SUMMARY

The first section of this thesis describes experiments leading to the preparation of a series of geometrical isomers of tricarbonyl-mono-7-substituted-cyclohepta(1,3,5)trienechromium.

Direct reaction of a substituted cycloheptatriene with hexacarbonylchromium (or molybdenum) is shown to lead normally to the 'exo' configurational isomer, whilst anionic addition to tricarbonyltropyliumchromium (or molybdenum) salts leads normally to formation of the corresponding 'endo' isomer. Nuclear magnetic resonance studies are described in support of these suggestions and possible mechanistic pictures of the two reactions are given.

The second section reports the results of studies on the ring-contraction of certain tricarbonyl-mono-7-substituted-cyclohepta(1,3,5)trienechromium derivatives to tricarbonylbenzenechromium. It is shown that the substituent, which must have an acidic hydrogen on the carbon atom α to the C_7 carbon atom of the cycloheptatriene ring, can be in either the exo or endo configuration. A possible mechanism for the rearrangement is given. It has not been possible to characterise the second fragment from the ring-contraction.

In the third section, the results of unsuccessful attempts to elucidate the structure of tricarbonylanthracenechromium and tricarbonylphenanthrenechromium by chemical reactions (in the former case by formation from tricarbonyl 9:10-dihydroanthracenechromium

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by dehydrogenation and in the latter case by hydrogenation to the previously unknown tricarbonyl 9:10-dihydrophenanthrenechromium) are reported.

Finally, in additional experiments the reaction of phenylethynyllithium with tricarbonyltropyliumchromium fluoroborate is shown to yield tricarbonylphenylethynylcyclohepta(1,3,5)trienechromium, the reaction of sodium methoxide with tricarbonyltropyliummolybdenum fluoroborate is shown to give tricarbonylmethoxycycloheptatrienemolybdenum and the reaction of hexacarbonylmolybdenum and 6:6'-dimethylfulvene is shown to give a complex mixture separable by chromatography on alumina. Two of these compounds have been identified as hexacarbonyldi(isopropylcyclopentadienyl)dimolybdenum and hexacarbonyl(isopropylcyclopentadienyl)-(isopropenylcyclopentadienyl)dimolybdenum.

SOME ORGANIC DERIVATIVES OF CHROMIUM AND MOLYBDENUM

A Thesis presented for the Degree of

Doctor of Philosophy

in the

University of Glasgow

by

Geoffrey Harold Smith

July, 1962.

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INTRODUCTION

Hein's polyphenylchromium compounds.

Although attempts were made, by Sand and Singer[1] in 1903 and by Bennett and Turner[2] in 1914 to form stable derivatives of chromium by reaction of phenylmagnesium bromide with chromyl chloride[1] and chromic chloride[2] it was not until 1919 that Hein reported[3] the first successful preparation of a series of organochromium compounds, nowadays known by the trivial name of the "polyphenylchromium compounds".

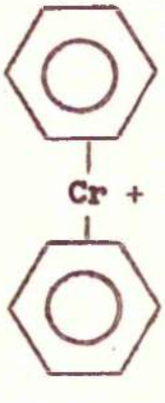
Whilst these compounds have been known for over forty years it is only within the last eight years that their structures have been elucidated.[4,5,6]

Under Hein's original conditions, the reaction is assumed to take the following course:-

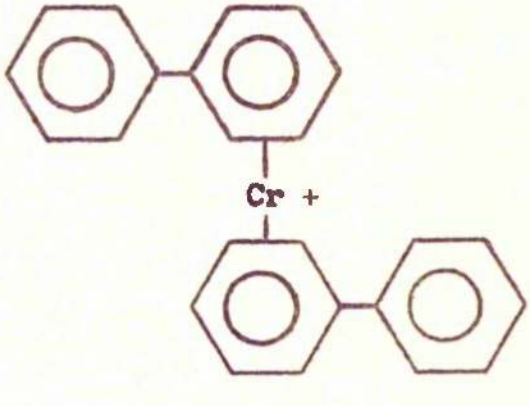
$$3\ \mathrm{PhMgBr} + \mathrm{CrCl_3} \xrightarrow{\mathrm{Et_2O}} \mathrm{Ph_3Cr(OEt_2)_3}$$

(I)

giving an unstable σ-bonded etherate (I), which undergoes an oxidation-reduction reaction with rearrangement to yield π-bonded complexes of chromium(I) with both benzene (II) and biphenyl (III).



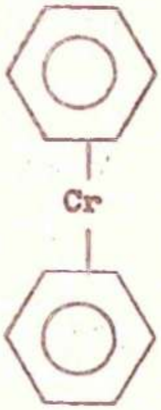
(II)



(III)

Bisbenzene derivatives of chromium and molybdenum.

The cation (II) was first prepared by Fischer[7,8] in 1955 by the reduction of chromic chloride with aluminium powder at 150°C in the presence of benzene and aluminium trichloride, a reaction system which, with the addition of carbon monoxide, was being investigated with a view to synthesising hexacarbonylchromium[9]. Without the carbon monoxide, a mixture resulted from which (II) was isolated as the picrate or reineckate. Reduction of (II) with sodium dithionite gave the parent compound bisbenzenechromium (IV) as a black-brown solid.



(IV)

Subsequent research led to the isolation of the bisbiphenylchromium(I) cation (III),[10] and the mixed benzenebiphenylchromium(I) cation,[11] from similar reductions of chromic chloride using biphenyl, and a mixture of benzene and biphenyl in place of benzene. These complexes were found to be identical with those from the Grignard reaction, thus proving conclusively the π-bonded nature of the "polyphenylchromium compounds".

The properties of (II) and (IV) have been studied in great detail. (II) is diamagnetic[7] and thermodynamically stable (although less so than ferrocene[99,100]). The infrared spectra[108] of $(C_6H_6)_2Cr$ and $(C_6D_6)_2Cr$ have been interpreted[12] as suggesting D_{3d} symmetry rather than the six-fold symmetry about the Z axis which might be expected, and this has been confirmed by X-ray analysis.[13]

A study of the solid-state spectrum[14] of (IV) has led to the conclusion that there is some motion in the solid state, but that this appears to be rotation of the whole molecule in the crystal lattice rather than rotation of the rings in the complex.

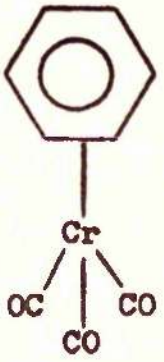
Further confirmation of structure (IV) comes from electron-spin resonance studies on (II)[16,17,18,19] whence it is found that the unpaired electron in (II) is not localised on the chromium atom, but interacts equally with all twelve hydrogens on the two benzene rings.

Chemical properties of (IV) are largely negative. Friedel-Crafts, Chichibabin and metalation reactions failed[20] to give the substitution products as did reaction with diazonium salts. Attempted nitration or sulphonation and treatment with peroxides resulted[20] in decomposition of the molecule. Metalation has, however, been achieved recently.[21,105]

Analogous bisarenechromium compounds of toluene, o, m and p-xylenes, tetralin, mesitylene and hexamethylbenzene have been prepared.[8] Bisarenemolybdenum compounds of benzene and mesitylene have been made.[71,73]

Preparation of tricarbonylarenechromium (and molybdenum) compounds.

Reaction of (IV) with hexacarbonylchromium gave the first tricarbonylarenechromium, tricarbonylbenzenechromium[22] (V) in 27% yield.



(V)

A more general method, devised independently by Fischer,[23,24] Natta[25,26] and Whiting[27,29] is to heat the aromatic compound with hexacarbonylchromium under reflux or in an autoclave under pressure in a solvent such as diethylene glycol dimethyl ether, (diglyme):-

$$\mathrm{Ar} + \mathrm{Cr(CO)_6} \xrightarrow{\text{diglyme}} \mathrm{ArCr(CO)_3} + 3\mathrm{CO}$$

Using diglyme as solvent, the intermediate tricarbonyldiglymemolybdenum has been isolated[74] as a fairly stable yellow solid. Table I lists some of the compounds which have been made by this general method.

Table I

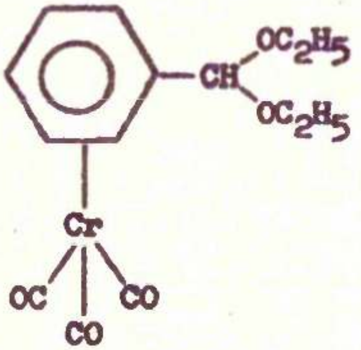
Some tricarbonylarenechromiums

Arene	M.p.(^{o}C).	Reference	Arene	M.p.(^{o}C).	Reference
C_6H_6 *	161.5-163	22,24,26 27,29,30	$C_6H_5CH_2OH$	95.5- 96.5	27
$C_6H_5NHCOCH_3$	134 -135.5	30	$C_6H_5OCH_3$	86 - 87	23,24,27 30
C_6H_5Cl	102 -103	23,27,30	o-$C_6H_4(CH_3)(OCH_3)$	75 - 77	27
C_6H_5F *	122.5-124	27	p-$C_6H_4(CH_3)(OCH_3)$	52 - 53.5	27
$C_6H_5C(CH_3)_3$	83.5- 84	27	$C_6H_5COCH_3$	91 - 92.5	27
$C_6H_5CH_3$ *	80 - 81	23,24,26 27,29,30	$C_6H_5COOCH_3$	97.5- 98.5	24,27,29 30
sym-$C_6H_3(CH_3)_3$ *	177.5-178	23,24,26 27,29,30	$C_6H_5N(CH_3)_2$	145.8-146.5	27,29,30
C_6H_5OH	113 -115	23,24,30	$C_6(CH_3)_6$	211 -213	24,27

23,24,88

* The corresponding molybdenum compounds also known

Limitations of this method have been encountered with the substituents -COOH, -CHO, -CN, -NO_2 and -Br which promote decomposition of hexacarbonylchromium before the complexing reaction becomes prominent. However, the benzoic[24] and phenylacetic acid[29] complexes have been isolated by hydrolysis of the corresponding ester derivatives and the benzaldehyde complex has been isolated[35] by acid hydrolysis of tricarbonyldi(ethoxy)methylbenzenechromium (VI).



(VI)

Tricarbonylbenzaldehydechromium forms an oxime, a dinitrophenylhydrazone derivative and undergoes normal Cannizzaro reaction.

Properties of tricarbonylarenechromium complexes.

Tricarbonylarenechromium (and molybdenum) compounds are generally yellow to orange in colour and the chromium compounds are stable in air unless there are sensitive substituents in the benzene ring (such as -OH). The reaction between hexacarbonylchromium and arenes is facilitated by the presence of electron-releasing substituents, and retarded by electron-attracting and by bulky (Bu^t) substituents. Tricarbonyl-

(benzoic acid)chromium (pK 4.77 in 50% ethanol) is a considerably stronger acid than benzoic acid (pK 5.68) and only a little weaker than p-nitrobenzoic acid (pK 4.48). Tricarbonyl(phenylacetic acid)-chromium is almost as strong as p-nitrophenylacetic acid, and these results suggest that a $-Cr(CO)_3$ group bound to an aromatic ring withdraws electrons almost as much as a nitro group, and that it has also a steric effect comparable with that of a large ortho-substituent.[27]

The electrically positive character of the aromatic ring in these compounds hinders electrophilic substitution reactions and promotes nucleophilic reactions. For example, tricarbonylchlorobenzene-chromium can be converted into tricarbonylanisolechromium under very mild conditions and in good yield.[27]

Since the tricarbonylchromium group can be displaced from the arene by the reaction of the π-bonded complex with pyridine, tertiary arsines, tertiary phosphines[27] or diethylenetriamine[36] giving compounds like $(Ph_3P)_3Cr(CO)_3$ the possibility arises of attaching temporarily the π-bonded $Cr(CO)_3$ group to carry out otherwise impossible nucleophilic substitution reactions on aromatic compounds.[24]

The dipole moments of several of these π-bonded $Cr(CO)_3$ complexes have been measured;[78,37] they are large, and the benzene ring is the positive end of the dipole. Representative moments are given in Table II, and it can be seen that electron-releasing substituents on the benzene ring increase the overall dipole moment.

Table II

Dipole moments of AreneCr(CO)$_3$ compounds.

Arene	Dipole Moment
C_6H_6	5.08
$C_6H_5CH_3$	5.26
p-$C_6H_4(CH_3)_2$	5.52
1,3,5-$C_6H_3(CH_3)_3$	5.81
1,2,4,5-$C_6H_2(CH_3)_4$	6.04
$C_6(CH_3)_6$	6.48
$C_6H_5N(CH_3)_2$	6.30
Cycloheptatriene	4.52

Cycloheptatriene, apparently, has a lower donor character than benzene.

The tricarbonylarenechromium complexes all show two strong C-O stretching vibrations at 1980 and 1895 cm.$^{-1}$ [27,29,38,39,110] Ercoli and Mangini[40] have recorded the ultraviolet spectra of a series of these compounds and find three characteristic absorption areas, 315-325 mμ (logϵ 4.0), 250-270 mμ (logϵ = 3.7-4.0) and 220-230 mμ (logϵ = 4.3-4.8).

Tricarbonylbenzenechromium.

This compound is formed in 80% yield from hexacarbonylchromium and benzene in an autoclave at 210-240°C.[26] It forms bright yellow needles, m.p. 161.5-163°C., stable in air, but slowly decomposed in organic solvents to chromium oxide. X-ray analysis [41,111] indicated structure (V) for the molecule, in which the carbon atoms have a fixed position and are all equidistant (2.25 ± 0.05 Å) from the chromium atom. The plane in which the oxygen atoms are contained has been found to be parallel, within experimental error, to the benzene ring, the carbon and oxygen atoms of each CO group being collinear with the chromium atom, and the angles CO-Cr-CO very near to 90°.

Tricarbonylbenzenechromium has been acetylated[32,33] to give tricarbonylacetophenonechromium.

