled off under vacuum at room temperature and the solid extracted 3 times with 15 ml. of benzene. Fractional crystallisation from the benzene solution produced the white solid $C_6F_5SC_2H_4SC_6F_5$, (1.99g, 4.67 mmol) in 87% yield.

Preparation of $CH_3SCF_2CH_2SCH_3$. Method A. The apparatus used for the reaction is shown on the following diagram.



5 ml. of CH_3SSCH_3 were condensed under vacuum on the quartz finger A and allowed to warm to room temperature. CF_2CH_2 was admitted to the system until the internal pressure was ca 1.5 atms.. A peristaltic (P) pump was used to bubble the gas in the liquid. The liquid phase was

irradiated for 27 days and during this period the internal pressure dropped to 1.1 atms.. The reaction mixture was then vacuum distilled and $\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3$ (0.69g, 4.36 mmol.) was retained in a trap cooled to 213 K. Method B. CHBrCF_2 (3g, 21.1 mmol), CH_3SH 81g, 20.8 mmol) and 5 ml. of 2×10^{-2} M sodium hydroxide solution were vigorously shaken for 24 hrs. The aqueous layer was then separated and the reaction mixture distilled under vacuum to produce $\text{CH}_3\text{SCF}_2\text{CH}_2\text{Br}$ (3.7g, 19.47 mmol) in 92.5% yield. The sulphide was refluxed in 10 ml. of ethanol and NaSCH_3 (2g, 28.5 mmol) in 10 ml. of ethanol was added dropwise over 20 minutes. The reaction mixture was stirred continuously and a white precipitate appeared soon after the first addition. After the addition was complete the reaction mixture was cooled and filtered, the precipitate was washed with 10 ml. of ethanol. The solvent was distilled off under reduced pressure (water pump) to yield a white paste that was washed with diethyl-ether (30 ml.). The solvent was evaporated under a current of nitrogen and the remaining liquid distilled under vacuum to produce $\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3$ (2.7g, 17 mmol) in 88% yield.

Addition of CH_3SH to acetylenes. The reactions of CH_3SH with $\text{CF}_3\text{C}\equiv\text{CCF}_3$, $\text{CF}_3\text{C}\equiv\text{CH}$, $\text{CH}_3\text{C}\equiv\text{CCH}_3$ and $\text{CH}_3\text{C}\equiv\text{CH}$ were all carried out similarly. A 3:1 excess of CH_3SH (typically 40 mmol) and the corresponding acetylene were condensed in a quartz vessel and irradiated until the internal pressure was constant. Time of reaction and yields are shown in table 24.

Table 24

Times of irradiation and yields for the reaction of CH_3SH and acetylenes

Acetylene	Time of reaction hrs.	Yield %
$\text{CF}_3\text{C}\equiv\text{CCF}_3$	24	95
$\text{CF}_3\text{C}\equiv\text{CH}$	14	96
$\text{CH}_3\text{C}\equiv\text{CCH}_3$	16	98
$\text{CH}_3\text{C}\equiv\text{CH}$	12	98

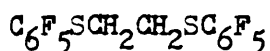
Volatiles were pumped off from the reaction vessel cooled to 263 K and the remaining liquids distilled under vacuum.

Table 25

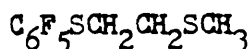
Analyses

Compound	b.p./mp. K Torr	Found		
		C	H	S
$\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{CF}_6\text{F}_5$	140-141 760	39.6 39.4	1.1 0.9	15.1 15.0
$\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SCH}_3$	353-354 12	39.3 39.4	2.7 2.5	23.1 23.4
$\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$	333-335 32	27.0 27.2	4.2 4.0	36.1 36.4
$\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3$	348-349 25	30.3 30.3	5.1 5.0	40.5 40.6
$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$	352-353 29	27.6 27.9	3.3 3.1	24.7 24.8
$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3$	351-353 18	31.4 31.6	4.6 4.7	33.8 33.7
$\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3$	363-364 31	47.9 48.0	9.2 9.3	42.5 42.7
$\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3$	357-358 20	44.0 44.1	8.8 8.8	47.3 47.1

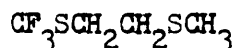
Table 26

i.r. data (cm^{-1})

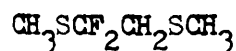
1639, s; 1624, w; 1517, vs; 1476, vs, br;
 1421, m; 1397, w; 1376, w; 1294, w; 1213, m;
 1132, w; 1094, vs; 1028, w; 977, vs; 970, vs;
 866, vs; 746, w; 726, w; 685, w; 639, w;
 321, w; 313, w.



2976, w; 2922, m; 2838, w; 1637, s; 1625, m, sh;
 1507, vs; 1483, vs; 1436, s, sh; 1426, s; 1400, w;
 1370, w; 1354, w; 1320, w; 1290, m; 1263, m;
 1204, s; 1141, w; sh; 1127, m; 1089, vs; 1014, m;
 977, vs; 912, w; 861, vs; 730, w; 719, w; 681, m;
 627, w; 513, w.



2975, w; 2919, m; 2835, w; 1425, s; 1321, w;
 1293, w; 1273, m; 1214, s; 1157, vs, br; 1127, vs,
 sh, br; 1108, vs, br; 1014, w; 993, w; 952, w;
 909, w; 841, w; 754, s; 722, w; 685, w; 460, m.

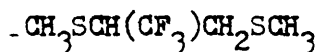


2990, w, br; 2928, m; 2864, w; 2836, w; 1590, w, br;
 1437, s; 1424, s; 1401, m; 1323, m; 1269, m;
 1224, s; 1209, m, sh; 1160, vs, br; 995, vs, br;
 960, vs, br; 874, w; 836, m; 815, w; 791, m, br;
 756, w, sh; 748, m; 712, w; 697, w; 631, w; 566, m;
 549, w; 535, w; 441, w.

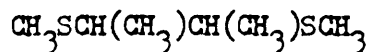
Table 26 Contd.

$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$	2996, w; 2931, w; 1625, w; 1435, m; 1429, m; 1351, s; 1321, s; 1260, vs, sh; 1239, s; 1227, s; 1202, s; 1156, vs; 1104, vs; 1047, w; 959, w, br; 881, w; 851, w; 809, w; 798, w; 758, w; 711, w; 690, w; 661, m; 640, m; 622, m; 529, w; 510, w.
$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3$	2981, m; 2920, s; 2837, w; 1620, w; 1567, w; 1424, s; 1330, vs; 1320, vs; 1276, vs; 1242, vs; 1205, s; 1170, vs; 1138, vs; 1101, vs; 1045, m; 978, s; 960, s; 890, m; 851, w; 838, m; 769, w; 742, w; 705, w; 695, w; 660, s; 560, w; 533, w; 437, w.
$\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3$	2970, vs; 2919, vs; 2858, m; 2835, w; 1443, s; 1435, s; 1422, s; 1371, w; 1317, w; 1306, w; 1240, w; 1213, m; 1189, w; 1179, w; 1101, m; 1078, w; 1059, m; 1001, w; 952, s, br; 844, w; 722, w; 663, w; 641, w; 562, w.
$\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3$	2968, vs; 2919, vs; 2864, s; 2836, s; 1430, vs, sh; 1371, vs; 1318, m; 1261, m; 1243, m; 1223, m; 1181, s, sh; 1101, m; 1063, m; 1016, m; 956, s; 890, w; 844, w; 819, w; 747, w; 722, w; 689, w; 672, m, sh; 651, w.
$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$	2996, w; 2931, w; 1435, m; 1429, m; 1351, s; 1321, s; 1260, vs; 1239, s; 1227, s; 1202, s; 1156, vs; 1104, vs; 661, m; 640, m; 622, m.

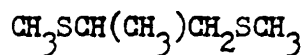
Table 26 Contd.



2981, m; 2920, s; 2837, w; 1424, s; 1330, vs;
1320, vs; 1276, vs; 1242, vs; 1205, s; 1170, vs;
1138, vs; 1101, vs; 1045, m; 978, s; 960, s;
660, s.



2970, vs; 2919, vs; 2858, s; 2835, m; 1443, s;
1435, s; 1422, s; 1371, s; 1317, m; 1213, m;
1101, m; 1059, m; 952, s.



2968, vs; 2919, vs; 2864, s; 2836, s; 1430, vs, sh;
1371, vs; 1318, m; 1261, m; 1243, m; 1223, m;
1181, s, sh; 1101, m; 1063, m; 1016, m; 956, s;
672, m, sh.

Table 27

Mass Spectra data

(compound, m/e, intensity %, assignment.)

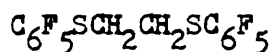
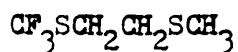
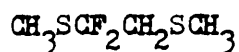
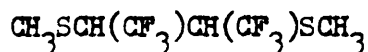
426, 22, $\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SC}_6\text{F}_5$ 227, 100, $\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2$ 213, 8, $\text{C}_6\text{F}_5\text{SCH}_2$ 199, 59, $\text{C}_6\text{F}_5\text{S}$ 155, 8, $(\text{C}_6\text{F}_5-\text{C})$ 274, 42, $\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SCH}_3$ 227, 8, $\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2$ 213, 16, $\text{C}_6\text{F}_5\text{SCH}_2$ 199, 55, $\text{C}_6\text{F}_5\text{S}$ 75, 100, $\text{CH}_3\text{SCH}_2\text{CH}_2$ 61, 39, CH_3SCH_2 47, 32, CH_3S 176, 98, $\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$ 129, 33, $\text{CF}_3\text{SCH}_2\text{CH}_2$ 115, 10, CF_3SCH_2 107, 17, $\text{CH}_3\text{SCH}_2\text{CH}_2\text{S}$ 75, 73, $\text{CH}_3\text{SCH}_2\text{CH}_2$ 69, 57, CF_3 61, 100, CH_3SCH_2 47, 64, CH_3S

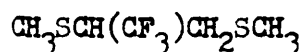
Table 27 , Contd.