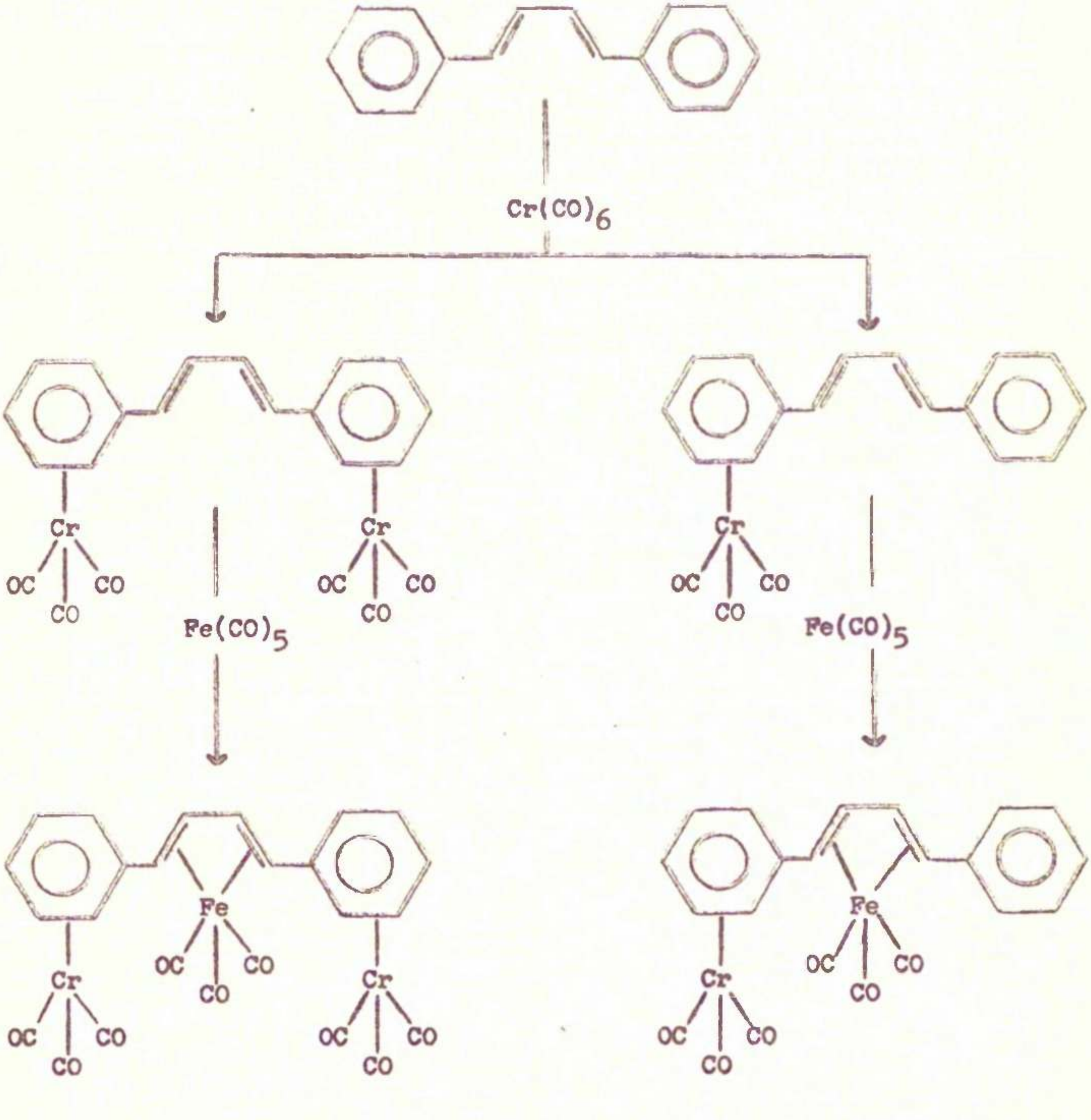
Arene exchange reactions of tricarbonylbenzenechromium with binuclear aromatics have led[42] to the synthesis of a series of bis(tricarbonylchromium)complexes:- Table III

Table III

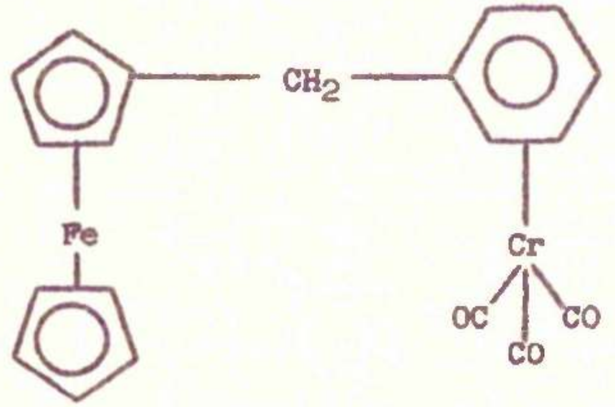
Binuclear aromatic compound	M.p.(°C).	Yield (%).
Ph-Ph	215-216	55
$H_2N-C_6H_4-C_6H_4-NH_2$	253-255	31
$Ph-CH_2-Ph$	216-217	24
Ph-NH-Ph	210-212	61
$Ph-CH_2-CH_2-Ph$	236-238	79
Ph-CH=CH-Ph	243-245	72

Miscellaneous benzenoid derivatives of chromium and molybdenum.

Cais and Feldkimel[43] and Stone, et al[15] have isolated mixed-metal complexes of chromium and iron by the following reactions:-



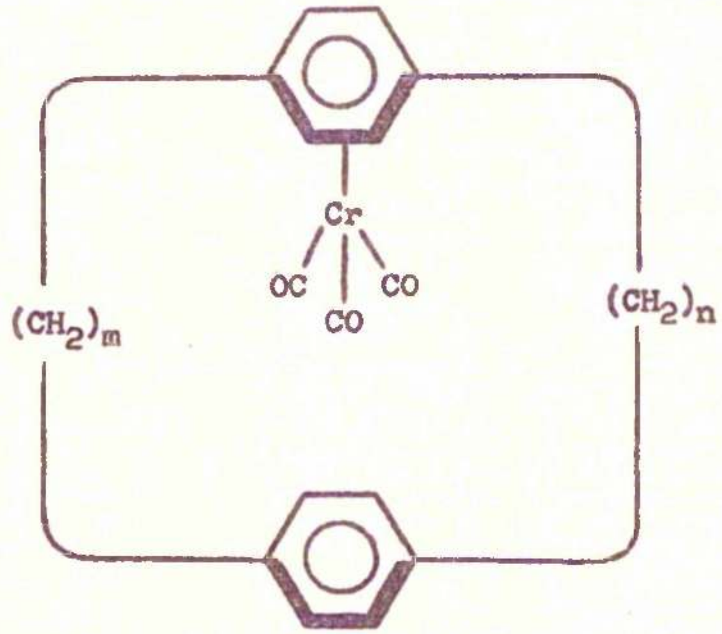
and also compound (VII) from hexacarbonylchromium and benzylferrocene,



(VII)

whilst Munro[56] has prepared an analogous compound from phenylferrocene.

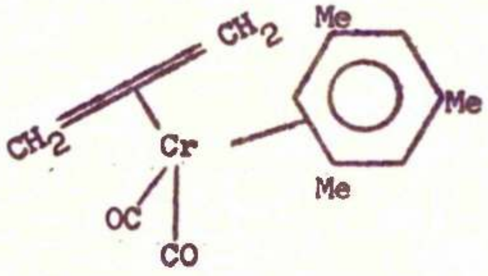
In an attempt to obtain paracyclophane analogues of bisbenzenechromium, Cram and Wilkinson[44] reacted hexacarbonylchromium with a series of paracyclophanes to yield compounds of type (VIII), in some cases having two $Cr(CO)_3$ residues in the molecule. However, they were unable to link two benzene rings through a chromium atom.



(VIII)

A variety of tricarbonylchromium complexes have been made from compounds having 2, 3 or 4 benzene rings fused together. Thus, naphthalene,[31] anthracene,[31] phenanthrene,[31,77] chrysene,[31] 9:10-dihydroanthracene[31] and a dihydrotetracene[34] have given tricarbonylchromium complexes. Other systems which have given tricarbonylchromium derivatives include indene,[48] fluorene,[48] thianaphthene,[77] acenaphthylene[77] and thiophene.[47]

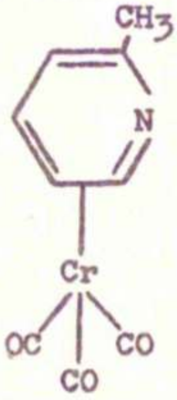
Fischer, et al[49,69] have also prepared the dicarbonyl compound (IX) which is unique in being the only chromium complex known in which the ligand is a simple olefin.



(IX)

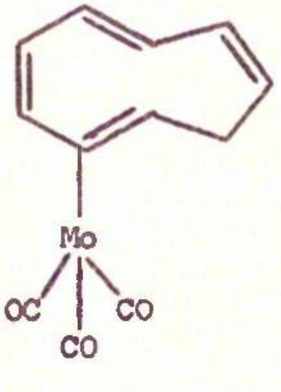
Tricarbonyl-N-(benzaldehyde-anil)chromium derivatives have been made[35] with the $Cr(CO)_3$ group on 1) the phenyl ring and 2) the aniline ring, and each of these has been hydrogenated to the corresponding benzylaniline complex.

By reaction of hexacarbonylchromium (or molybdenum) with methylpyridinium iodide, Fischer and Öfele[50,51] isolated the corresponding methylpyridinium(pentacarbonyliodo)metal complexes. Upon heating in vacuo., the chromium compound gave a low yield of the π-bonded tricarbonylmethylpyridinechromium (X).



(X)

Fischer and Fröhlich[75] have reported that hexacarbonylmolybdenum reacts with 1,3-cyclohexadiene to give a compound $(C_6H_8)_2Mo(CO)_2$, and King and Stone[76] reacted 8:9-dihydroindene with hexacarbonylmolybdenum to give a compound thought to be the cyclononatetraene derivative (XI)



(XI)

6:6'-Diphenylfulvene has given[53] a tricarbonylchromium derivative in which it is suggested that the tricarbonylchromium group is bound to one of the phenyl rings rather than the fulvene.

Strohmeier has recently reported[88] the results of kinetic studies on the synthesis of tricarbonylarenemolybdenum compounds of benzene, fluorobenzene, toluene and xylenes.

Chromium and molybdenum derivatives of miscellaneous olefins.

Table IV lists some of the olefins from which carbonylmetal complexes have been prepared:-

Table IV

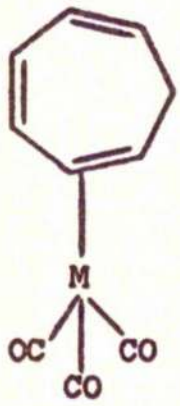
Olefin	Metal	No of CO groups displaced	Reference
cyclooctatriene	Cr	4	45,46
cyclooctatriene	Mo	3* or 4	45,46
5,6-dimethylenebicyclo(2,2,1)heptene-2	Cr	3	28
5,6-dimethylenebicyclo(2,2,1)heptene-2	Mo	3	28
1,5-cyclooctadiene	Cr	2	52
1,5-cyclooctadiene	Mo	2	80,82
norbornadiene	Cr	2	82
norbornadiene	Mo	2	79,81,82
bicyclo(2,2,2)octa2,5-diene	Mo	2	82
1,2-diphenylacrylonitrile	Mo	2	84
acrylonitrile	Mo	2	85

* this compound has been shown to be a tricarbonylmolybdenum derivative by its conversion, in boiling mesitylene, into tricarbonylmesitylenemolybdenum.[45]

Reaction of hexacarbonylmolybdenum with azulene, 4,6,8-trimethylazulene and guaiazulene has led to compounds formulated as $AzMo_2(CO)_6$. The structures of these compounds are unknown.[101,102]

Chromium and molybdenum derivatives of cycloheptatriene.

During an abortive attempt to prepare tricarbonyltropylium derivatives of chromium and molybdenum, Wilkinson, et al. isolated[54,55] a series of tricarbonylcyclohepta(1,3,5)triene derivatives of chromium and molybdenum. Recently, many more derivatives of these parent molecules (XII) have been prepared and Table V lists some of these.



(XII)

Structure (XII) is deduced not only from the red colour, but from the infrared spectrum which shows three intense carbonyl stretching modes as opposed to the two stretching modes shown by all the tricarbonylbenzenechromium (and molybdenum) compounds. Initially it was suggested[54,55] that the electrons of the six carbon atoms in the

Table V

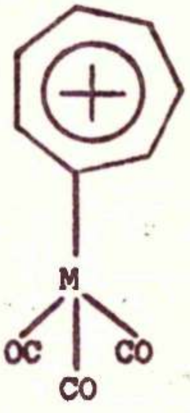
Some 7-substituted tricarbonylcycloheptatrienechromiums.

Substituent	Metal	M.p.(°C).	Reference
H	Cr	129 -130	54,55
H	Mo	101 -101.5	54,55
CH_3	Cr	72 - 73	54,55
CH_3	Mo	d 150	54,55
C_6H_5	Cr	-----	54,55
C_6H_5	Mo	d 150	54,55
C_7H_7 *	Cr	-----	54,55
C_7H_7 *	Mo	d 150	54,55
OCH_3	Cr	107 - 109	58,56
CN	Cr	118-119	58,56
$CH(COOC_2H_5)_2$	Cr	122-133	58-56
$C(CH_3)(COOC_2H_5)_2$	Cr	91- 92	58,56

* cyclohepta(1,3,5)trienyl.

plane of the ring were delocalised to form a quasi-aromatic system which by-passed the exo-methylene group and were π -bonded to the d-orbitals of the metal atom. However, recent nuclear magnetic resonance studies have led Wilkinson to retract this suggestion and state[55] that bonding is from three distinct sets of double bonds, and this is fully confirmed by detailed X-ray analysis[107] (for the molybdenum compound).

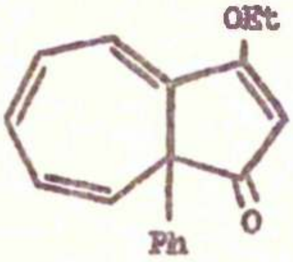
Treatment of tricarbonylcyclohepta(1,3,5)trienechromium (or molybdenum) (XII) with trityl salts has led [57,58,59] to the isolation of the much sought after tricarbonyltropyliumchromium (and molybdenum) cations (XIII, M = Cr or Mo).



(XIII)

The high symmetry and structure of (XIII, M = Mo) has been confirmed by the presence of only one proton resonance line in the N.M.R. spectrum of its solution in D_2SO_4.[59] The symmetrical tropylium cation has six π electrons which form an aromatic sextet and interact with the $Mo(CO)_3$ group in much the same way as do those of benzene.

A novel use of the tricarbonylchromium group in helping to determine structure has recently been published.[83] Reaction of a compound thought to have structure (XIV) with hexacarbonylchromium gave a compound having infrared absorption typical of a tricarbonylcyclohepta(1,3,5)-trienechromium derivative.