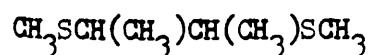
158, 40, $\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3$
 111, 19, $\text{CH}_3\text{SCF}_2\text{CH}_2$ / $\text{CH}_3\text{SCH}_2\text{CF}_2$
 97, 9, CH_3SCF_2
 64, 7, CF_2CH_2
 61, 100, CH_3SCH_2
 47, 54, CH_3S



258, 50, $\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$
 211, 93, $\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)$
 129, 100, $\text{CH}_3\text{SCH}(\text{CF}_3)$
 95, 4, $\text{CH}(\text{CF}_3)\text{CH}$
 69, 4, CF_3
 47, 7, CH_3SH



190, 51, $\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3$
 143, 21, $\text{CH}(\text{CF}_3)\text{CH}_2\text{SCH}_3$
 129, 6, $\text{CH}_3\text{SCH}(\text{CF}_3)$
 96, 3, $\text{CH}(\text{CF}_3)\text{CH}_2$
 69, 3, CF_3
 61, 100, CH_3SCH_2
 47, 12, CH_3S



150, 49, $\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3$
 103, 25, $\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)$
 75, 100, $\text{CH}_3\text{SCH}(\text{CH}_3)$
 55, 30, $\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)$
 47, 3, CH_3S

Table 27, Cont.

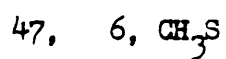
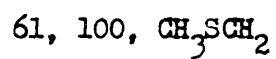
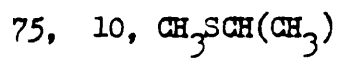
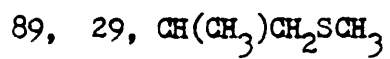
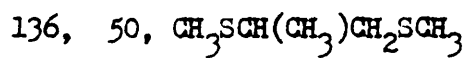
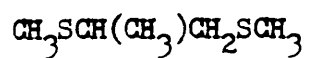


Table 28

Nuclear Magnetic Resonance Parameters

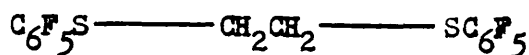
 ^1H Chemical Shifts^a / multiplicity: s singlet

d doublet

t triplet

m multiplet

br broad



3.41

s

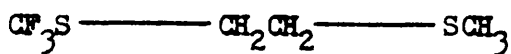


3.35

2.56

m

s



3.5

2.62

m

s



2.78

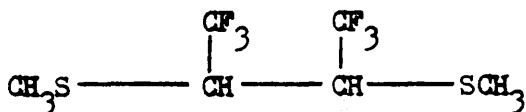
3.72

2.87

s, br

t

s



meso

2.88

4.17

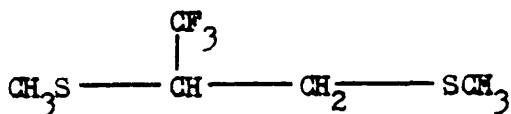
s

m

 \pm

2.83

s



2.77

3.87

3.46

2.71

s, br

m

m

s

Table 28, continued.

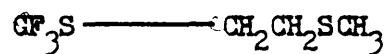
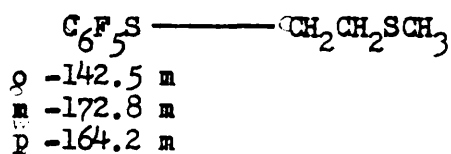
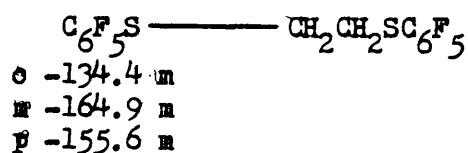
meso	1.56	$ \begin{array}{ccccccc} & & \text{CH}_3 & & \text{CH}_3 & & \\ & & & & & & \\ & & \text{CH} & - & \text{CH} & - & \text{SCH}_3 \\ \text{CH}_3\text{S} & - & & & & - & \end{array} $		
d				
(+)	1.43			
d				
meso	2.31	3.00		
s		m		
(±)	1.90			
s				
	1.77	$ \begin{array}{ccccccc} & & \text{CH}_3 & & & & \\ & & & & & & \\ & & \text{CH} & - & \text{CH}_2 & - & \text{SCH}_3 \\ \text{CH}_3\text{S} & - & & & & - & \end{array} $		
d				
	2.52	3.12	2.54	
s		m	s	

a) ppm from external TMS.

Table 29

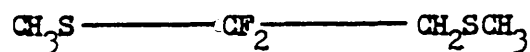
Nuclear Magnetic Resonance Parameters

¹⁹F Chemical Shifts^a /multiplicity: s singlet
 d doublet
 t triplet
 m multiplet
 br broad



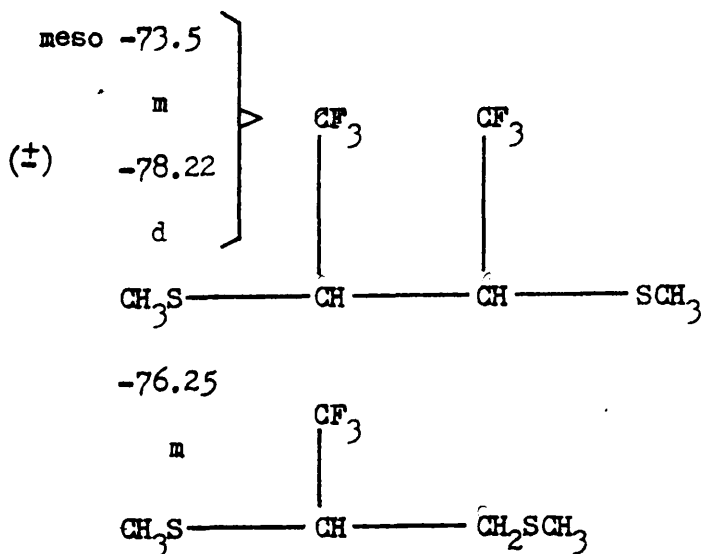
-43.2

s, br



-80.7

t



a) ppm positive to low field of external CCl_3F .

Table 30

Parameters of Nuclear Magnetic Resonance Spectra

Coupling Constants. Hz.

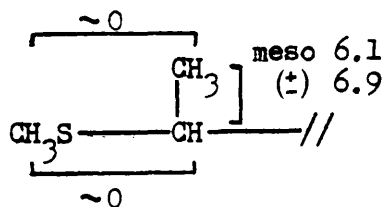
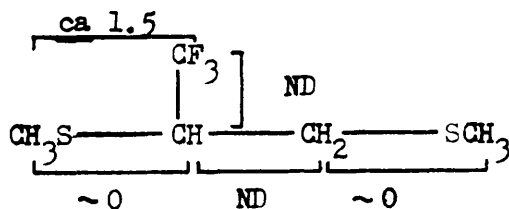
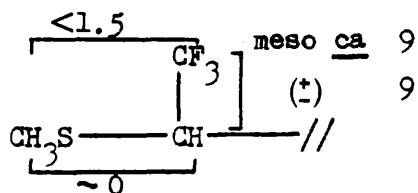
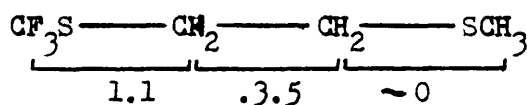
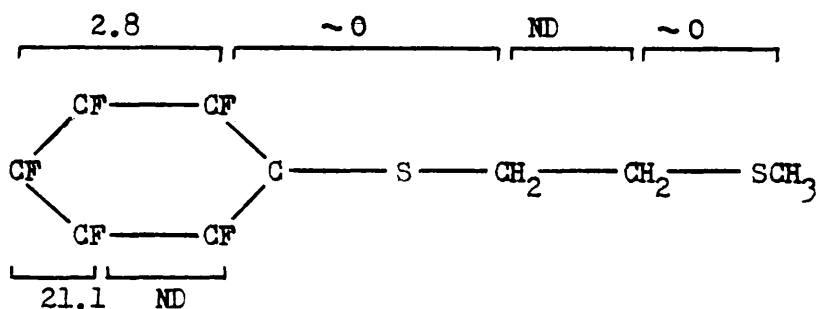
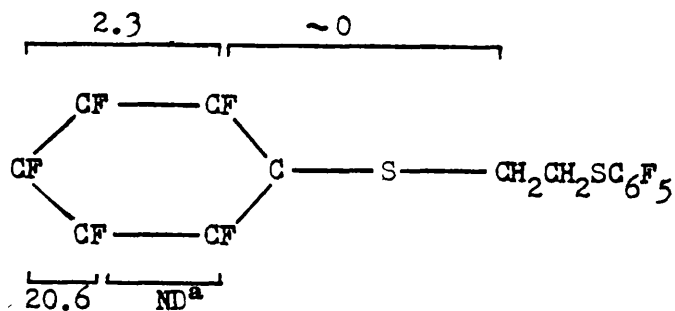
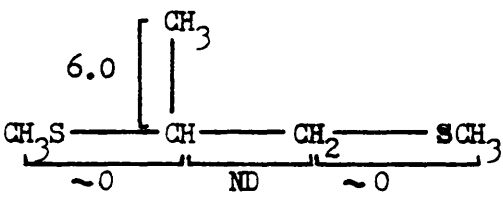


Table 30, continued.



a) ND: not determined

Preparation of platinum and palladium complexes.