(XIV)

<u>Chromium and molybdenum derivatives of cyclopentadiene</u>.[93]

Biscyclopentadienechromium (XV, M = Cr) was first prepared[60] by

(XV)

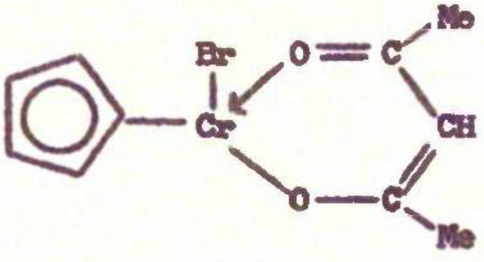
thermal decomposition of the hexamminechromiumcyclopentadienide $Cr(NH_3)_6(C_5H_5)_3$ and independently by reaction of hexacarbonylchromium with cyclopentadiene.[94] A better method is the action of cyclopentadienylsodium on either chromous or chromic chloride.[61] Although unattacked by water, it is decomposed by acids and is very sensitive to oxygen. The "chromocinium" cation $(C_5H_5)_2Cr^+$ is obtained by oxidation with iodine,[86] but is not stable in water. The reineckate and tetraphenylborate are known.[86] The analogous molybdenum compound (XV, M = Mo) is not known. Table VI lists some of the known cyclopentadienylmolybdenum compounds.

Table VI

Compound	Reference
$[(C_5H_5)_2Mo^{IV}Cl]^+$	89
$[(C_5H_5)_2Mo^{V}Cl_2]^+$	89
$(C_5H_5)_2MoCl_2$	89
$(C_5H_5)_2MoH_2$	90
$(C_5H_5)_4Mo$*	72

* this compound is thought to have one π-bonded cyclopentadienyl group and three σ-bonded cyclopentadiene groups.

An interesting monocyclopentadienylchromium compound (XVI) is formed[62] from chromium(III) acetylacetonate and one equivalent of cyclopentadienylmagnesium bromide in benzene. It is instantly hydrolysed in water.

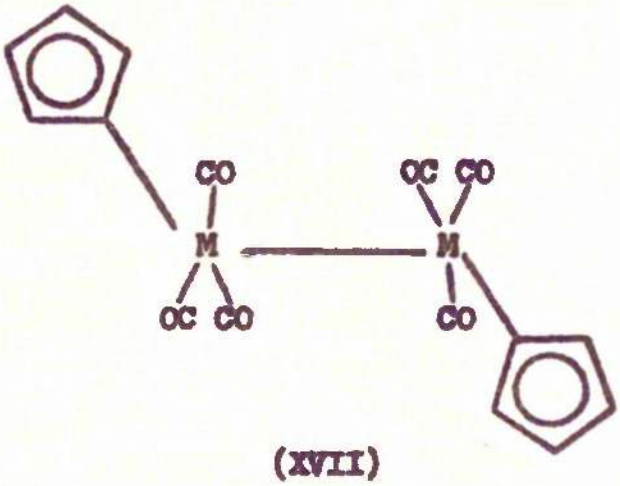


(XVI)

If carbon monoxide is allowed to react under pressure with biscyclopentadienylchromium, the first product formed, at 100-110°C is a salt

$$(C_5H_5)_2Cr \xrightarrow{CO} \left[(C_5H_5)_2Cr\right]^+\left[C_5H_5Cr(CO)_3\right]^-$$

At 150-170°C., the further action of carbon monoxide results in formation of the dimeric carbonyl[63] (XVII, M = Cr).



(XVII)

This structure has been confirmed for M = Mo by X-ray analysis.[64,103] The temperature dependence of the proton magnetic resonance spectrum shows that rotation of the cyclopentadienyl rings begins about 100°K. and is then practically free.[98]

(XVII, M = Cr and Mo), and a variety of substituted cyclopentadiene derivatives, in the case where M = Mo, have also been obtained[65,95,96,97] from fulvenes and the metal carbonyls and by the following series of reactions:-

$$\begin{tikzcd}
C_5H_5Na + Cr(Mo)(CO)_6 \arrow[r] & \underset{\text{(XVIII)}}{Na[C_5H_5Cr(Mo)(CO)_3]} \arrow[dl, "HX"'] \\
{[C_5H_5Cr(Mo)(CO)_3]H} &
\end{tikzcd}$$

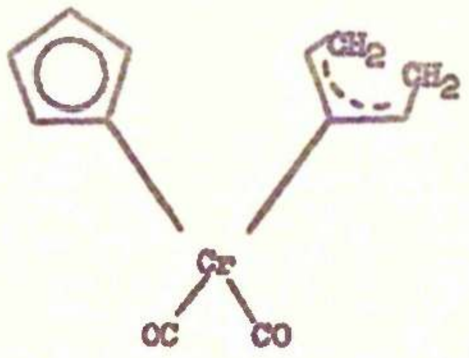
$$[C_5H_5Cr(CO)_3]H \xrightarrow[-H_2]{\text{heat}} [C_5H_5Cr(CO)_3]_2$$

(XVII)

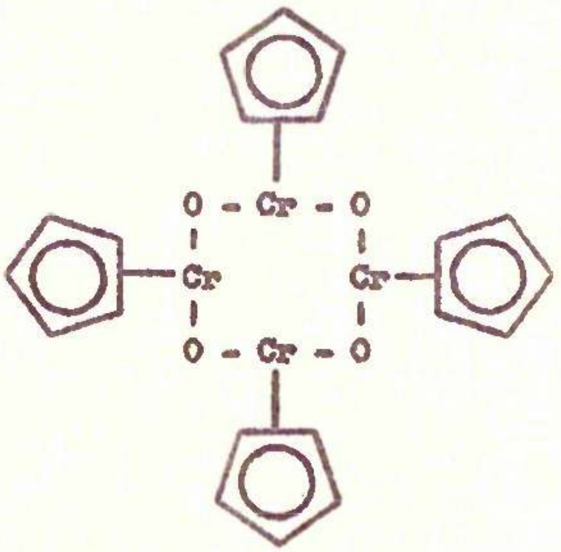
Treatment of (XVIII) with alkyl halides leads to σ-bonded alkyl derivatives e.g., methyl, ethyl and isobutyl compounds for M = Mo[91] and methyl for M = Cr.

Amongst the other interesting cyclopentadienylchromium and molybdenum compounds which have been made are (XIX) - (XXIII) made by Fischer and co-workers[66-70]

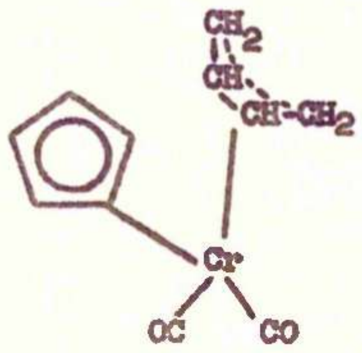
(XIX)



(XX)



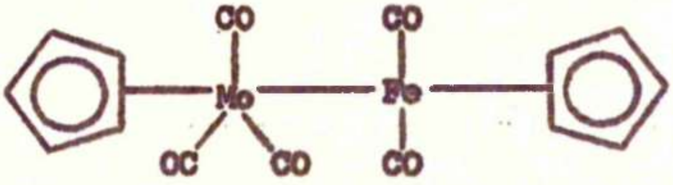
(XXI)



(XXII)

(XXIII)

and the mixed-metal bonded complex (XXIV) made[104] from sodiumtricarbonylcyclopentadienylmolybdenum and (dicarbonylcyclopentadienyliron) iodide in tetrahydrofuran.



(XXIV)

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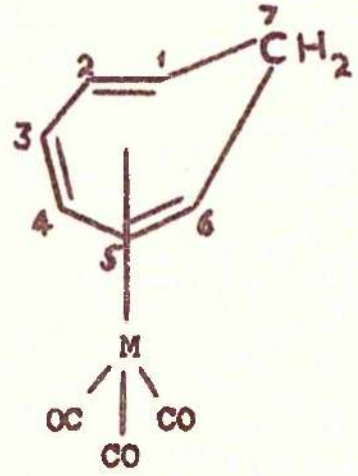
DISCUSSION

PAGE NO

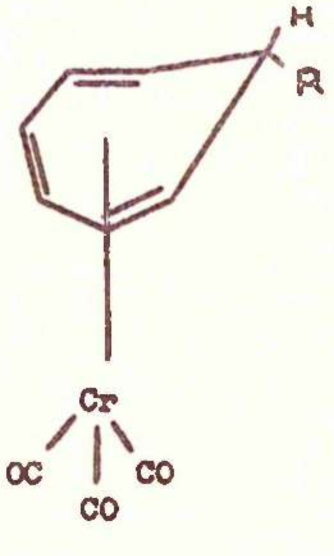
Geometrical stereoisomers of mono-7-substituted tricarbonylcyclohepta-(1,3,5)trienechromium.

The tricarbonylcyclohepta(1,3,5)trienechromium molecule can be assumed to have structure (XXV, M = Cr),

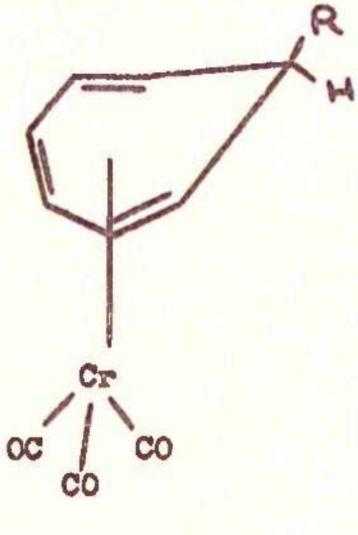


(XXV)

by analogy with the corresponding molybdenum compound whose structure has been shown to be (XXV, M = Mo) by X-ray analysis.[107] It is therefore apparent that mono-7-substituted, [for numbering see (XXV)], derivatives might exist in two geometrically isomeric forms: (XXVI) and (XXVII).



(XXVI)



(XXVII)

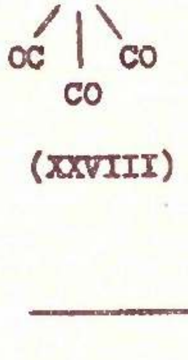
At the beginning of the work described in this thesis, various mono-7-substituted derivatives of (XXV) had been prepared (Table V), but no suggestion had been made as to the configuration of these compounds. It was therefore decided to attempt to characterise the structures of the known compounds and to synthesise pairs of isomers having structures (XXVI) and (XXVII).

Two general methods have previously been used in the preparation of mono-7-substituted derivatives of (XXV), and these are illustrated by equations 1 and 2.

The first method[54,55] involved heating the metal carbonyl with a 7-substituted cycloheptatriene under reflux, or in a suitable solvent:-

$$C_7H_7R \quad + \quad Cr(CO)_6 \quad \longrightarrow \quad C_7H_7RCr(CO)_3 \quad + \quad 3\,CO \;....1$$

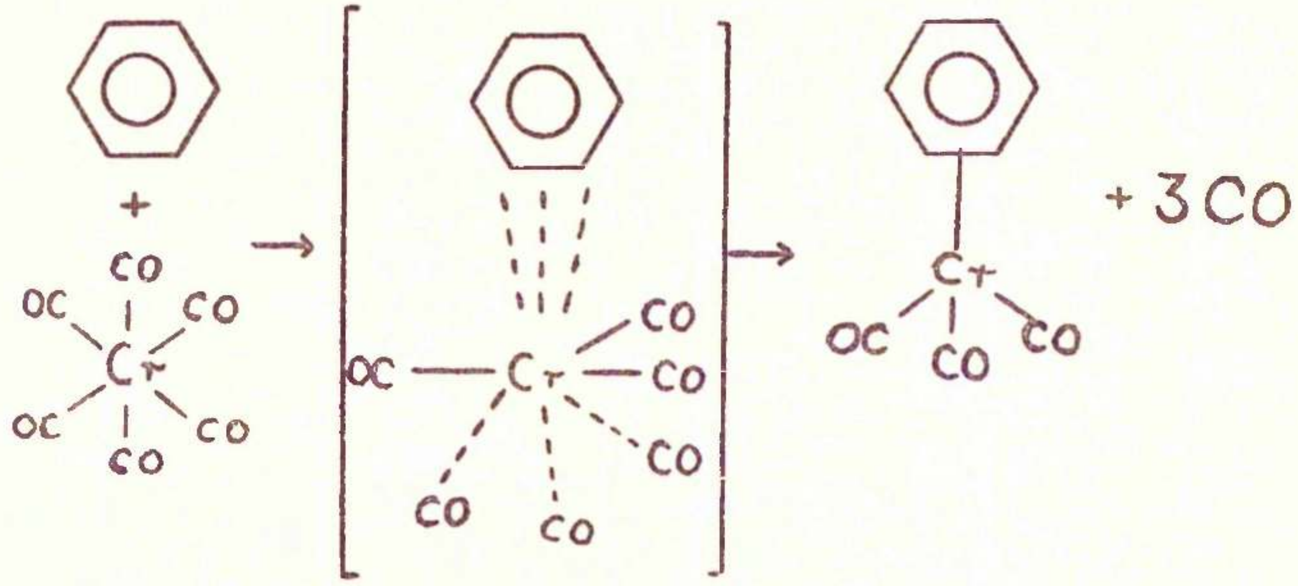
The second method[56,58] involved reaction of the tricarbonyltropyliumchromium cation (XXVIII) with suitable anions:-



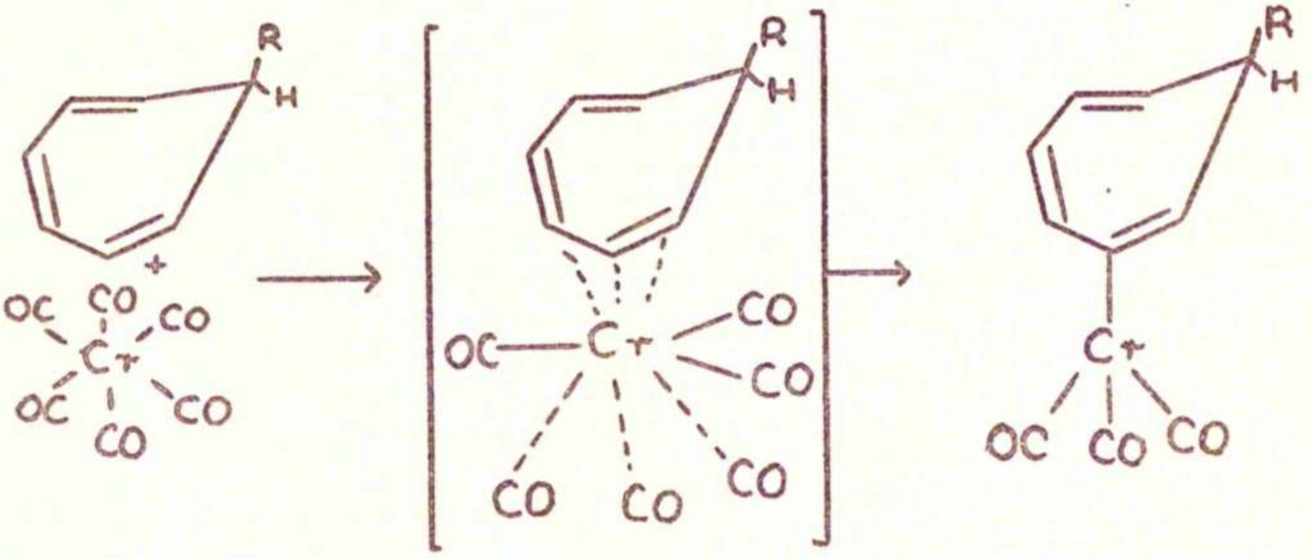
(XXVIII)

$$C_7H_7Cr(CO)_3{}^{+} \quad + \quad R^{-} \quad \longrightarrow \quad C_7H_7RCr(CO)_3 \;..............2$$