Reagents. K_2PtCl_4 and H_2PtCl_6 from Johnson Matthey Chem. Ltd.

and KBr and KI from B.D.H. Ltd. were used as supplied. K_2PtCl_4 and K_2PdCl_4 from Research Organic-Inorganic Chemical Corp. were contaminated with K_2MCl_6 and were recrystallised from aqueous solutions before use.

Na_2PtCl_4 was prepared by reduction of Na_2PtCl_6 ³³⁹. Dithioethers used as ligands were prepared as described in the previous section or by published syntheses as follows: $CF_3SCH_2CH_2SCF_3$ ³⁷; $CF_3SCH(CH_3)CH_2SCF_3$ ³⁷.

Experimental methods. Were as described in the preceding section.

Preparation of complexes. The preparation of all complexes was very similar differing only in the solvents, relative proportion of reactants, and temperatures. In each case, the first preparation was carried out under anhydrous conditions and under nitrogen. Na_2MCl_4 (M=Pt or Pd) was used in these preparations since both salts are soluble in alcohols. The complexes however were found to be stable to oxidation and hydrolysis at ambient conditions and subsequent preparations were carried out using K_2MCl_4 (M=Pt or Pd) and aqueous-ethanolic solutions which produce higher yields.

A typical example is described below and conditions for other reactions are listed in table 31. The bromide and iodide derivatives were obtained by metathetical reaction of the appropriate chloro-complex with a large excess of KBr or KI in acetone.

Preparation of $(CF_3SCH_2CH_2SCF_3)_2PtCl_2$. K_2PtCl_4 (0.8g, 1.9 mmol) was dissolved in 25 ml. of water and 20 ml. of ethanol added.

$CF_3SCH_2CH_2SCF_3$ (0.5g, 2.1 mmol) in 5 ml. of ethanol was added to the solution. No immediate reaction occurred but the colour of the solution slowly changed from red to yellow with deposition of crystals. After 24 hrs. bright yellow crystal of $(CF_3SCH_2CH_2SCF_3)_2PtCl_2$ (0.7g, 1.4 mmol) deposited in 70% yield and were filtered and washed with cold ethanol and dried under vacuum at room temperature for 2 hrs., the complex

obtained gave a satisfactory analysis without further purification.

$(\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ + KBr. This reaction was carried out in n.m.r. tubes in order to follow the effect of increasing the concentration of KBr, relative to that of the complex on the ^{19}F n.m.r. resonances of the reaction products.

1.5 ml. of 0.1 M solution of $(\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCF}_3)\text{PtCl}_2$ in acetone were placed in a n.m.r. tube and 3 ml. of 0.1 M solution of KBr in 1:1 aqueous-acetone were added in 20 additions of 0.15 ml. At least 10 minutes were allowed between each addition of KBr and several spectra run, to ensure equilibration of the reaction mixture, before a final spectrum was recorded. The solution slowly changed colour from clear yellow to orange as the concentration of KBr increased.

Table 31

PREPARATION OF COMPLEXES

N_2PtCl_4 Solvent	m mols ml	ligand Solvent	m mols ml	Conditions	Product	Yield %
Na_2PtCl_4	1.9	$CF_3SC_2H_4SCF_3$	2.0	standing 24 hrs.	$(CF_3SC_2H_4SCF_3)_2PtCl_2$	43
C_2H_5OH	25	C_2H_5OH	25			
K_2PtCl_4	1.9	$CF_3SC_2H_4SCF_3$	2.1	standing 24 hrs.	$(CF_3SC_2H_4SCF_3)_2PtCl_2$	70
H_2O/C_2H_5OH	25/20	C_2H_5OH	5			
Na_2PtCl_4	2.0	$CF_3SCH(CH_3)CH_2SCF_3$	2.0	standing 24 hrs.	$(CF_3SCH(CH_3)CH_2SCF_3)_2PtCl_2$	47
C_2H_5OH	25	C_2H_5OH	25			
K_2PtCl_4	2.0	$CF_3SCH(CH_3)CH_2SCF_3$	2.0	standing 24 hrs.	$(CF_3SCH(CH_3)CH_2SCF_3)_2PtCl_2$	71
H_2O/C_2H_5OH	25/20	C_2H_5OH	25			
K_2PtCl_4	2.1	$C_6F_5SC_2H_4SCF_5$	2.1	standing 48 hrs. evaporate solvent	$(C_6F_5SC_2H_4SCF_5)_2PtCl_2$	78
$H_2O/acetone$	25/40	acetone	20	acetone extraction		
K_2PtCl_4	4.0	$CF_3SC_2H_4SCH_3$	2.4	two liquid phases stirred 24 hrs.	$(CF_3SC_2H_4SCH_3)_2PtCl_2$	63
H_2O	35	acetone	5			
K_2PtCl_4	2.1	$CH_3SC_2H_4SCF_3$	6.1	two liquid phases stirred 24 hrs.	ois, trans $(CH_3SC_2H_4SCF_3)_2PtCl_2$	66
H_2O	25	acetone	5			

Table 31, Continued.

N_2PtCl_4 Solvent	m mols		ligand		m mols ml	Conditions	Product	Yield %
	ml		Solvent					
K_2PtCl_4 H_2O	4.3 35		$CH_3SC_2H_4SC_6F_3$ acetone		2.0 5	two liquid phases stirred 24 hrs.	$(CH_3SCH_2CH_2SC_6F_5)PtCl_2$	161
K_2PtCl_4 H_2O	2.2 25		$CH_3SC_2H_4SC_6F_5$ acetone		5.9 5	two liquid phases stirred 24 hrs.	cis, trans $(CH_3SCH_2CH_2SC_6F_5)_2PtCl_2$	62
K_2PtCl_4 H_2O/C_2H_5OH	2.0 25/20		$CH_3SCF_2CH_2SCH_3$ C_2H_5OH		2.1 5	standing 24 hrs.	$(CH_3SCF_2CH_2SCH_3)PtCl_2$	79
K_2PtCl_4 H_2O	2.1 25		$CH_3SCH(CF_3)CH_2SCH_3$ acetone		2.2 5	two liquid phases	$(CH_3SCH(CF_3)CH_2SCH_3)PtCl_2$	81
K_2PtCl_4 H_2O	2.2 25		$CH_3SCH(CF_3)CH(CF_3)SCH_3$ acetone		2.2 25	two liquid phases stirred 24 hrs.	$(CH_3SCH(CF_3)CH(CF_3)SCH_3)PtCl_2$	81
K_2PtCl_4 H_2O	2.1 25		$CH_3SCH(CH_3)CH_2SCH_3$ acetone		2.2 5	pink precipitate initially formed Refluxed for 8 hrs Precipitate filtered	$(CH_3SCH(CH_3)CH_2SCH_3)PtCl_2$	76
K_2PtCl_4 H_2O	2.1 25		$CH_3SCH(CH_3)CH(CH_3)SCH_3$ acetone		2.1 5	pink precipitate initially formed Refluxed for 8 hrs Precipitate filtered	$(CH_3SCH(CH_3)CH(CH_3)SCH_3)PtCl_2$	81

Table 32

COMPOUND	COLOUR	ANALYSES				
		C	H	S	X	M
$\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$	Yellow	9.7	0.85	12.9	14.3	496
PtCl_2		9.7	0.80	12.9	14.3	496
PtBr_2	Yellow	8.4	0.70	27.0	11.2	585
		8.2	0.68	27.3	11.0	585
$\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3$	Yellow	11.7	1.2	12.5	13.8	510
PtCl_2		11.7	1.2	12.6	13.9	510
PtBr_2	Yellow	9.6	0.82	10.0	25.4	599
		10.0	1.0	10.7	26.6	599
$\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$	Yellow	10.9	1.60	14.7	16.0	442
PtCl_2		10.9	1.58	14.5	16.0	442
$(\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCH}_3)_2$	Yellow	15.6	2.31	20.4	11.2	618
PtCl_2		15.5	2.26	20.7	11.5	618
$(\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCH}_2\text{PdCl}_2)_2$	Orange-Red	13.9	2.1	18.4	19.7	706
		13.6	2.0	18.2	20.0	706
$\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SCF}_5$	Yellow	24.5	0.61	9.6	10.2	692
PtCl_2		24.3	0.57	9.3	10.2	692
$\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SCF}_5$	Yellow	21.7	0.73	8.5	20.6	781
PtBr_2		21.5	0.51	8.2	20.5	781
PtI_2	Yellow-Brown	19.4	0.76	7.1	29.3	
		19.2	0.45	7.3	29.0	875

Table 32, continued.

COMPOUND	COLOUR	ANALYSES					
		d	H	Found			M
				S	X		
$\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SCH}_3$	Yellow	20.2	1.5	11.8	13.8	540	
		20.0	1.3	11.9	13.1	540	
	Yellow	17.4	1.13	10.2	25.6	629	
		17.2	1.11	10.2	25.4	629	
$(\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SCH}_3)_2$	Yellow	26.6	1.63	16.0	8.9	814	
		26.5	1.72	15.8	8.7	814	
	Yellow	24.2	1.74	14.5	17.8	903	
		23.9	1.55	14.2	17.7	903	
	Yellow-Brown	21.6	1.57	12.6	25.3		
		21.7	1.40	12.8	25.4	997	
$(\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SCH}_3)_2$	Orange-Red	30.0	2.09	17.9	10.1	725	
		29.8	1.93	17.7	9.8	725	
	Red	26.7	1.58	15.6	19.8	814	
		26.5	1.72	15.7	19.6	814	
	Violet	23.8	1.37	14.3	27.7		
		23.8	1.54	14.1	28.0	908	

Table 32, Continued.