Fischer[24] and Whiting[117] have suggested that reaction of substituted benzenes with hexacarbonylchromium occurs by a "broadside" attack accompanied by an intramolecular shift and extrusion of carbon monoxide groups, represented diagramatically as follows:-



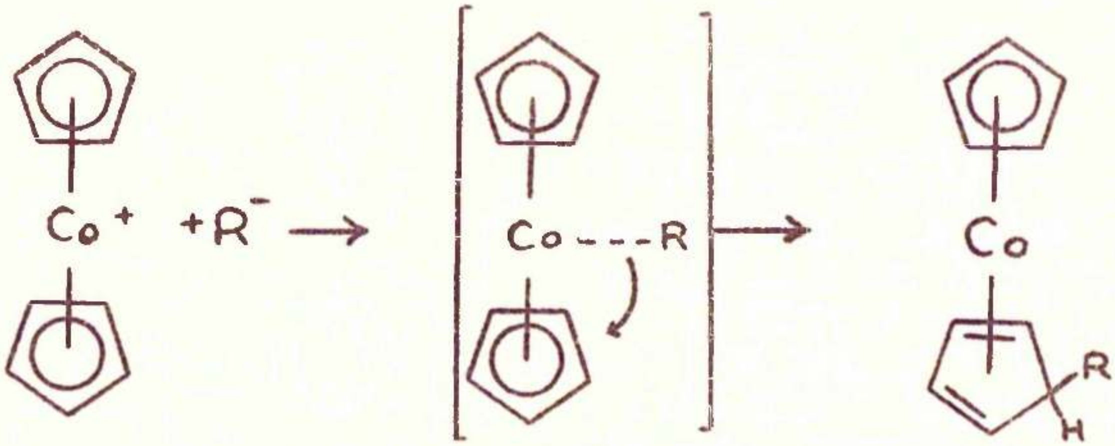
It seems reasonable to assume that mono-7-substituted cycloheptatrienes should react with hexacarbonylchromium in a similar manner, steric factors assuring that the product is the 'exo' isomer (XXVII):-



In no case has it been observed that reaction of a mono-7-substituted cycloheptatriene with hexacarbonylchromium leads to more than one isomer, and it is therefore proposed that such a reaction leads normally to the exo-substituted product.

A parallel to reaction 2 can be found in the reaction of cobaltocinium salts with anionic reagents. Green, Pratt and Wilkinson[112] and Fischer and Herberich[119] have prepared various endo-substituted derivatives of cyclopentadienylcyclopentadienecobalt (XXIX) by nucleophilic attack on cobaltocinium salts, e.g. with deuteride ion and by the reaction of various halides, e.g. methyl iodide, with cobaltocene. The former authors[112] have presented evidence that the incoming group occupies the endo position, base mainly on the nuclear magnetic resonance spectra of the products. Thus, in the methylcyclopentadienecyclopentadienylcobalt compound (XXIX, R = Me) the proton resonance of the methyl group occurs at a high τ value (9.77) compared with normal aliphatic methyl protons. This is accounted for by assuming that the extra shielding resulting in this upfield shift is due to the proximity of the metal atom, which would not be the case if the group were in the exo configuration.

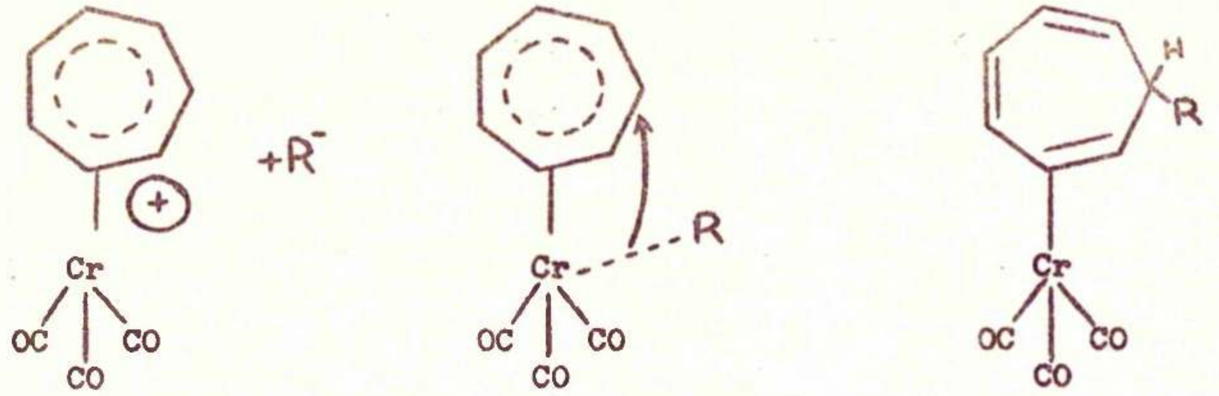
A mechanism to account for the reactions is not given by Wilkinson, et al.[112] However, in a footnote to a paper dealing with the stabilization of carbonium ions by metallocenes, Hill and Richards[118] suggest that the mechanism probably involves initial attack of the methyl group on the free electrons of the metal followed by an intramolecular shift to give the desired compound. This type of mechanism may be represented diagramatically as follows:-



(XXIX)

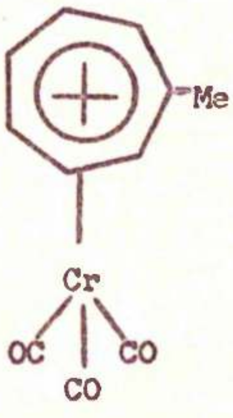
In further experiments, Jones and Wilkinson[120] and Green, Pratt and Wilkinson[113] obtained endo-substituted products by reaction of lithium aluminium deuteride with $[C_6H_6(C_5H_5)Fe]I$ and of phenyllithium with $[C_6H_6Mn(CO)_3]^+ ClO_4$ and with $[C_6H_6(C_5H_5)Fe]Br_3$. They observed that the product from the latter reaction, namely endo-phenylcyclohexadienylcyclopentadienyliron(II), $(C_6H_5\text{-}C_6H_5)Fe(C_5H_5)$ showed a phenyl proton resonance in the nuclear magnetic resonance spectrum at a τ value of 3.25, again a relatively high value for this type of proton, and accounted for by the shielding effect of the metal atom.

In view of these results, it seems probable that reaction of the tricarbonyltropyliumchromium cation with anions takes the following course, leading solely to the endo-substituted isomer. The positive charge on the cation is presumed to be distributed between the ring carbon atoms and the metal atom.



Experiments by Munro and Pauson[56,58] and to be described in this thesis, involving anionic addition to tricarbonyltropyliumchromium (and molybdenum) cations, gave in all cases only a single product. It will be shown that these products have different properties from the isomeric products formed by the direct reaction of the corresponding substituted cycloheptatriene with the metal carbonyls, and N.M.R. data are given in support of the suggestion just made regarding the configuration of these compounds.

Reaction of 7-methylcycloheptatriene[54] with hexacarbonylchromium under Wilkinson's conditions[54,55] gave a single product formulated as tricarbonyl-7-exo-methylcyclohepta(1,3,5)trienechromium, [(XXVII), R = Me]. This compound was converted into tricarbonylmethyltropyliumchromium fluoroborate (XXX), by hydride abstraction using triphenylmethyl fluoroborate

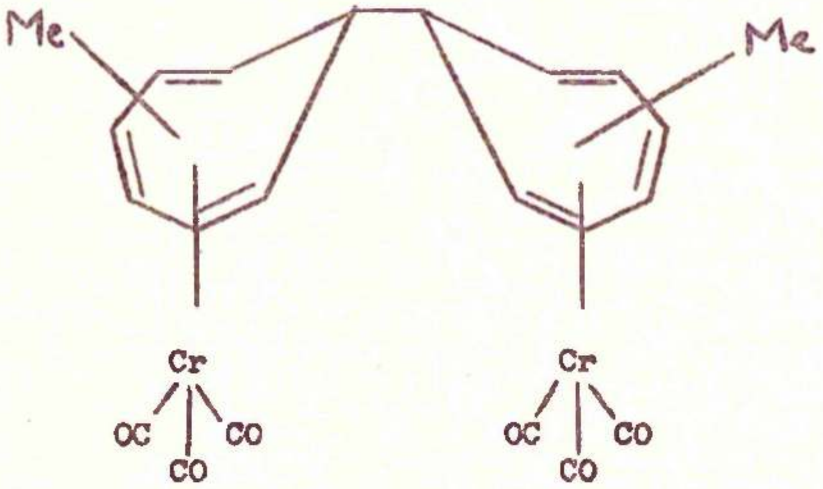


(XXX)

and this was treated with sodium borohydride in an attempt to see if the sequence $-H^-/+H^-$ would give a) a new isomer or b) the starting methyl compound.

The reaction product was a deep-red oily substance which was separated, by chromatography on alumina, into a non-crystalline fraction and a red crystalline compound.

To eliminate the possibility that the crystalline compound was of a type (XXXI), resulting from the reducing action of the borohydride,

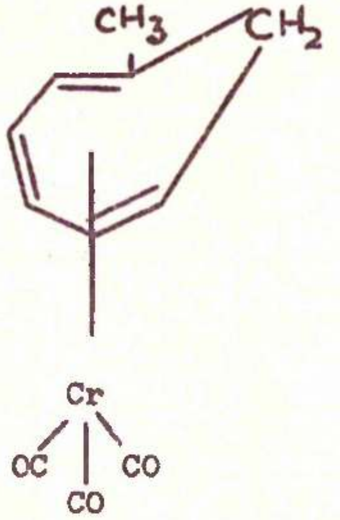


(XXXI)

tricarbonylmethyltropyliumchromium fluoroborate (XXX) was treated with zinc dust. This gave a compound whose properties were more similar to those expected of a compound of type (XXXI), viz. low solubility in organic solvents and high m.p., than those of the borohydride reaction product.

The low solubility of this zinc dust reduction product, in organic solvents, has precluded its study by nuclear magnetic resonance and the positions of the methyl groups are not known.

A study of the N.M.R. spectrum (No 2, page 40) of this borohydride reaction product indicated that it probably has the structure (XXXII), tricarbonyl-1-methylcyclohepta(1,3,5)trienechromium.



(XXXII)

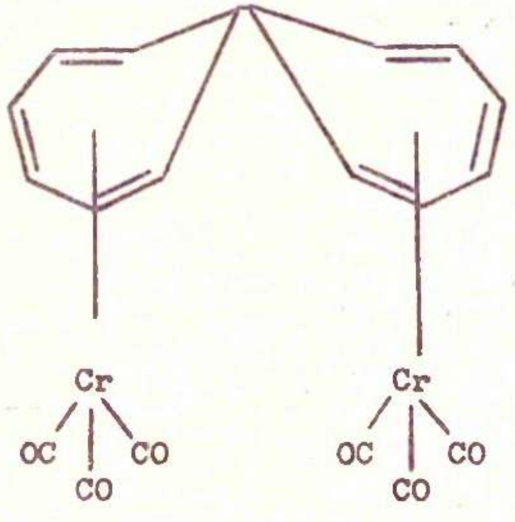
The singlet at τ = 8.03 is clearly due to the methyl protons, and this methyl group must be on position 1,2 or 3, since a doublet would be expected if the group were at position 7. The relative intensities of the 3,4 2,5 and 1,6 protons, relative to those in the parent compound tricarbonylcyclohepta(1,3,5)trienechromium[82] (No 1, page 40), together with the relative disturbances of these groups suggest that the methyl group is at position 1.

Structure (XXXII) is in harmony with recently published[115] work by Conrow who treated methyltropylium salts with sodium borohydride and obtained a mixture of the four expected position isomers in the following ratio:-

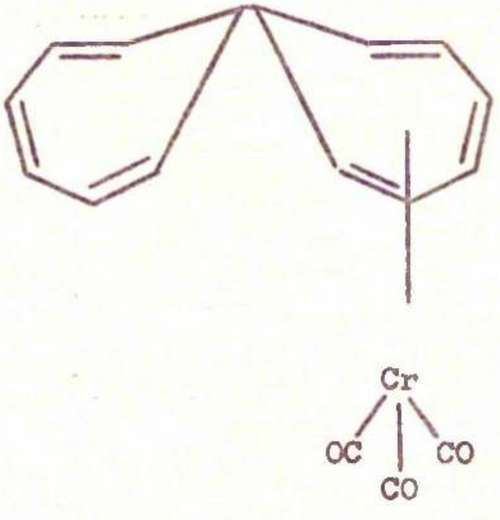
Isomer	1	2	3	7
%. formed	60	20	15	2.5

The non-crystalline material from the reaction of sodium borohydride with tricarbonylmethyltropyliumchromium fluoroborate is thus probably a mixture of 2,3 and 7 position isomers.

The action of methyllithium on tricarbonyltropyliumchromium fluoroborate gave the two di(cycloheptatrienyl) compounds (XXXIII) and (XXXIV), by the 'abnormal'route,[56,114] whilst reaction of methylmagnesium



(XXXIII)



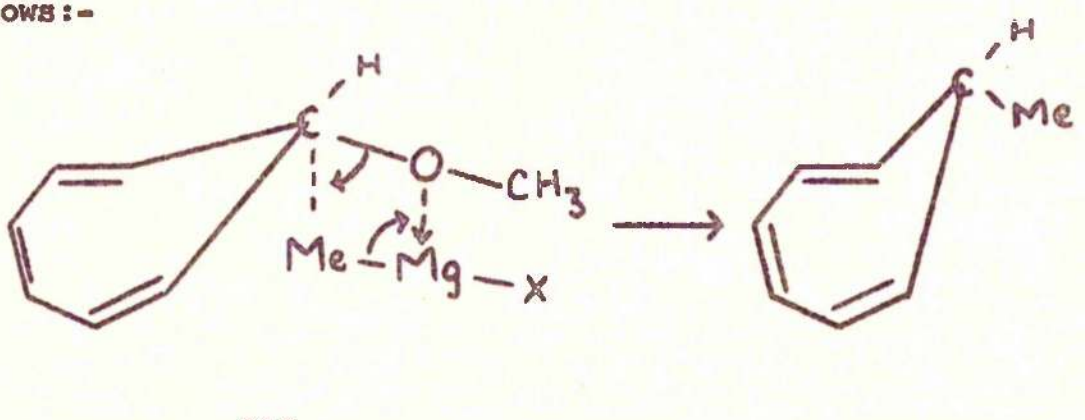
(XXXIV)

iodide gave the required tricarbonyl-7-endo-methylcyclohepta(1,3,5)-trienechromium [(XXVI), R = Me] in 13% yield.