COMPOUND	COLOUR	ANALYSES				
		Found		Calculated		
		C	H	S	X	M
$\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3$	PtCl_2	11.1	1.69	15.3	16.9	424
		11.3	1.88	15.1	16.7	424
	PtBr_2	9.3	1.38	12.4	31.1	513
		9.4	1.55	12.5	31.1	513
	PtI_2	8.3	1.35	10.5	42.2	
		7.9	1.31	10.6	41.8	607
	PdCl_2	14.5	2.15	19.2	21.3	335
		14.3	2.38	19.1	21.1	335
	PdBr_2	11.3	2.01	15.2	37.6	424
		11.3	1.88	15.1	37.7	424
$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$	PdI_2	9.2	1.50	12.6	48.8	
		9.3	1.54	12.4	49.0	518
	PtCl_2	13.7	1.52	13.5	12.2	524
		13.9	1.7	13.0	12.8	524
	PtBr_2	11.7	1.30	26.1	10.5	613
		11.6	1.5	26.0	10.6	613
	PtI_2	10.2	1.13	35.9	9.1	
		10.4	1.2	36.6	9.5	707
	PdCl_2	16.5	1.87	16.3	14.7	435
		16.6	1.9	16.6	15.0	435
$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3$	PdBr_2	13.7	1.52	30.5	12.2	524
		13.9	1.7	30.2	12.5	524
	PdI_2	11.6	1.29	41.0	10.4	
		11.3	1.5	39.8	10.8	618

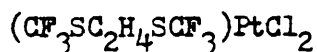
Table 32, Continued.

COMPOUND	COLOUR	ANALYSES					
		C	H	Found			M
				S	X		
$\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3$	PtCl_2	Yellow	13.2	1.97	14.1	15.5	456
			13.4	2.2	14.3	15.6	456
	PtBr_2	Yellow-Brown	11.0	1.65	11.8	29.3	545
			11.3	1.7	12.0	30.0	545
	PtI_2	Brown	9.4	1.40	10.0	39.7	
			9.6	1.6	11.0	40.7	639
	PdCl_2	Yellow	16.3	2.44	17.5	19.3	367
			16.6	2.6	17.5	19.4	367
	PdBr_2	Orange	13.1	1.97	14.1	35.0	456
			13.2	2.0	14.0	34.6	456
PdI_2	Violet	10.9	1.63	11.7	46.1		
			11.0	1.9	11.7	45.8	550
$\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3$	PtCl_2	Yellow	17.3	3.36	15.4	17.0	416
			17.2	3.8	15.0	17.2	416
	PtBr_2	Yellow-Brown	14.3	2.77	12.7	31.6	505
			14.2	2.6	12.5	30.1	505
	PtI_2	Brown	12.0	2.33	10.7	42.4	
			12.0	2.3	10.9	42.5	599
	PdCl_2	Yellow	22.0	4.27	19.6	21.7	327
			22.1	4.1	19.5	21.6	327
	PdBr_2	Orange	17.3	3.36	15.4	38.4	416
			17.6	3.3	15.9	38.0	416
PdI_2	Violet	11.6	1.29	10.4	41.0		
			11.3	1.5	10.8	39.8	618

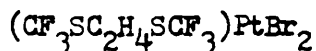
Table 32, Continued.

COMPOUND	COLOUR	ANALYSES						
		Found						
		Calculated						
		C	H	S	X	M		
$\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3$	Yellow	14.9	2.98	15.9	17.6	402		
		15.0	3.0	16.3	17.9	402		
PtBr_2	Yellow-Brown	12.2	2.44	13.1	32.5	491		
		12.1	2.6	13.3	32.9	491		
PtI_2	Brown	10.3	2.05	11.0	43.4			
		10.1	2.1	11.0	43.3	585		
PdCl_2	Yellow	19.1	3.82	20.5	22.6	313		
		19.7	4.0	20.5	22.6	313		
PdBr_2	Orange	14.9	2.98	15.9	39.7	402		
		15.1	3.1	15.8	39.5	402		
PdI_2	Violet	12.1	2.41	12.9	51.1			
		12.1	2.8	13.0	52.0	496		

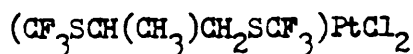
Table 33
i.r. data (cm^{-1})



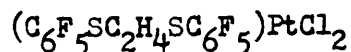
2953, w, br; 2920, w, br; 1412, w, br;
1303, w, br; 1190, vs, br; 1170, vs, br;
1130, s; 1070, vs; 936, w; 827, w; 753, s;
654, w, br; 500, w; 431, w; 390, w; 342, m;
336, m.



2960, w, br; 2929, w, br; 1420, w, sh;
1414, m; 1316, w, sh; 1300, m; 1201, vs, br;
1170, vs, br; 1135, s; 1085, vs, br; 934, m;
831, m; 757, vs; 656, w; 648, w; 503, w;
436, w; 392, w.

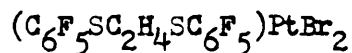


2967, w, br; 2909, w; 1444, m, br; 1384, w;
1327, w, br; 1296, w, br; 1269, m; 1202,
1202, vs, sh, br; 1185, vs, sh, br;
1161, vs, br; 1080, vs, br; 990, m; 976, w;
912, w, br; 864, w; 754, s; 707, w, br;
606, w; 547, w; 487, w; 453, w; 439, w;
360, w; 346, m; sh; 336, s; 313, w.

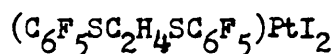


2994, w; 2940, w; 1642, s; 1518, vs; 1495, vs;
1415, m, sh; 1406, s; 1374, w; 1297, m;
1152, w; 1115, m, sh; 1096, vs; 1008, m;
986, vs; 937, w; 855, m; 841, m; 727, w;
529, w; 342, m; 334, m; 314, w.

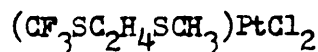
Table 33, continued.



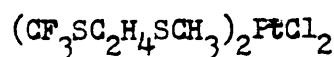
2980, w; 2828, w; 1640, m; 1515, vs; 1494, vs;
1412, w, sh; 1402, m; 1396, m, sh; 1369, w;
1295, w; 1150, w; 1114, w, sh; 1094, vs;
1003, w, sh; 984, vs; 931, w; 851, w; 839, m;
723, w; 525, w; 328, w; 310, w.



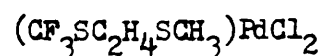
2980, w; 2924, w; 1641, m; 1517, vs; 1494, vs;
1404, m; 1369, w; 1294, m; 1150, w; 1094, vs;
1000, m, sh; 984, vs; 933, w; 851, m; 721, w;
526, w; 306, w.



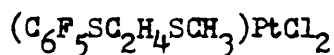
2994, w; 2969, m; 2936, w, sh; 2925, w;
1423, m, sh; 1413, s; 1330, w, sh; 1309, w;
1297, w, sh; 1255, w; 1199, vs; 1179, vs;
1164, vs, br; 1137, s; 1088, vs, br; 1014, w;
975, m, sh; 966, m; 934, m; 928, w, sh;
832, w; 755, s; 657, w; 637, w; 499, w;
486, w; 440, w; 401, w; 334, m; 323, m; 240, w;
227, w;



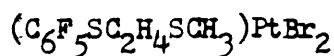
2990, w; 2962, w, sh; 2923, w; 1418, m, br;
1315, w; sh; 1307, w; 1295, w, sh; 1164, s, br;
1104, vs, br; 1088, vs; 1011, w; 969, m, br;
830, w; 756, m; 462, w; 439, w; 330, w, br;



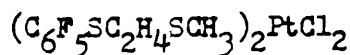
2990, w; 2985, w; 2961, w; 2926, w; 2919, w;
1422, w, sh; 1414, m; 1318, w, br; 1295, w;
1254, w; 1195, s; 1179, s; 1166, vs; 1132, m;
1088, vs, br; 1016, w; 972, m, br; 930, w; 835, w;
756, m; 439, w; 336, w, br; 329, w, sh; 304, w, br.



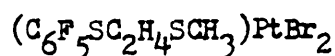
3011, w; 2979, w; 1640, m; 1624, w; 1511, vs;
1480, vs, br; 1424, s; 1416, m; 1405, m; 1372, w;
1364, w, sh; 1355, w, sh; 1321, w; 1293, w;
1286, m; 1268, w; 1214, s; 1138, m; 1090, vs;
1027, m; 990, s; 974, vs; 966, vs, sh; 930, w;
862, vs; 767, w; 726, w; 718, w; 711, w; 679, w;
635, w; 350, s; 321, m; 315, sh.



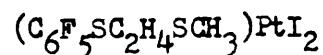
3010, w; 2920, w; 1642, m; 1626, w, sh; 1515, vs;
1482, vs, br; 1424, s; 1417, s; 1407, s;
1373, w; 1366, w; 1357, w; 1349, w; 1321, w;
1288, m; 1269, w; 1216, s; 1140, m; 1091, vs;
1029, m; 995, s; 978, vs; 964, s; 930, m; 865, vs;
768, w; 729, w; 720, w; 711, w; 680, w; 636, w.



2964, w; 2916, w; 1640, m; 1516, vs; 1490, vs;
1419, vs; 1405, w; 1311, w; 1291, w, br; 1092, vs;
1014, w, sh; 1004, w; 981, vs; 861, w, br;
340, m, br; 331, w, sh.



2996, w; 2960, w; 2920, w; 1641, m; 1519, vs;
1495, vs; 1427, m, sh; 1418, m; 1404, m;
1311, w; 1292, br; 1095, vs; 1013, w, sh;
1004, w; 983, vs; 857, w, br.

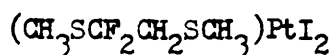


1640, w; 1514, vs; 1492, vs, sh; 1485, vs;
1424, m; 1418, m; 1402, w; 1311, w; 1290, w, br;
1208, w; 1090, s, br; 1013, w, sh; 980, vs; 862, s

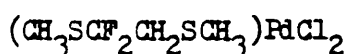
Table 33, continued.

$(C_6F_5SC_2H_4SCH_3)_2PdCl_2$	2915, w, br; 1640, m; 1515, vs; 1494, vs, sh; 1486, vs; 1413, m, br; 1320, w; 1289, w, br; 1248, w; 1211, m; 1140, w, br; 1090, vs; 980, vs; 963, m, sh; 866, s; 267, m, sh; 251, m, br
$(C_6F_5SC_2H_4SCH_3)_2PdBr_2$	2910, w, br; 1641, m; 1516, vs; 1492, vs, sh; 1490, vs; 1414, m, br; 1312, w; 1286, w, br; 1090, vs; 975, vs, br; 860, s; 850, m, sh.
$(C_6F_5SC_2H_4SCH_3)_2PtI_2$	3000, w; 2960, w; 1639, w; 1513, vs; 1491, vs, sh; 1482, vs; 1419, w, br; 1401, m; 1292, w; 1285, w; 1212, w; 1138, w; 1090, s; 975, vs, br; 861, s; 845, w.
$(CH_3SCF_2CH_2SCH_3)PtCl_2$	3028, w; 3006, w; 2976, m; 2925, m; 1630, w, br; 1427, m, sh; 1418, s; 1316, w; 1276, m; 1222, s; 1167, s; 1093, vs; 1024, vs; 982, m, sh; 971, s; 962, s; 860, w; 640, w; 589, w; 440, w; 338, m; 324, m.
$(CH_3SCF_2CH_2SCH_3)PtBr_2$	3028, w; 2999, w; 2987, m; 2918, m; 1625, w, br; 1424, m, sh; 1416, s; 1399, m, br; 1313, m; 1276, s; 1219, vs; 1166, s; 1089, vs; 1022, vs; 980, s; 969, s; 960, s; 954, s; 856, m; 639, m; 583, m; 438, m, sh; 434, m.

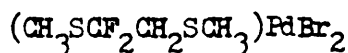
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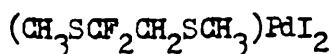
3020, w; 3000, w; 2979, w; 2958, w; 2919, m;
1623, w, br; 1430, w; 1416, s; 1390, w;
1316, w, sh; 1309, m; 1276, m; 1270, m;
1210, m; 1160, m; 1080, vs; 1016, vs; 974, m;
969, m; 956, s; 847, m; 633, w; 580, w;
434, w; 427, w.



3026, w, sh; 3008, w; 2970, m; 2922, s;
1628, w, br; 1419, s; 1414, s; 1319, m;
1312, m; 1274, m; 1217, m, sh; 1208, s;
1163, s; 1092, vs, br; 1025, vs; 1005, m;
974, s; 959, s; 852, m; 639, w; 578, m;
431, m; 360, m; 341, s; 330, s.



3010, w; 2969, m; 2919, m; 1625, w, br;
1417, s, sh; 1414, s; 1317, m; 1311, m;
1273, m; 1218, m, sh; 1208, m; 1161, m;
1090, vs, br; 1024, vs; 1004, m; 971, s, br;
958, s; 851, w; 638, w; 576, m; 431, w.



3000, w; 2953, w; 2918, m; 1620, w, br;
1418, s, sh; 1413, s; 1316, m; 1310, m;
1271, m; 1214, s; 1206, m, sh; 1161, m;
1090, s, br; 1080, s, sh; 1020, vs; 1000, m;
971, s; 957, s; 851, w; 638, w; 576, w; 430, w;

Table. 33, continued.

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$	3010, w; 2970, m; 2928, m; 1416, s, br; 1350, vs; 1318, m; 1282, vs; 1255, vs; 1239, vs, sh; 1181, vs; 1152, vs; 1121, vs; 1092, s; 1059, w; 975, s; 915, w; 894, w; 867, m; 759, w; 686, w; 664, m; 334, m, sh; 321, s.
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}_2$	3015, w; 2969, w; 2920, m; 898, w; 1410, vs; 1343, vs; 1317, m; 1306, m; 1279, vs; 1249 vs; 1233, vs; 1209, m; 1180, vs; 1165, s, sh; 1154, s; 1120, vs; 1108, vs; 1049, w; 970, vs; 927, w; 893, w; 864, m; 760, w; 709, w; 690, w; 682, w; 665, m;.
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtI}_2$	3000, w; 2960, w; 2919, m; 2906, w, sh; 1413, s, br; 1346, vs; 1319, m; 1306, m; 1280, vs; 1252, vs; 1238, vs, sh; 1212, m; 1183, vs; 1154, s; 1128, vs, br; 1052, w; 972, s; 968, s, sh; 911, w; 892, w; 865, w; 759, w; 691, w; 681, w; 665, w.
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PdCl}_2$	3000, w; 2960, w; 2918, m; 1416, m, br; 1348, s; 13166, w; 1279, s; 1251, vs; 1238, vs, sh; 1179, vs; 1150, s; 1120, vs; 1055, w; 973, m, br; 911, w; 891, w; 863, w; 755, w; 685, w; 661, w; 379, w; 342, w; 323, m; 310, w.

Table 33, continued.

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PdBr}_2$ 2998, w; 2957, w; 2915, m; 2844, w; 1411, m, br;
1343, s; 1316, w; 1306, w; 1279, s; 1250, vs;
1234, vs, sh; 1181, vs; 1150, s; 1120, vs;
1110, vs, sh; 1052, w; 970, m; 910, w; 891, w;
861, w; 760, w; 684, w; 662, w;

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PdI}_2$ 2988, w; 2944, w; 2900, w; 1407, s, br;
1338, s; 1314, m; 1304, m; 1274, s; 1245, vs;
1233, vs, sh; 1175, vs; 1146, s; 1110, vs, br;
1049, w; 968, s, br; 904, w; 886, w; 857, w;
754, w; 706, w; 680, w; 660, m.

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtCl}_2$ 3011, w; 2917, m; 1414, m; 1363, s; 1330, s, sh;
1318, s; 1260, vs; 1240, vs; 1220, vs, sh;
1174, vs; 1130, vs, sh; 1116, vs; 1046, w;
973, m; 762, w; 683, w; 673, w, sh; 667, w;
626, w; 527, w; 510, w; 329, m, br;

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtBr}_2$ 3000, w; 2895, m; 1412, m; 1360, m; 1329, m, sh;
1315, m; 1256, vs; 1239, vs, sh; 1214, vs, sh;
1183, vs, sh; 1170, vs; 1128, s, sh; 1114, vs;
1044, w; 973, m; 762, w; 681, w; 664, w; 625, w;
505, w.

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtI}_2$ 2998, w; 2903, m; 2880, w, sh; 1413, m, br;
1406, w, sh; 1358, m; 1329, m; 1310, m, br;
1258, vs; 1244, vs, sh; 1220, s; 1207, s;
1181, vs; 1170, vs; 1128, s; 1116, vs; 1041, w;
980, w, sh; 971, m; 964, w, sh; 887, w; 761, w;
680, w; 665, w; 624, w; 506, w.

Table 33, continued.

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PdCl}_2$	3010, w; 2914, m; 1417, m; 1364, s; 1330, m, sh; 1322, s; 1259, vs; 1242, vs; 1216, vs; 1179, vs; 1130, vs; 1115, vs; 1047, w; 979, m; 891, w; 763, w; 684, w; 667, w; 626, w; 371, w; 334, m; 307, m; 231, m, br.
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PdBr}_2$	3008, w; 2900, m, br; 1416, m, br; 1364, s; 1332, m, sh; 1320, s, br; 1259, vs; 1240, vs, sh; 1230, vs, sh; 1216, s, sh; 1173, vs, br; 1130, vs, sh; 1114, vs; 1046, w; 978, m, br; 888, w; 764, w; 684, m; 666, w; 627, w; 371, w.
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PdI}_2$	3008, w; 2902, w; 1414, m, br; 1359, s; 1329, m; 1318, m, sh; 1311, m; 1259, vs; 1242, vs; 1220, s; 1208, s, sh; 1182, vs; 1169, vs; 1127, vs; 1114, vs; 1046, w; 971, m; 864, w, sh; 885, w; 764, w; 681, w; 665, w; 624, w; 369, w.
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$	2984, w; 2940, m; 2899, w; 2851, w; 1444, m; 1408, vs; 1369, m; 1307, m; 1253, w; 1231, w; 1156, w; 1064, w; 1010, s; 959, vs; 904, w; 324, vs; 312, vs.
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}_2$	2991, w; 2955, w; 2914, w; 1446, s; 1409, vs, br; 1374, m; 1310, m; 1259, w; 1241, w; 1161, w; 1069, w; 1015, s; 977, s, sh; 965, s; 910, w.

Table 33, continued.