Conrow had reported[115] that reaction of methylmagnesium iodide with 7-ethoxycyclohepta(1,3,5)triene gives a quantitative yield of

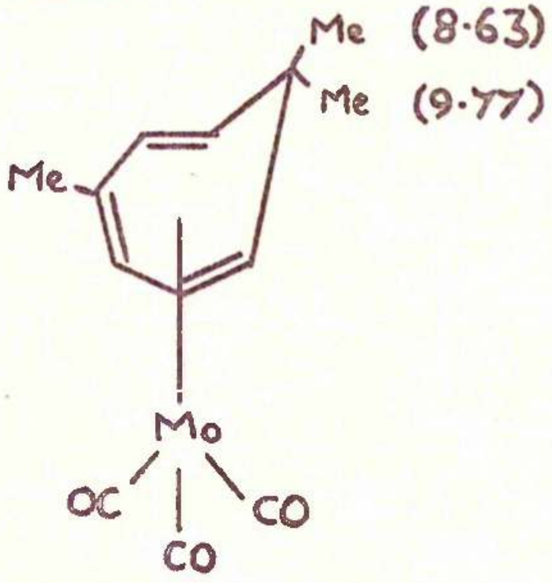
7-methylcycloheptatriene, uncontaminated with 1,2 or 3 position isomers. Since tricarbonyl-7-endo-methoxycycloheptatrienechromium [(XXVI), R = OMe] had been made previously by the action of sodium methoxide on tricarbonyltropyliumchromium salts[56,58] it was decided to react this compound with methylmagnesium iodide. The main product, formed in 80% yield was again tricarbonyl-7-endo-methylcycloheptatrienechromium.

Conrow[115] does not suggest a mechanism for the reaction of the Grignard reagent with 7-ethoxycycloheptatriene. However, it seems reasonable to assume that the mechanism involves a four-centered cyclic attack by the Grignard reagent on the alkoxyl group with (in the case where there is a $Cr(CO)_3$ residue) retention of configuration. It is not known at which point the incoming methyl group becomes attached, although it should be possible to clarify this point by the use of suitably labelled reactants. The proposed mechanism can be illustrated as follows:-



Wilkinson has stated[112] that in the cyclopentadienylcyclopentadienecobalt compounds (XXIX), the substituent group, and the groups replacing it are probably in the endo configuration. Thus, by an extension of this statement to cover exo and endo derivatives of tricarbonyl-7-substituted cycloheptatrienechromiums it seemed probable that whereas the 7-exo-methyl derivative should react with triphenylmethyl fluoroborate to yield the corresponding tricarbonylmethyltropyliumchromium cation (and this does in actual fact occur), the 7-endo-methyl compound should not react with triphenylmethyl salts.

Upon treatment of tricarbonyl-7-endo-methylcycloheptatrienechromium with triphenylmethyl fluoroborate, the chromium complex was recovered unchanged in 78% yield, and no trace of triphenylmethane was found. Unequivocal proof of the structure of the 7-endo-methyl compound came from a study of the nuclear magnetic resonance spectrum, (No 4, page 40). The methyl proton resonance occurred at a τ value of 10.2., which high value is attributable only to metal-proton interaction and consequent shielding by the metal atom. Comparison with the spectrum of the 7-exo-methyl compound (No 3, page 40) showed the latter to have methyl proton absorption at $\tau = 8.45$, in accordance with Wilkinson's assignments [82] for the endo ($9.77\,\tau$) and exo ($8.63\,\tau$) 7-methyl groups in the similar molybdenum compound (XXIVa)



(XXIVa)

Similarly, the product formed by reaction of sodium methoxide and tricarbonyltropyliumchromium salts was shown to have the endo configuration from its nuclear magnetic resonance spectrum (No10, page 42) the methyl proton resonance occurring at a τ value of 7.2, which is quite high for methyl protons in such an environment (usually 6.2 - 6.3τ),[145] and which is again explainable on the basis of shielding by the metal atom.

In attempts to prepare tricarbonyl-7-exo-methoxycycloheptatrienechromium, 7-methoxycycloheptatriene was treated with hexacarbonylchromium and with tricarbonylcycloheptatrienechromium but in each case decomposition occurred with scission of the metal-ring bond.

Wilkinson and co-workers had reported[54,55] that reaction of phenylcycloheptatriene[116] with hexacarbonylchromium gives a compound formulated as tricarbonylphenylcycloheptatrienechromium. The only properties of the compound to be published were the three metal-carbonyl stretching frequencies in the infrared. Repetition of the reaction by Munro[56,58] afforded a low yield of a substance which melted over 7 degrees. It was concluded[56,58] that this substance was probably a mixture of several isomers.

Reaction of phenylmagnesium bromide with tricarbonyl-7-endo-methoxycycloheptatrienechromium gave tricarbonyl-7-endo-phenylcyclohepta(1,3,5)trienechromium [(XXVI), R = Ph] in 95% yield. The compound was homogeneous, highly crystalline and possessed a sharp melting point. It was also obtained (in only 7% yield) by the reaction of phenylmagnesium bromide with tricarbonyltropyliumchromium fluoroborate.

The phenyl proton resonance occurred at a τ value of 3.53 in the nuclear magnetic resonance spectrum (No 9, page 42), which value is abnormally high for phenyl group protons in most organic molecules. It should be compared, however, with the value of $\tau = 3.25$ in (C_6H_5-C_6H_5)Fe(C_5H_5)[120] and $\tau = 3.2$ in C_5H_5Co(C_5H_5-endo-Ph),[119] and hence it seems highly probable that our compound is the endo-phenyl derivative.

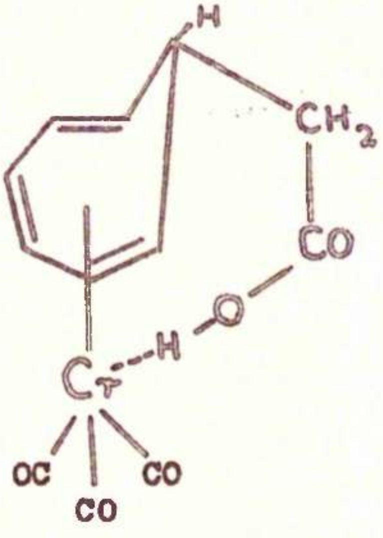
In the study of the rearrangement to tricarbonylbenzenechromium of certain tricarbonylcycloheptatrienechromium derivatives (part 2 of this discussion), Munro had prepared tricarbonyl-7-endo-di(ethoxycarbonyl)-methylcycloheptatrienechromium [(XXVI), R = CH($COOEt)_2$], by reaction of diethylsodiomalonate with tricarbonyltropyliumchromium perchlorate. It was therefore decided to try and obtain the corresponding exo-isomer by direct reaction of 7-di(ethoxycarbonyl)methylcycloheptatriene[121] with hexacarbonylchromium. The expected product, tricarbonyl-7-exo-di(ethoxycarbonyl)methylcycloheptatrienechromium, [(XXVII), R = CH($COOEt)_2$] was isolated in 50% yield.

In view of its possibilities as a model rearrangement compound tricarbonyl-7-exo-(ethoxycarbonyl)methylcycloheptatrienechromium, [(XXVII), R = CH_2COOEt], had been prepared by direct reaction of 7-(ethoxycarbonyl)methylcycloheptatriene[121] with hexacarbonylchromium. Attempts were made to prepare the corresponding endo-derivative by means of a pseudo Reformatsky[122] reaction using zinc and ethyl bromoacetate upon tricarbonyltropyliumchromium fluoroborate and tricarbonyl-7-endo-methoxycycloheptatrienechromium, similar to the above-mentioned

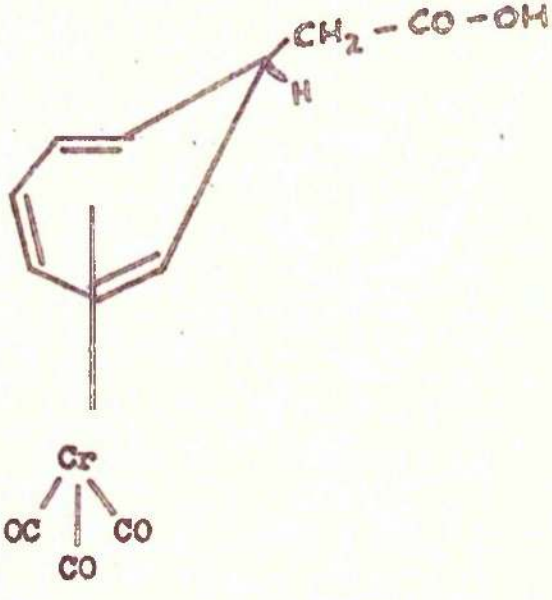
Grignard reactions. By using rigorously purified materials, the required compound, tricarbonyl-7-endo-(ethoxycarbonyl)methylcyclohepta-(1,3,5)trienechromium [(XXVI), R = CH_2COOEt] was finally prepared from zinc turnings, ethyl bromoacetate and tricarbonyl-7-endo-methoxycycloheptatrienechromium in tetrahydrofuran, in 88% yield.

The nuclear magnetic resonance spectra of the two malonate and the two acetate complexes (Nos 5-8, page 41) show the same displacements of chemical shifts, but the spectra are so complex that detailed assignments could not be made.

Alkaline hydrolysis of tricarbonyl-7-endo-(ethoxycarbonyl)methylcycloheptatriene chromium gave tricarbonyl-7-endo-carboxymethylcyclohepta(1,3,5)-trienechromium in 93% yield. Determination of the pK value of this acid and of the corresponding exo-acid, might add further confirmation as to the configurations assigned to these compounds, provided that the endo-acid has structure (XXXV) and that the exo-isomer has structure (XXXVI)



(XXXV)

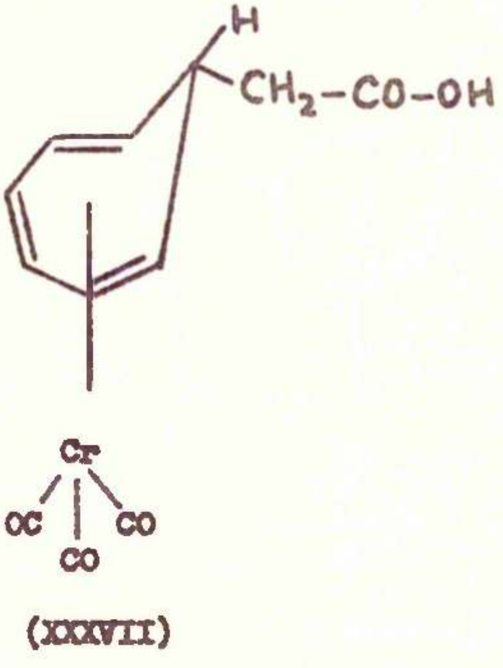


(XXXVI)

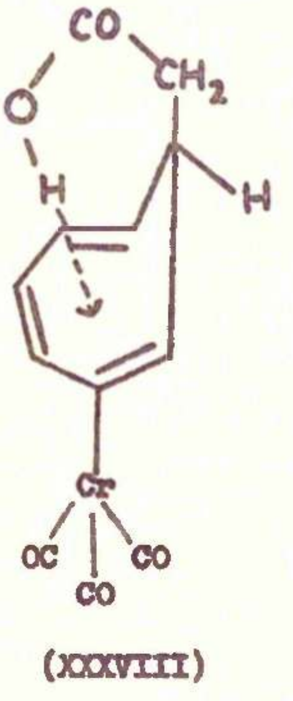
for whereas (XXXVI) would be expected to be a slightly stronger acid than acetic acid, the tricarbonylchromium group having been shown[27] to be powerfully electron-withdrawing, the possibility of interaction between the hydroxyl hydrogen and the chromium atom in (XXXV) would tend to make (XXXV) a weaker acid than acetic acid.

Signifigant differences in hydroxyl absorption in the infrared have been noted[118,123] for similar exo and endo isomeric alcohols in the ferrocene series.

However, there is the possibility that the endo-acid could have the structure (XXXVII) and the exo-acid could have structure (XXXVIII) where back-bonding with the π electrons of the ring might lead to a reversal of the results.