$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PtI}_2$	2975, m; 2957, m; 2940, m; 2909, w, sh; 2885, w; 1450, m; 1441, m; 1417, vs, sh; 1411, vs; 1399, vs; 1380, m, sh; 1321, m; sh; 1311, m, sh; 1253, w; 1238, w; 1160, w; 1070, w, br; 1016, s; 987, s; 976, vs; 965, s, sh; 920, w.
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PdCl}_2$	2994, w; 2965, w; 2946, m; 2913, m; 2862, w; 1452, m, sh; 1448, m; 1418, vs; 1376, m; 1314, s; 1259, m; 1237, w; 1161, m; 1106, w; 1068, w; 1015, s; 969, s; 961, s; 910, w; 339, m; 326, s; 304, m; 299, m.
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PdBr}_2$	2989, w; 2950, m; 2913, w; 1446, s; 1410, vs; 1374, w; 1312, m; 1260, w; 1240, w; 1163, w; 1108, w; 1066, w; 1014, s; 977, s, sh; 962, s, sh 910, w.
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PdI}_2$	2990, w; 2942, w; 2902, w; 1419, m, sh; 1444, m; 1410, vs, br; 1374, w; 1310, w; 1260, w; 1240, w; 1160, w; 1064, w; 1013, m; 964, s, br; 910, w.
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PtCl}_2$	3000, w; 2963, w; 2910, m; 2860, w; 1445, vs; 1419, vs; 1409, vs, sh; 1384, m; 1316, m; 1308, m; 1260, w; 1244, w; 1211, m; 1086, w; 1070, w; 1004, w; 996, w; 969, vs; 964, vs; 953, vs; 706, w; 685, w; 647, w; 330, vs; 320, vs.

Table 33, continued.

$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PtBr}_2$	2995, w; 2986, w; 2915, m, sh; 2904, m; 1447, vs; 1423, vs; 1383, m; 1379, m, sh; 1314, m; 1308, m; 1252, w, br; 1210, m; 1071, w, br; 1004, w, br; 966, vs, br; 962, vs; 950, s; 707, w; 684, w; 647, w.
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PtI}_2$	2964, vs; 2914, m; 2868, s; 1442, vs; 1413, vs; 1404, vs, br; 1385, s, sh; 1323, m, sh; 1314, m; 1298, m; 1235, w; 1211, m; 1079, m; 974, vs; 962, s; 681, w; 643, w; 529, w,
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PdCl}_2$	2998, m; 2967, m; 2913, m; 2898, m; 2860, w; 1446, vs; 1415, vs; 1379, m; 1311, m; 1284, w; 1256, m; 1245, m; 1207, w; 1068, m, br; 1000, w; 962, vs, br; 709, w; 685, w; 649, w; 366, w; 350, w; 324, vs; 317, vs.
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PdBr}_2$	3000, w; 2968, w; 2920, w; 2904, m; 2865 w; 1447, vs; 1418, vs; 1381, m; 1311, s; 1285, m; 1261, m; 1242, m; 1213, m; 1076, m; 1068, m, sh; 1054, m; 1004, w; 964, vs, br; 710, w; 686, w; 651, w; 534, w.
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PdI}_2$	2985, w; 2953, w; 2904, w; 1442, vs; 1410, vs; 1382, m; 1376, m, sh; 1312, m, sh; 1301, m; 1246, w, sh; 1235, w; 1201, w; 1075, m; 1050, w; 1003, w; 970, vs, sh; 961, vs; 946, s; 708, w; 686, w; 647, w; 531, w.

Table 34

Mass Spectra data

(compound, m/e, intensity %, assignment.)

$(\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3)\text{PtCl}_2$	495,	11,	$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2$
	460,	8,	$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}$
	427,	9,	$(\text{CF}_3\text{SC}_2\text{H}_4\text{S}-)\text{PtCl}_2$
	425,	7,	$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{Pt}$
	397,	40,	$(\text{CF}_3\text{S})_2\text{Pt}$
	391,	9,	$(\text{CF}_3\text{SC}_2\text{H}_4\text{S}-)\text{PtCl}$
	366,	5,	$(\text{CF}_3\text{S}-)\text{PtCl}_2$
	357,	3,	$(-\text{SC}_2\text{H}_4\text{S}-)\text{PtCl}_2$
	356,	3,	$(\text{CF}_3\text{SC}_2\text{H}_4\text{S}-)\text{Pt}$
	331,	5,	$(\text{CF}_3\text{S}-)\text{PtCl}$
	322,	5,	$(-\text{SC}_2\text{H}_4\text{S}-)\text{PtCl}$
	297,	14,	$(\text{S})\text{PtCl}_2$
	296,	100,	$(\text{CF}_3\text{S}-)\text{Pt}$
	255,	5,	$(-\text{C}_2\text{H}_4\text{S}-)\text{Pt}$
	241,	7,	$(-\text{CH}_2\text{S}-)\text{Pt}$
$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtBr}_2$	583,	8,	$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtBr}_2$
	514,	10,	$(\text{CF}_3\text{SC}_2\text{H}_4\text{S}-)\text{PtBr}_2$
	504,	7,	$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtBr}$
	445,	1,	$(-\text{SC}_2\text{H}_4\text{S}-)\text{PtBr}_2$
	435,	12,	$(\text{CF}_3\text{SC}_2\text{H}_4\text{S})\text{PtBr}$
	425,	5,	$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{Pt}$
	397,	30,	$(\text{CF}_3\text{S}-)_2\text{Pt}$
	375,	11,	$(\text{CF}_3\text{S}-\text{PtBr})$
	366,	4,	$(-\text{SC}_2\text{H}_4\text{S}-)\text{PtBr}$

Table 34, continued.

356, 5, $(\text{CF}_3\text{SC}_2\text{H}_4\text{S}-)\text{Pt}$
 296, 100, $(\text{CF}_3\text{S}-)\text{Pt}$
 255, 1, $(-\text{CH}_4\text{S}-)\text{Pt}$
 241, 3, $(-\text{CH}_2\text{S}-)\text{Pt}$

$(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$

509, 24, $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2$
 474, 14, $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}$
 440, 5, $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{S}-)\text{PtCl}_2$
 439, 5, $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{S}-)\text{PtCl}$
 405, 7, $(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{S}-)\text{PtCl}$
 301, 8, $(-\text{SCH}(\text{CH}_3)\text{CH}_2\text{S}-)\text{Pt}$
 296, 100, $(\text{CF}_3\text{S}-)\text{Pt}$

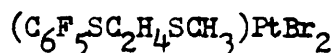
$(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{SC}_6\text{F}_5)\text{PtBr}_2$

779, 12, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{SC}_6\text{F}_5)\text{PtBr}_2$
 700, 25, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{SC}_6\text{F}_5)\text{PtBr}$
 621, 100, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{SC}_6\text{F}_5)\text{Pt}$
 533, 4, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{S}-)\text{PtBr}$
 454, 15, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{S}-)\text{Pt}$

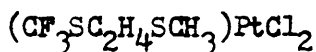
$(\text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$

539, 15, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtCl}_2$
 489, 8, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{S}-)\text{PtCl}$
 469, 21, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{SCH}_3)\text{Pt}$
 464, 4, $(\text{C}_6\text{F}_5\text{S}-)\text{PtCl}_2$
 429, 2, $(\text{C}_6\text{F}_5\text{S}-)\text{PtCl}$
 394, 71, $(\text{C}_6\text{F}_5\text{S}-)\text{Pt}$
 372, 100, $(-\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtCl}_2$
 337, 10, $(-\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtCl}$
 322, 7, $(-\text{SC}_2\text{H}_4\text{S})\text{PtCl}$
 302, 7, $(-\text{SC}_2\text{H}_4\text{SCH}_3)\text{Pt}$

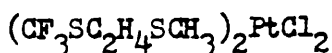
Table 34, continued.



- 627, 13, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtBr}_2$
 548, 8, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtBr}$
 552, 1, $(\text{C}_6\text{F}_5\text{S})\text{PtBr}_2$
 533, 8, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{S-})\text{PtBr}$
 469, 6, $(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{S-})\text{Pt}$
 460, 12, $(-\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtBr}_2$
 394, 100, $(\text{C}_6\text{F}_5\text{S-})\text{Pt}$
 381, 41, $(-\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtBr}$
 302, 5, $(-\text{SC}_2\text{H}_4\text{SCH}_3)\text{Pt}$

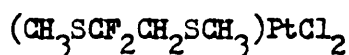


- 441, 15, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtCl}_2$
 406, 23, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtCl}$
 391, 100, $(\text{CF}_3\text{SC}_2\text{H}_4\text{S-})\text{PtCl}$
 356, 9, $(\text{CF}_3\text{SC}_2\text{H}_4\text{S-})\text{Pt}$
 337, 3, $((-\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtCl}$
 322, 1, $(-\text{SC}_2\text{H}_4\text{S-})\text{PtCl}$
 296, 80, $(\text{CF}_3\text{S-})\text{Pt}$
 287, 10, $(-\text{SC}_2\text{H}_4\text{S-})\text{Pt}$

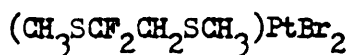


- 617, 24, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)_2\text{PtCl}_2$
 582, 100, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)_2\text{PtCl}$
 446, 21, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)\text{Pt}(\text{CH}_3\text{SC}_2\text{H}_4\text{-})$
 441, 68, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtCl}_2$
 432, 37, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)\text{Pt}(\text{CH}_3\text{SCH}_2\text{-})$
 418, 37, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)\text{Pt}(\text{CH}_3\text{S-})$
 416, 79, $(-\text{C}_2\text{H}_4\text{S-})\text{Pt}(-\text{SC}_2\text{H}_4\text{SCF}_3)$
 406, 63, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtCl}$
 371, 53, $(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)\text{Pt}$

Table 34, continued.



422, 100, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2$
 391, 9, $(-\text{SCF}_2\text{CH}_2\text{S}-)\text{PtCl}_2$
 386, 89, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtCl}$
 372, 20, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{S}-)\text{PtCl}$
 351, 63, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{Pt}$
 338, 9, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{S}-)\text{Pt}$
 323, 20, $(-\text{CH}_2\text{CF}_2\text{S}-)\text{Pt}$
 277, 19, $(-\text{CF}_2\text{S}-)\text{Pt}$



511, 6, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtBr}_2$
 449, 9, $(-\text{CH}_2\text{CF}_2\text{S}-)\text{PtBr}_2$
 435, 15, $(-\text{CF}_2\text{S}-)\text{PtBr}_2$
 432, 11, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtBr}$
 402, 18, $(-\text{SCH}_2\text{CF}_2\text{S}-)\text{PtBr}$
 385, 12, $(-\text{S}-)\text{PtBr}_2$
 370, 9, $(-\text{CH}_2\text{CF}_2\text{S}-)\text{PtBr}$
 356, 14, $(\text{CF}_2\text{S}-)\text{PtBr}$
 353, 100, $(\text{CH}_3\text{SCH}_2\text{CF}_2\text{SCH}_3)\text{Pt}$
 338, 20, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{S}-)\text{Pt}$
 323, 27, $(-\text{SCH}_2\text{CF}_2\text{S}-)\text{Pt}$
 306, 11, $(-\text{S}-)\text{PtBr}$
 291, 42, $(-\text{CH}_2\text{CF}_2\text{S}-)\text{Pt}$
 277, 24, $(-\text{CF}_2\text{S}-)\text{Pt}$
 227, 32, $(-\text{S}-)\text{Pt}$

Table 34, continued.

$(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PdCl}_2$	335, 75, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PdCl}_2$
	317, 75, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{S-})\text{PdCl}_2$
	297, 50, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PdCl}$
	282, 38, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{S-})\text{PdCl}$
	221, 81, $(-\text{CF}_2\text{S-})\text{PdCl}$
	206, 88, $(-\text{S-})\text{PdCl}_2$
	186, 100, $(-\text{CF}_2\text{S-})\text{Pd}$
	171, 38, $(-\text{S-})\text{PdCl}$
$(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PdBr}_2$	424, 79, $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PdBr}_2$
	279, 81, $(-\text{CH}_2\text{CF}_2\text{S-})\text{PdBr}$
	265, 81, $(-\text{CF}_2\text{S-})\text{PdBr}$
	188, 100, $(-\text{CF}_2\text{S-})\text{Pd}$
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtCl}_2$	523, 61, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtCl}_2$
	488, 36, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtCl}$
	453, 47, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{Pt}$
	406, 85, $(\text{CH}_3\text{SCH}(\text{CF}_3))(-\text{SCH}_3)\text{PtCl}$
	324, 79, $(\text{CH}_3\text{S-})_2\text{PtCl}$
	289, 100, $(\text{CH}_3\text{S-})_2\text{Pt}$
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtBr}_2$	611, 54, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtBr}_2$
	532, 100, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtBr}$
	517, 25, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{S-})\text{PtBr}$
	453, 36, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{Pt}$
	368, 79, $(\text{CH}_3\text{S-})_2\text{PtBr}$
	306, 43, $\text{Br-Pt}(-\text{S-})$

Table 34, continued.

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PdCl}_2$ 434, 31, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtCl}_2$
 399, 100, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtCl}$
 364, 12, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{Pt}$
 352, 19, $(\text{CH}_3\text{SCH}(\text{CF}_3))(-\text{SCH}_3)\text{PtCl}_2$
 349, 23, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{S-})\text{Pt}$

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PdBr}_2$ 522, 15, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PdBr}_2$
 507, 8, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{S-})\text{PdBr}_2$
 443, 100, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PdBr}$
 364, 73, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{Pd}$
 282, 30, $(\text{CH}_3\text{SCH}(\text{CF}_3))(-\text{SCH}_3)\text{Pd}$
 232, 49, $(\text{CH}_3\text{S-})\text{PdBr}$

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$ 455, 24, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$
 440, 19, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{S-})\text{PtCl}_2$
 420, 100, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}$
 370, 54, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{S-})\text{Pt}$
 324, 15, $(\text{CH}_3\text{SCH}(\text{CF}_3))\text{Pt}$

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}_2$ 543, 39, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}_2$
 464, 100, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}$
 449, 19, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{S-})\text{PtBr}$
 403, 12, $(\text{CH}_3\text{SCH}(\text{CF}_3))\text{PtBr}$
 385, 45, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{Pt}$
 370, 23, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{S-})\text{Pt}$

Table 34 , continued.

$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PdCl}$	366, 32, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PdCl}_2$
	351, 17, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{S-})\text{PdCl}_2$
	331, 100, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PdCl}$
	296, 49, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{Pd}$
	235, 18, $(\text{CH}_3\text{SCH}(\text{CF}_3))\text{Pd}$
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PdBr}_2$	454, 34, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PdBr}_2$
	375, 100, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PdBr}$
	360, 27, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{S-})\text{PdBr}$
	296, 21, $(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{S-})\text{Pd}$
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PtCl}_2$	415, 100, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PtCl}_2$
	380, 98, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PtCl}_2$
	365, 18, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{S-})\text{PtCl}$
	345, 28, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{Pt}$
	330, 15, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{S-})\text{Pt}$
	323, 28, $(-\text{CHCHS-})\text{PtCl}_2$
	300, 28, $(\text{CH}_3\text{SCHCHS-})\text{Pt}$
	285, 30, $(-\text{SCHCHS-})\text{Pt}$
	240, 48, $(-\text{CHS-})\text{Pt}$
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PtBr}_2$	503, 100, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PtBr}_2$
	424, 86, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PtBr}$
	411, 7, $(-\text{CHCHS-})\text{PtBr}_2$
	345, 14, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{Pt}$
	332, 9, $(-\text{CHCHS-})\text{PtBr}$
	330, 12, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{S-})\text{Pt}$
	285, 43, $(-\text{SCHCHS-})\text{Pt}$

Table 34, continued.

$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PdCl}_2$	326, 100,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PdCl}_2$
	291, 90,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PdCl}$
	276, 31,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{S-})\text{PdCl}$
	256, 37,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{Pd}$
	226, 12,	$(\text{CH}_3\text{SCHCHSCH}_3)\text{Pd}$
	211, 16,	$(\text{CH}_3\text{SCHCHS-})\text{Pd}$
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PdBr}_2$	414, 100,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PdBr}_2$
	335, 87,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{PdBr}$
	256, 41,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCH}_3)\text{Pd}$
	241, 8,	$(\text{CH}_3\text{SCH}(\text{CH}_3\text{CHSCH}_3)\text{Pd}$
	226, 13,	$(\text{CH}_3\text{SCHCHSCH}_3)\text{Pd}$
	211, 9,	$(\text{CH}_3\text{SCHCHS-})\text{Pd}$
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$	401, 54,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$
	366, 30,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}$
	359, 65,	$(\text{CH}_3\text{S-})_2\text{PtCl}_2$
	331, 35,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{Pt}$
	324, 85,	$(\text{CH}_3\text{S-})_2\text{PtCl}$
	289, 100,	$(\text{CH}_3\text{S-})_2\text{Pt}$
	242, 64,	$(\text{CH}_3\text{S-})\text{Pt}$
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}_2$	489, 62,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}_2$
	447, 76,	$(\text{CH}_3\text{S-})_2\text{PtBr}_2$
	410, 57,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}$
	368, 100,	$(\text{CH}_3\text{S-})_2\text{PtBr}$
	331, 48,	$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{Pt}$
	289, 99,	$(\text{CH}_3\text{S-})_2\text{Pt}$
	242, 86,	$(\text{CH}_3\text{S-})\text{Pt}$

Table 34, continued.

$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PdCl}_2$	312, 58, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PdCl}_2$
	277, 30, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PdCl}$
	262, 12, $(\text{CH}_3\text{SCHCH}_2\text{SCH}_3)\text{PdCl}$
	242, 100, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{Pd}$
	235, 54, $(\text{CH}_3\text{S-})_2\text{PdCl}$:

$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PdBr}_2$	400, 62, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PdBr}_2$
	321 41, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PdBr}$
	306, 21, $(\text{CH}_3\text{SCHCH}_2\text{SCH}_3)\text{PdBr}$
	279, 15, $(\text{CH}_3\text{S-})_2\text{PdBr}$
	242, 100, $(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{Pd}$
	200, 8, $(\text{CH}_3\text{S-})_2\text{Pd}$

a) Values for ^{79}Br , ^{35}Cl , ^{195}Pt and ^{106}Pd . For clarity charges are not indicated.