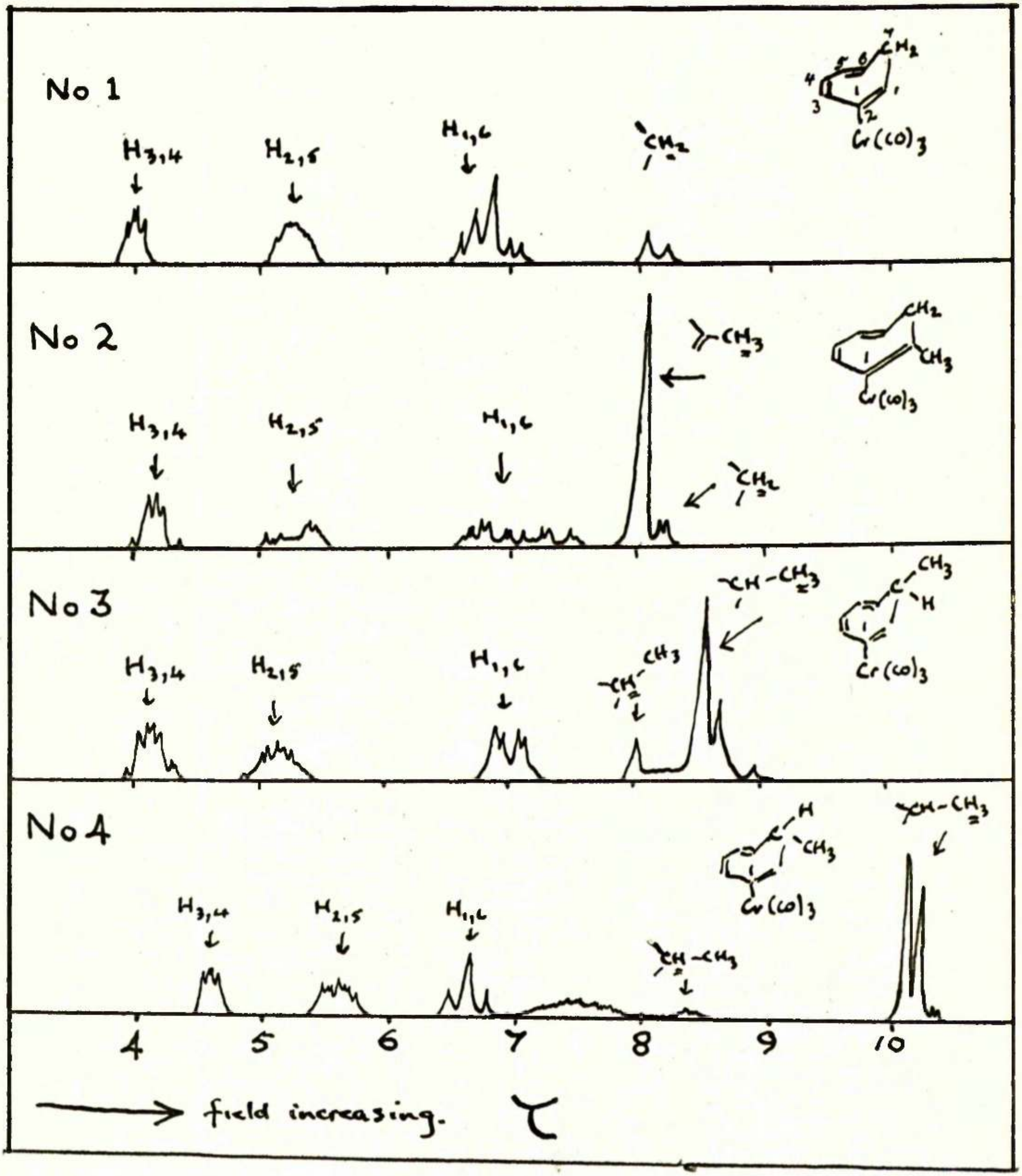
(XXXVII)

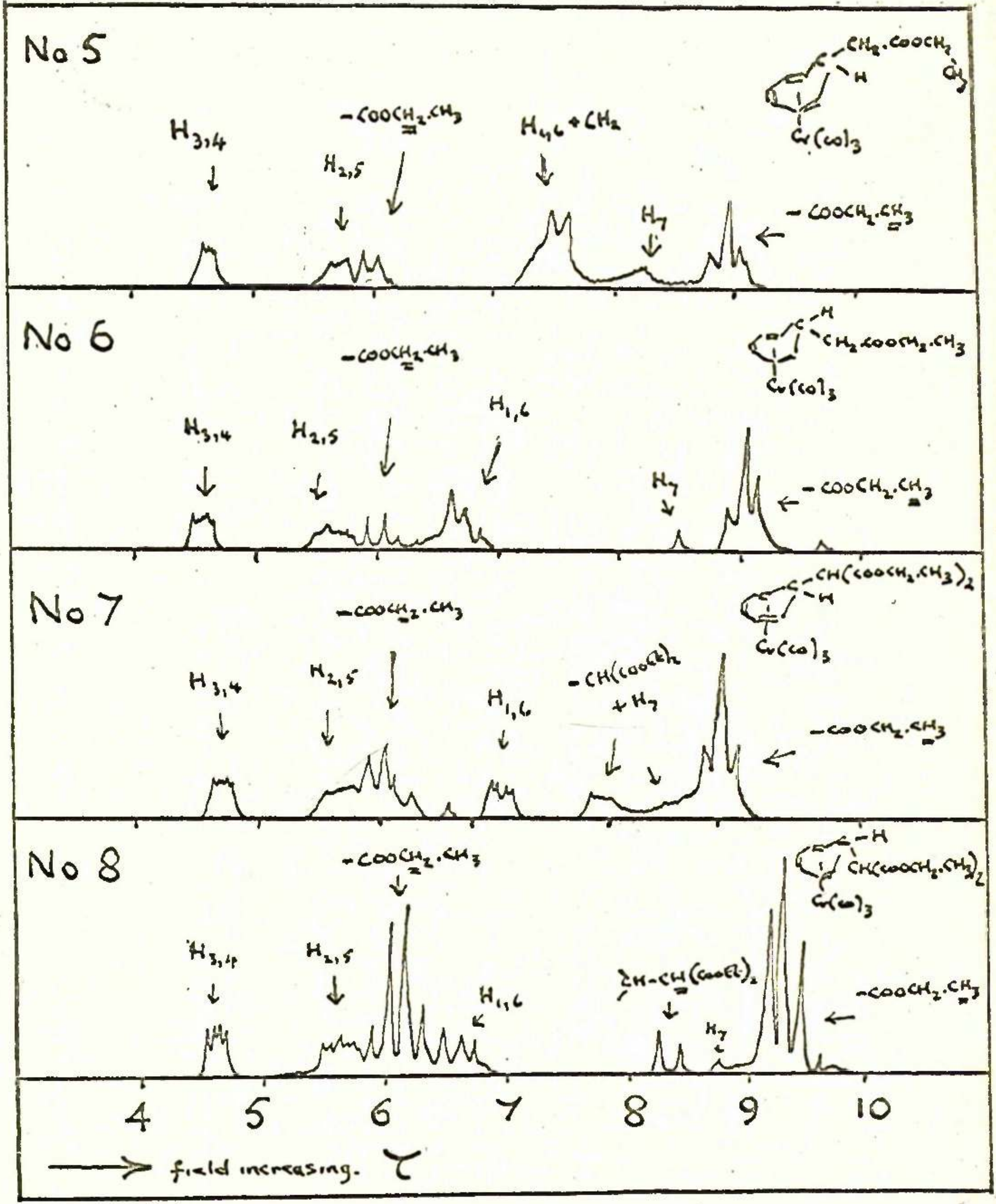


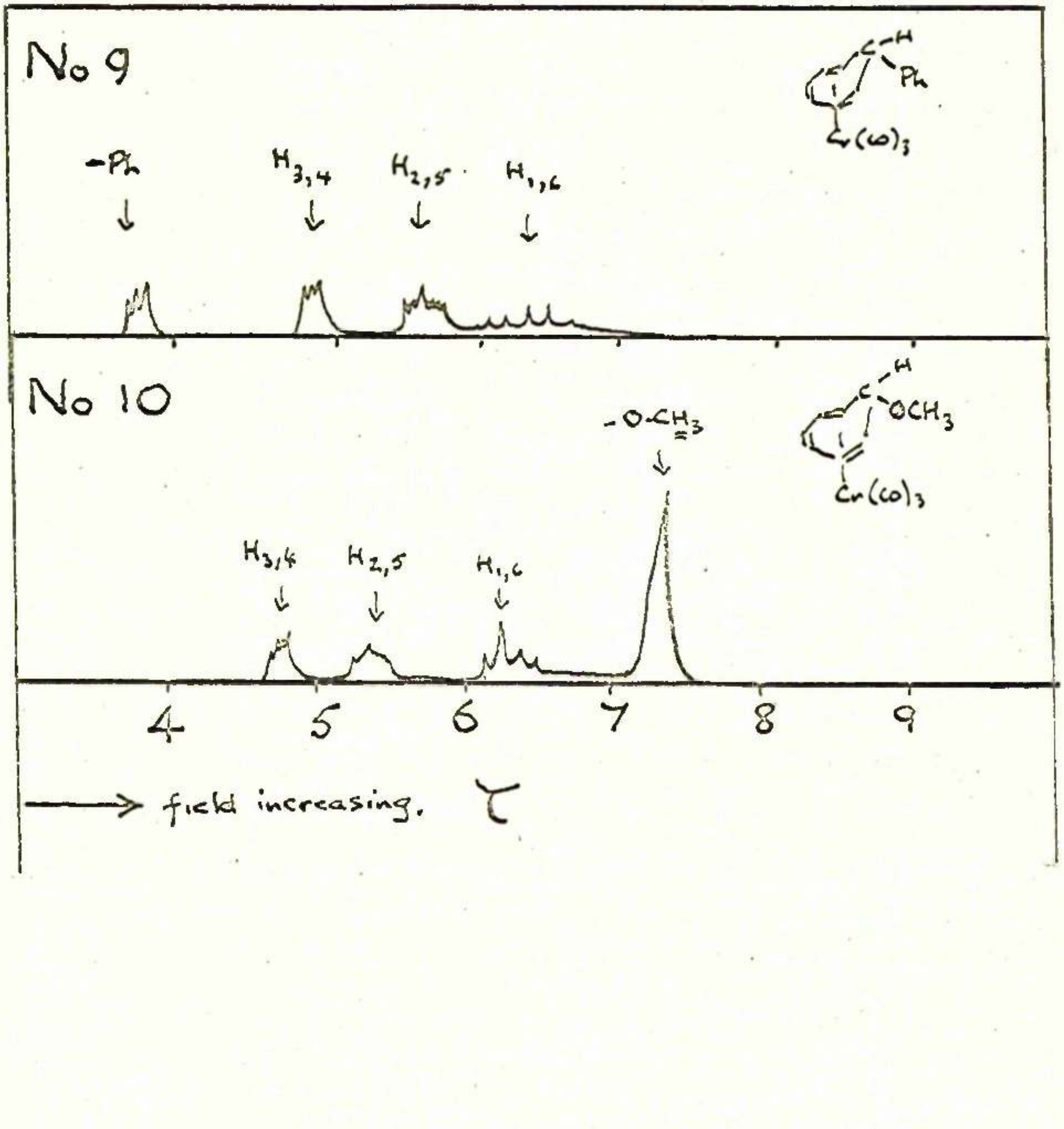
(XXXVIII)

NUCLEAR MAGNETIC RESONANCE SPECTRA.

Relevant spectra are shown overleaf. No. 1. is taken from the results of Wilkinson et al[82] and, like Nos 2 and 3, was obtained as CCl_4 solution using tetramethylsilane as internal reference, on a Varian Associates machine at Imperial College, London. Nos 4 - 10 were obtained as a benzene solution and were calibrated using the appropriate side-band of benzene. The difference in position of $H_{3,4}$ in Nos 1 - 3 from the position in Nos 4 - 10 is probably due to solution effects. Spectra Nos 4 - 10 were obtained on an A.E.I. machine at Glasgow University.


No 1
H3,4
H2,5
H1,6
CH2
7
1
2
3
4
5
6
Cr(CO)3
No 2
H3,4
H2,5
H1,6
CH3
CH2
Cr(CO)3
No 3
H3,4
H2,5
H1,6
CH–CH3
CH3
H
Cr(CO)3
No 4
H3,4
H2,5
H1,6
CH–CH3
H
CH3
Cr(CO)3
4
5
6
7
8
9
10
field increasing.
τ


No 5
$H_{3,4}$
$H_{2,5}$
$-COOCH_2.CH_3$
$H_{1,6} + CH_2$
H_7
$-COOCH_2.CH_3$
$CH_2.COOCH_2CH_3$
H
$Cr(CO)_3$
No 6
$-COOCH_2.CH_3$
$H_{3,4}$
$H_{2,5}$
$H_{1,6}$
H_7
$-COOCH_2.CH_3$
H
$CH_2.COOCH_2.CH_3$
$Cr(CO)_3$
No 7
$-COOCH_2.CH_3$
$H_{3,4}$
$H_{2,5}$
$H_{1,6}$
$-CH(COOEt)_2$
$+ H_7$
$-COOCH_2.CH_3$
$CH(COOCH_2.CH_3)_2$
H
$Cr(CO)_3$
No 8
$-COOCH_2.CH_3$
$H_{3,4}$
$H_{2,5}$
$H_{1,6}$
$\geq CH-CH(COOEt)_2$
H_7
$-COOCH_2.CH_3$
H
$CH(COOCH_2.CH_3)_2$
$Cr(CO)_3$
4
5
6
7
8
9
10
field increasing.
τ


No 9
C-H
Ph
Cr(CO)3
-Ph
H3,4
H2,5
H1,6
No 10
C-H
OCH3
Cr(CO)3
-O-CH3
H3,4
H2,5
H1,6
4
5
6
7
8
9
→ field increasing.
τ

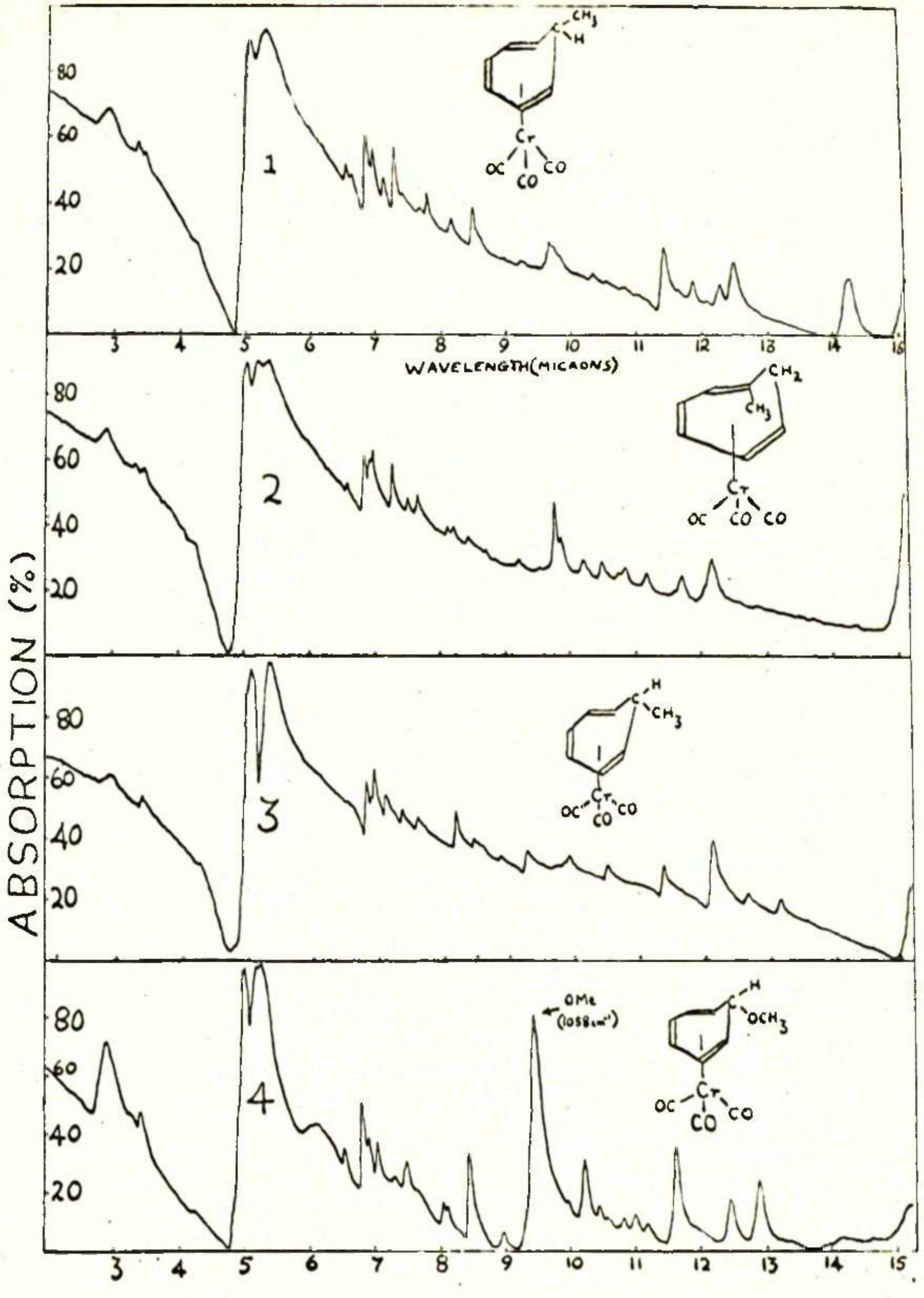
INFRARED SPECTRA

Representative spectra are shown on pages 43 and 44.

All were obtained as approx. 1.5 % KCl discs.

The intense metal carbonyl absorption at 5.0 - 5.5 microns was resolved by dilution of the samples and re-recording the spectra over that wavelength range.

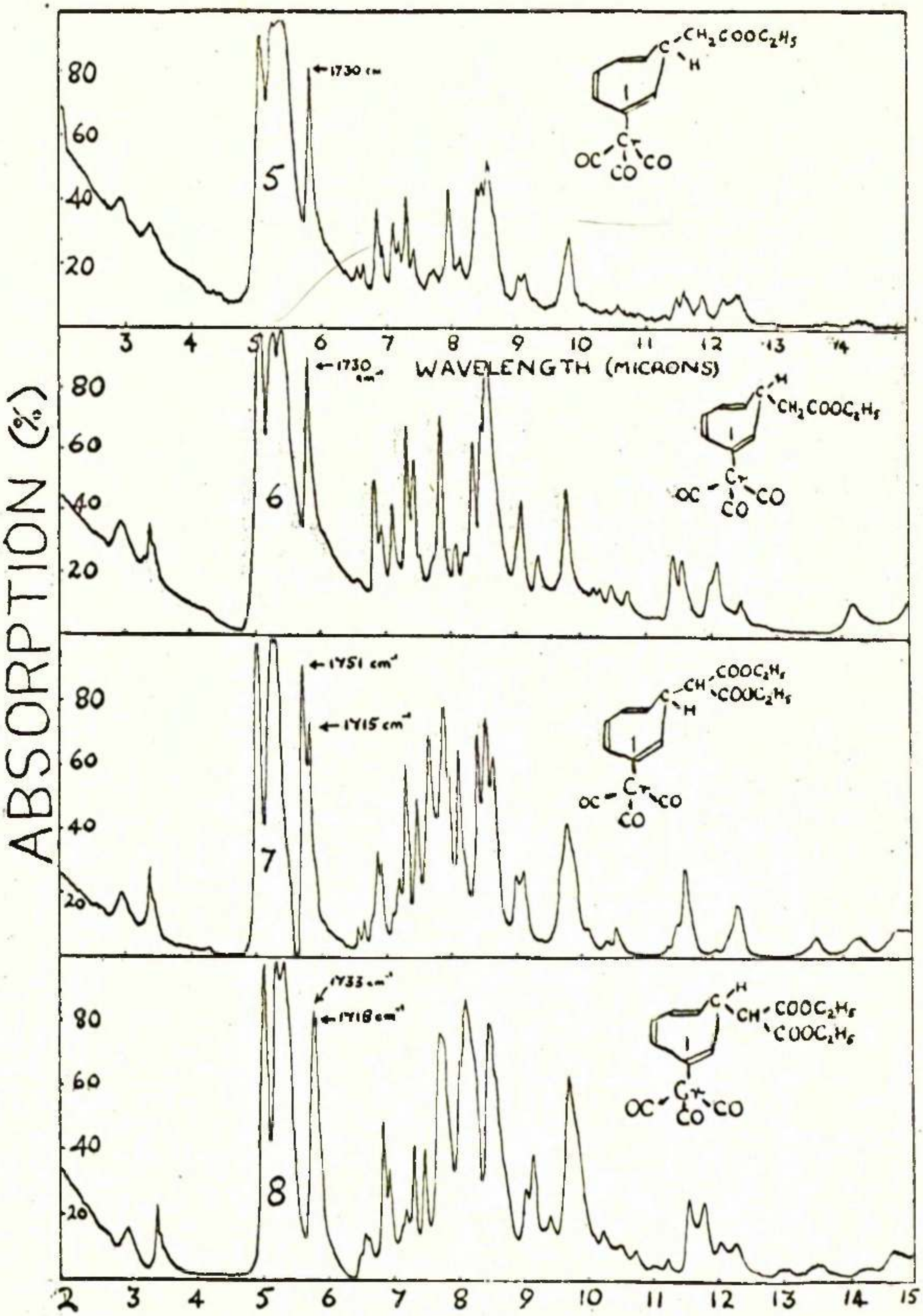
Peak positions are given in $cm.^{-1}$



Metal carbonyl frequencies:-

1. 2000, 1930 and 1908.
2. 2000, 1930 and 1908.
3. 1980, 1908 and 1876.
4. 1992, 1923 and 1894.

(as CCl_4 solution)



Metal carbonyl frequencies:-

5. 2000, 1934 and 1862.

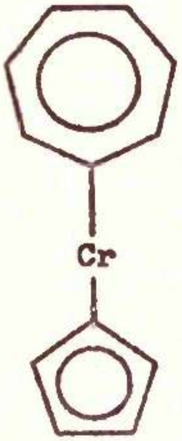
6. 1980, 1905 and 1859.

7. 1996, 1905 and 1887.

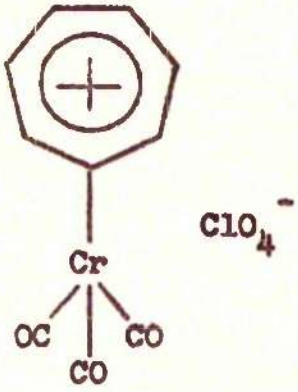
8. 1999, 1932 and 1905.

Rearrangement of 7-substituted tricarbonylcycloheptatrienechromium compounds to tricarbonylbenzenechromium.

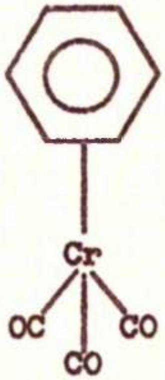
During an attempt to synthesise cycloheptatrienylcyclopentadienylchromium (XXXIX), Munro and Pauson[57,58,87] treated tricarbonyltropyliumchromium perchlorate (XIII) with an excess of cyclopentadienylsodium. The unexpected product, isolated in 46% yield was tricarbonylbenzenechromium (V).



(XXXIX)



(XIII)

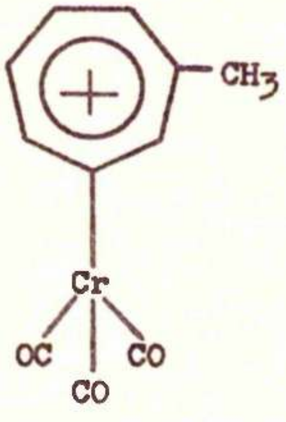


(V)

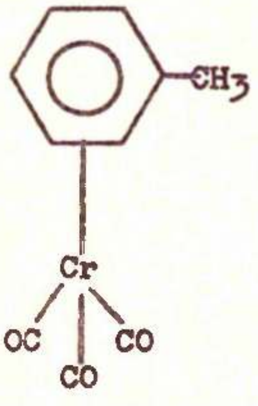
The molybdenum analogue was found to behave similarly. The reaction may be represented formally as :-

$$C_7H_7Cr(CO)_3{}^{+}ClO_4^{-} + C_5H_5^{-}Na^{+} \longrightarrow C_6H_6Cr(CO)_3 + C_6H_6 + NaClO_4$$

This equation shows that two C_6 fragments may be generated. It was therefore considered necessary to establish whether the benzene ring attached to chromium in the product was derived entirely from the seven-membered ring or in part from the cyclopentadiene ring. A decision in favour of the former view was reached qualitatively by repeating the reaction first with methylcyclopentadienylsodium, whereupon the benzene compound (V) was again the only chromium complex isolated; then with tricarbonylmethyltropyliumchromium cation (XL)[58,56] tricarbonyltoluene-chromium (XLI) was obtained. The conclusion was corroborated more quantitatively by labelling the tropylium complex (XIII) with tritium and showing that the derived product (V) contained the expected proportion of tritium.[87,56]



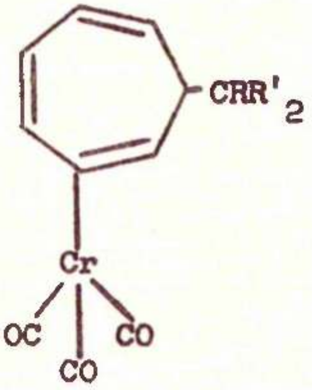
(XL)



(XLI)

The same ring contraction was observed when (XIII) was treated with an excess of diethylsodiomalonate. The simultaneous isolation of

tricarbonyl-7-endo-di(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium
[(XLII), R = H, R' = COOEt]

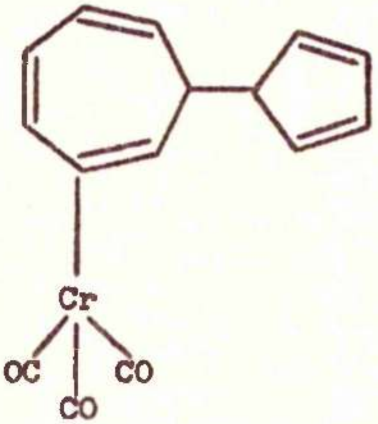


(XLII)

suggested that the 'normal' anion addition[58] is an intermediate step in these rearrangements. This was confirmed by showing that both the ester and the corresponding exo ester [(XLII), R = H, R' = COOEt] are transformed into tricarbonylbenzenechromium (V) by the further action of diethylsodiomalonate or other bases such as sodium methoxide. The molybdenum analogue of this endo ester has been made in a similar manner, but was found to be too unstable to be of use in the study of the rearrangement mechanism.

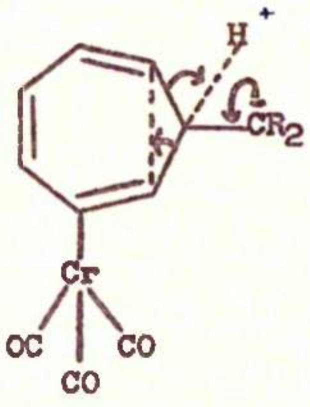
The corresponding intermediate (XLIII), in the cyclopentadienide reaction was readily isolated when an excess of the tropylium complex (XIII) was used and was similarly transformed into tricarbonylbenzenechromium (V) by sodium methoxide.

That tricarbonyl-7-endo-[1,1'-di(ethoxycarbonyl)]ethylcyclohepta(1,3,5)-trienechromium [(XLII), R = Me, R' = COOEt] fails to rearrange indicates that ionization of the acidic hydrogen [(XLII), R = H] induced by the base is an essential step in the ring contraction.



(XLIII)

The above observations led Munro and Pauson,[87,56] to propose that the electronic shifts indicated in (XLIV) represent a possible mechanistic picture for this ring contraction. On this basis, the

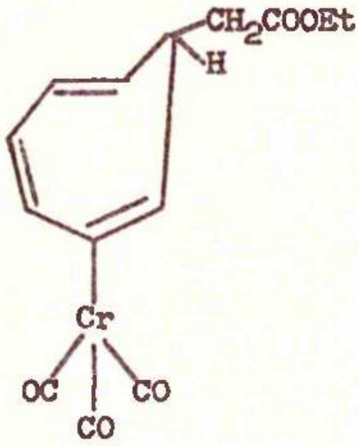


(XLIV)

'C_6H_6' fragment in the cyclopentadienylsodium reaction would be fulvene, and diethylmethylenemalonate would result similarly from $[(XLII), R = H, R' = COOEt]$. Neither of these products would be expected to survive the reaction conditions.[87]

Attempts have been made, therefore, to find a case where, by anionic addition to the tropylium salt (XIII) a compound could be synthesised which would, upon rearrangement by base, give two fragments which could be separately identified.

The first compound to be examined was tricarbonyl-7-exo-(ethoxycarbonyl)-methylcyclohepta(1,3,5)trienechromium (XLV), obtained in 67% yield from 7-(ethoxycarbonyl)methylcycloheptatriene and hexacarbonylchromium.



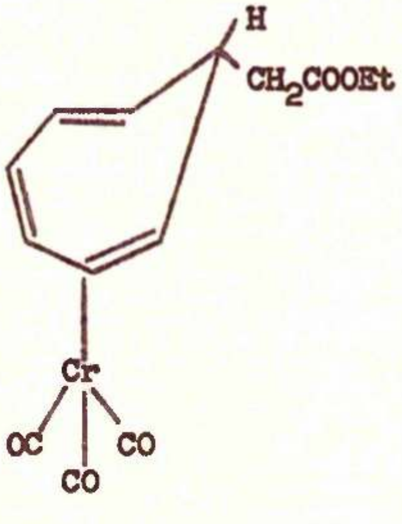
(XLV)

It was thought that treatment of this compound with base should give tricarbonylbenzenechromium (V) and ethyl acrylate. The latter compound would be isolable as an adduct with, e.g. phenyl azide.

However, treatment of (XLV) with sodium methoxide yielded no tricarbonylbenzenechromium (V) and the compound was recovered unchanged in 80% yield.

The analogous molybdenum compound was also synthesised but was found to be too unstable to be of use.

Pseudo-Reformatsky[122] conditions (part 1, page 36) gave tricarbonyl-7-endo-(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium (XLVI) in 88% yield from the reaction of zinc and ethyl bromoacetate



(XLVI)

with tricarbonyl-7-endo-methoxycycloheptatrienechromium. Attempts were made, using various bases, to effect rearrangement of this compound.

Treatment of (XLVI) with sodium methoxide gave no tricarbonylbenzenechromium (V), the compound (XLVI) being recovered unchanged in 90% yield.

The compound (XLVI) similarly survived treatment with an 0.5 molar equivalent quantity of potassium t-butoxide in t-butanol, being recovered in 42% yield. Again, no trace of tricarbonylbenzenechromium (V) was found.