Table 35

Parameters of Nuclear Magnetic Resonance

COMPOUND	Relative %	$\delta^{19}\text{F}^a$	$\delta^{195}\text{Pt}^b$	$J(\text{F-F})^c$	$J(\text{Pt-F})^d$
<hr/>					
$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtCl}_2^e$					
Isomer A	65	-44.1	-232.8	0	60.0
Isomer B	35	-44.7	-177.5	4	57.7
<hr/>					
$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCF}_3)\text{PtBr}_2^e$					
Isomer a	72	-43.7	-666.9	0	57.7
Isomer B	28	-44.2	-637.5	3.7	55.0
<hr/>					
$(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtCl}_2^f$					
Isomer A	6	-37.9 -43.9	-154.7	0	68.7 54.0
Isomer B	4	-38.5 -45.1	-100.5	+4.6	+65.5 +54.0
Isomer C	12	-42.1 -43.7	-202.3	0	53.0 62.0
Isomer D	78	-44.0 -44.4	- 98.3	+4.6	+59.0 +59.0
<hr/>					
$(\text{CF}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCF}_3)\text{PtBr}_2^f$					
Isomer A	17	-37.5 -43.8	-599.7	0	66.0 52.8
Isomer B	10	-38.2 -45.0	-	ca4.6	-
Isomer C	8	- -43.5	-	0	- 60.1
Isomer D	65	-43.9 -44.4	-570.3	ca4.6	57.2 57.2
<hr/>					
$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)\text{PtCl}_2$					
Isomer A	70	-41.6	-235.8	-	69.6
Isomer B	30	-41.8	-239.5	-	63.8
<hr/>					

Table 35, continued.

COMPOUND	Relative %	$\delta^{19}\text{F}^a$	$\delta^{195}\text{Pt}^b$	$J(\text{F-F})^c$	$J(\text{Pt-F})^d$
<hr/>					
$(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtCl}_2^g$					
Isomer A	58	-84.6 -82.2	-114.7	+ 221	+114.0 + 60.0
Isomer B	42	-83.5 -82.2	-122.1	+ 205	+ 29.0 +184.0
<hr/>					
$(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtBr}_2^h$					
Isomer A	-	-85.1 -81.4	-	223	118.0 43.0
Isomer B	-	-	-	205	-
<hr/>					
$(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtI}_2$					
Isomer A	54	-86.3 -79.9	-	225	113.5 22.5
Isomer B	46	-84.5	-	206	155.5 27.5
<hr/>					
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtCl}_2$					
Isomer A	18	-65.50	-231.2	0	6.1
Isomer B	13	-64.09 -59.82	-200.8	9.5	5.0 13.0
Isomer C	62	-61.25	-204.1	0	5.3
Isomer D	3	-60.11	-201.2	0	10.6
<hr/>					
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtBr}_2$					
Isomer A	18	-65.97	-628.4	0	<u>ca</u> 7
Isomer B	11	-64.13 -59.76		<u>ca</u> 9	
Isomer C	18	-61.51 -60.90		<u>ca</u> 9	
Isomer D	51	-61.18	-596.4	0	4.3
Isomer E	2	-59.94	-594.1	0	9.6
<hr/>					

Table 35, continued.

COMPOUND	Relative %	$\delta^{19}\text{F}^a$	$\delta^{195}\text{Pt}^b$	$J(\text{F}-\text{F})^c$	$J(\text{Pt}-\text{F})^d$
<hr/>					
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}(\text{CF}_3)\text{SCH}_3)\text{PtI}_2$					
Isomer A	13	-66.26	-1469.8 ⁱ	0	3.5 ⁱ
Isomer B	9	-63.9 -59.5	-1424.0 ⁱ	9 ⁱ	
Isomer C	73	-61.07	-1425.9	0	
Isomer D	5	-59.54	-1415.7	0	7.0
<hr/>					
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$					
Isomer A	4	-62.55	- 195.3	-	10.0
Isomer B	57	-66.00	- 192.8	-	6.2
Isomer C	8	-62.56	- 165.5	-	8.0
Isomer D	31	-65.96	-219.4	-	8.4
<hr/>					
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtBr}_2$					
Isomer A	6	-62.24	- 580.8	-	9.1
Isomer B	53	-65.75	- 580.43	-	5.7
Isomer C	13	-62.19	- 554.0	-	6.9
Isomer D	28	-65.67	- 618.9	-	7.4
<hr/>					
$(\text{CH}_3\text{SCH}(\text{CF}_3)\text{CH}_2\text{SCH}_3)\text{PtI}_2$					
Isomer A	5	-62.02	-1399.3	-	6.1
Isomer B	52	-65.55	-1397.9	-	3.6
Isomer C	19	-61.74	-1371.4	-	4.4
Isomer D	24	-65.49	-1427.3	-	5.1
<hr/>					

- a) p.p.m. positive to low field of external CCl_4
- b) p.p.m. positive to low field of cis- $(\text{Me}_2\text{S})_2\text{PtCl}_2$, for which $\nu(^{195}\text{Pt}) = 21\,420\,980\text{ Hz}^{278}$.
- c) Hz.
- d) Hz. signs are only shown when a relative sign determining experiment was performed.
- e) $J(\text{F}-\text{F})$ measured from ^{13}C satellites.
- f) Values of δCF_3 and $J(\text{Pt}-\text{F})$ for two chemical distinct CF_3 groups.
- g) For $(\text{CH}_3\text{SCF}_2\text{CH}_2\text{SCH}_3)\text{PtX}_2$, values of δCF_3 for two chemically distinct fluorine atoms $J(\text{F}-\text{F})$ represent the values of geminal coupling constants.
- h) See appendix A.
- i) Measured at 263 K.

Table 36

Nuclear Magnetic Resonance Parameters.

Compound	Relative %	$\delta^1\text{H}^a$	$\delta^{195}\text{Pt}^b$	$J(\text{Pt-H})^c$
<hr/>				
$(\text{CH}_3\text{SCH}(\text{CH}_3)\text{CH}_2\text{SCH}_3)\text{PtCl}_2$				
Isomer A	57	2.87 2.93	- 215.5	48.0 48.6
Isomer B	26	2.60 2.76	- 160.6	48.2 49.5
Isomer C	13	2.71 3.15	- 179.2	- 49.3
Isomer D	5			
<hr/>				
$(\text{CF}_3\text{SC}_2\text{H}_4\text{SCH}_3)_2\text{PtCl}_2$				
	<u>cis</u> 47	2.72	- 25.1	48.9
	<u>trans</u> 53	2.57	118.1	42.6
<hr/>				
$(\text{C}_6\text{F}_5\text{SC}_2\text{H}_4\text{SCH}_3)_2\text{PtCl}_2$				
	<u>cis</u> 31	2.61	- 36.5	49.2
	<u>trans</u> 69	2.44	116.1	42.3
<hr/>				

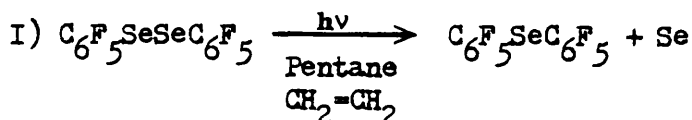
a) p.p.m. from external TMS.

b) p.p.m. positive to low field of cis-(Me₂S)₂PtCl₂ for which

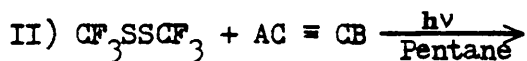
$$\Xi(^{195}\text{Pt}) = 21\,420\,980\text{ Hz}^{278}.$$

c) Hz.

Miscellaneous reactions.



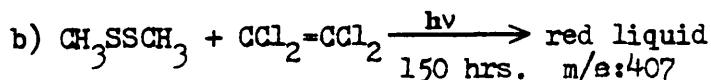
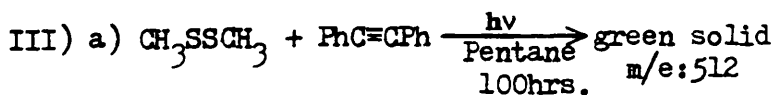
The reaction was similar whether Pyrex or quartz vessels were used. The diselenide was completely converted to monoselenide within three hours of irradiation. Similar reactions have been explained by invoking exclusive C-Se bond cleavage although formation of monoselenide can be rationalized by reactions of RSe• radicals as well³⁴⁰.



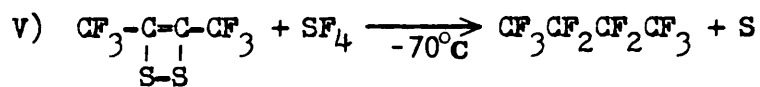
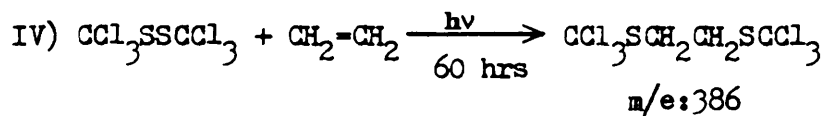
a) A=B=Ph or A=Ph, B=H. Although the products are probably different, the reactions of both acetylenes are very similar. After irradiation for ten hours in a sealed n.m.r. tube a brown grease was obtained. ¹⁹F n.m.r. spectra were identical with those of the starting materials although no CF₃SSCF₃ was present.

b) A=B=CF₃. After irradiation for five hours in a sealed n.m.r. tube, a white solid was formed. ¹⁹F n.m.r. spectrum showed a complex pattern containing 10 groups of signals.

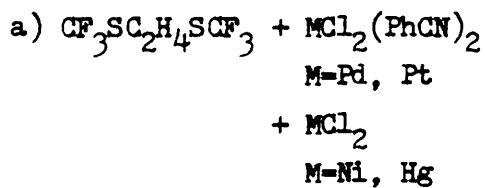
c) A=B=Me. When Pyrex apparatus was used, irradiation for five hours gave a brown grease. Using quartz apparatus however, two products were obtained: a red solid showing m/e at 603, (M of CF₃SC(Me)=C(Me)SCF₃=284) and a ¹⁹F n.m.r. spectrum showing a multiplet centered at ca 70 ppm. The second product was a brown solid with no fluorine n.m.r. resonances and m/e at 304.



Both products represented less than 2% of the total weight of the reaction mixture.



VI) No reaction took place in the following systems,



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