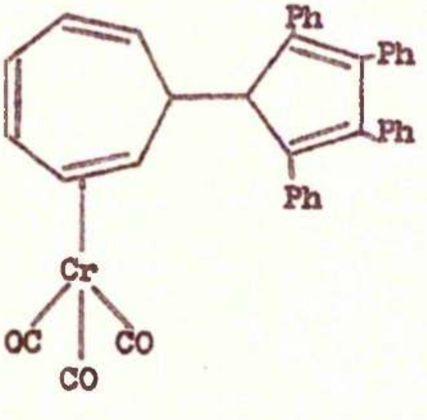
Treatment of (XLVI) with sodium hydride gave no tricarbonylbenzenechromium. In this case the addition of aqueous ethanol at the end of the reaction, to destroy the excess of sodium hydride caused hydrolysis and the corresponding acid (XXXV, or XXXVII, see part I) was isolated in 60% yield.

The use of a ten-fold excess of the much stronger base triphenylmethylsodium caused complete decomposition of the compound (XLVI). The only products isolated were triphenylmethane (60%) and a trace of a bright yellow crystalline hydrocarbon of unknown structure.

Repetition of this reaction using a catalytic amount of triphenylmethylsodium gave only unchanged (XLVI) in 94% yield.

At this stage it was decided to try and find another compound with a more acidic hydrogen on the α - carbon atom.

Reaction of tricarbonyltropyliumchromium fluoroborate with tetraphenylcyclopentadienyllithium[125] gave as the main product tricarbonyl-7-endo-(2',3',4',5'- tetraphenyl) cyclopentadienylcyclohepta(1,3,5)trienechromium (XLVII) in 43% yield.



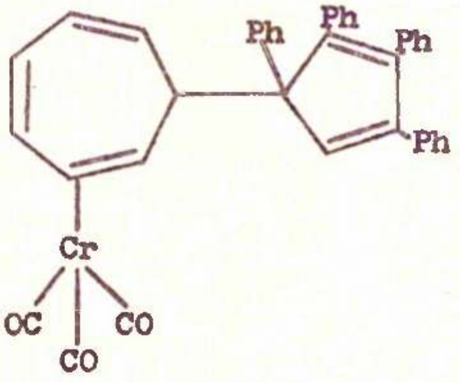
(XLVII)

Treatment of this compound with base should give tricarbonylbenzenechromium and 2,3,4,5-tetraphenylfulvene.[125] This latter compound is known to be stable to a boiling ethanolic solution of potassium hydroxide, and thus should withstand treatment at room temperature with bases such as sodium methoxide and potassium t-butoxide in t- butanol.

However, treatment of (XLVII) with sodium methoxide failed to cause rearrangement to take place the compound being recovered unchanged in 70% yield. No trace of tricarbonylbenzenechromium was found.

Treatment of (XLVII) with potassium t-butoxide in t-butanol likewise failed to effect rearrangement, the compound being recovered unchanged in 60% yield. Again, no trace of tricarbonylbenzenechromium was found.

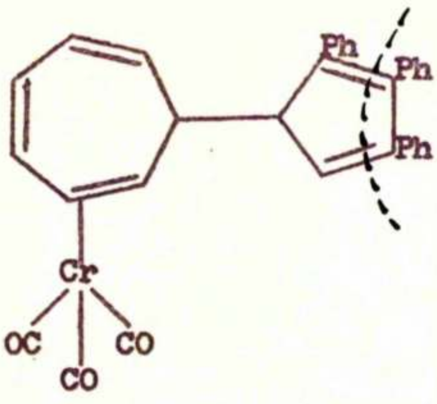
In view of the failure of these experiments, it seemed reasonable to suppose that (XLVII) did not represent the true structure of this compound. A less likely, but nevertheless perfectly feasible structure is (XLVIII):-



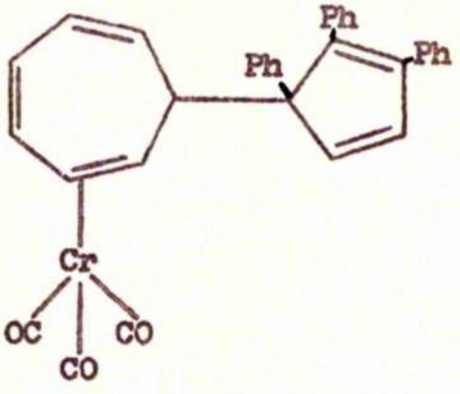
(XLVIII)

the presence of the phenyl group in place of hydrogen on the carbon atom α to the cycloheptatriene ring militating against the possibility of rearrangement according to the mechanism (XLIV).

The analogous triphenylcyclopentadiene complex (XLIX) was prepared



(XLIX)

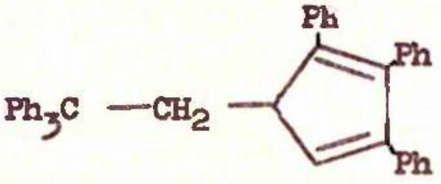


(L)

in 70% yield from tricarbonyltropyliumchromium fluoroborate and 2,3,4-triphenylcyclopentadienyllithium.[125] That it had, indeed, the structure (XLIX) and not (L) was easily shown by ozonolysis of the compound, when benzil was isolated from the complex mixture of reaction products. The benzil must have resulted from the breaking of the two double bonds indicated by the dotted line in (XLIX), and could not be formed if the molecule had structure (L).

Treatment of tricarbonyl-7-endo-(2', 3', 4'-triphenyl)cyclopentadienylcyclohepta(1,3,5)trienechromium (XLIX) with an 0.5 molar solution of sodium methoxide gave no trace of tricarbonybenzenechromium, the complex (XLIX) being recovered in 50% yield. But with triphenylmethylsodium a 30% yield of tricarbonylbenzenechromium was obtained. No trace of the second fragment -- 2,3,4-triphenylfulvene was found, and it was reasoned that if, indeed, the fulvene had been formed, it had reacted, in some way with triphenylmethylsodium.

Accordingly a sample of 2,3,4-triphenylfulvene[125] was prepared and treated with triphenylmethylsodium. An immediate reaction occurred and the deep red colour of the triphenylmethylsodium was discharged. Chromatography of the reaction mixture gave at least ten different compounds. The expected compound (LI) does not appear to have been



(LI)

formed as the major product, if at all. Triphenylmethane, triphenylmethyl peroxide, and a compound which is probably hexaphenylpropane constituted the major fraction of the material, and it is not known what happened to the triphenylcyclopentadiene grouping.

Also, it had not been possible to locate the triphenylcyclopentadiene moiety from the reaction of triphenylmethylsodium with (XLIX).

It was therefore decided to find another base which would effect rearrangement of (XLIX) at the same time lending itself to easy identification of the triphenylcyclopentadiene moiety.

Cram and Knox[126] have recently investigated the base-system potassium t-butoxide in dimethyl sulphoxide, and stated that it is approximately as strong as triphenylmethylsodium. This system was thus used in an attempt to rearrange compound (XLIX).

The complex (XLIX) was treated with a solution of excess potassium t-butoxide in dimethylsulphoxide at room temperature. After seventeen hours, the reaction mixture was poured into water and extracted with ether. The extract was chromatographed on alumina to yield tricarbonylbenzenechromium (30%). However, no trace of a compound posessing the triphenylcyclopentadiene grouping was found in this extract.

The aqueous solution was acidified and extracted with ether, and this extract was chromatographed on alumina to yield a brown oil which showed intense absorption in the metal carbonyl stretching frequency region of the infrared. That this is a derivative of tricarbonylbenzenechromium is suggested by the presence of only two stretching modes in the metal carbonyl region of the infrared. What is probably the same compound was also formed during a study of the rearrangement of (XLIX) using sodium hydride in tetrahydrofuran. In this latter case, the major product, (isolated in almost quantitative yield) was a vivid purple solid. (Tricarbonylbenzenechromium, 5%, was also isolated from this reaction). The purple compound was sensitive to oxygen, being converted into a brown solid. It showed intense absorption in the metal carbonyl stretching frequency region of the infrared, and in the hydroxyl region. Acidification of an aqueous ethanolic solution of this compound followed by extraction with methylene chloride yielded an orange-brown gum whose infrared spectrum was identical with that of the brown compound from the reaction of (XLIX) with the Cram and Knox reagent.[126]

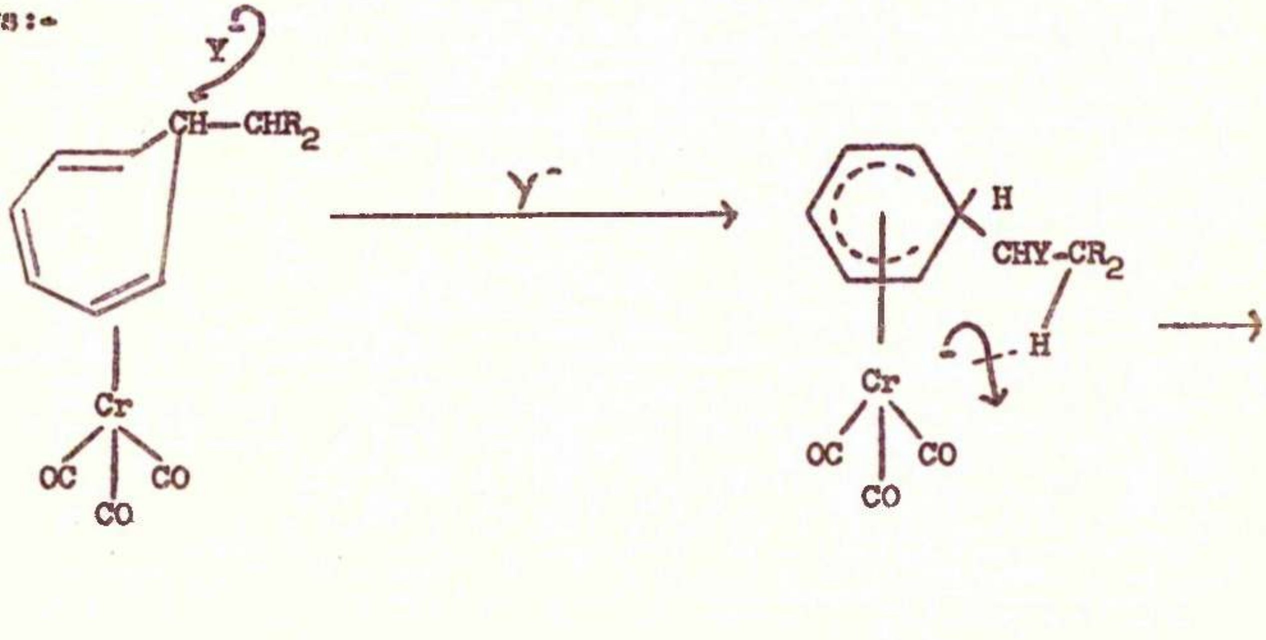
It thus appears that the purple solid is probably the sodium salt of an intermediate in the rearrangement, its unusual stability being due to the particular substituent (triphenylcyclopentadienyl).

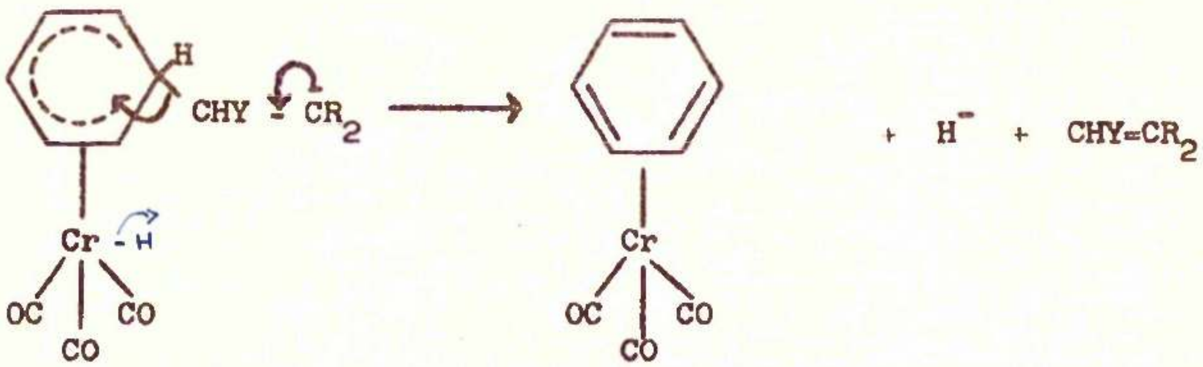
It was suggested by Munro and Pauson, that the mechanism (XLIV) was only to be treated as an indication of the course of the rearrangement, in view of the fact that whereas tricarbonylcyclopentadienylcycloheptatrienechromium (XLIII) rearranged to tricarbonylbenzenechromium upon treatment with base, the metal-free cyclopentadienylcycloheptatriene did not rearrange to benzene under the same conditions.[56,87]

We have found that, in a similar manner, whereas tricarbonyl-7-di(ethoxycarbonyl)methylcycloheptatrienechromium (exo and endo) rearranges to tricarbonylbenzenechromium, the metal-free compound, **7**-di(ethoxycarbonyl)methylcycloheptatriene does not rearrange to benzene.

The mechanism (XLIV) suggests that the base is a catalyst, and as a corollary, trace amounts should effect rearrangement. That this is not the case is seen from the fact that whereas a trace of potassium t-butoxide failed to effect rearrangement of tricarbonyl-7-exo-di(ethoxycarbonyl)methylcycloheptatrienechromium, an excess of sodium methoxide caused rearrangement to tricarbonylbenzenechromium to occur.

A possible mechanism to account for all these observations is as follows:-

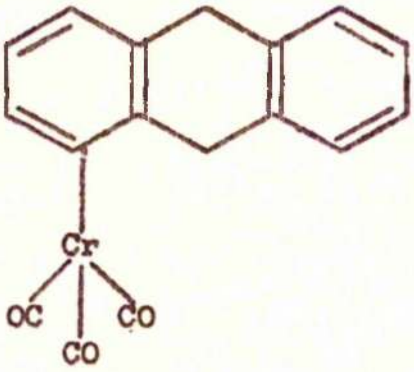




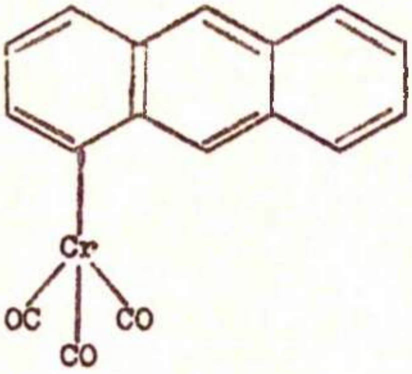
However, it is rather surprising that the fragment $CHY{=}CR_2$ is not isolated, and the above mechanism can not be considered to give a true picture of the reaction until or unless this fragment is isolated.

Attempted elucidation of the structures of tricarbonylanthracenechromium and tricarbonylphenanthrenechromium by chemical means.

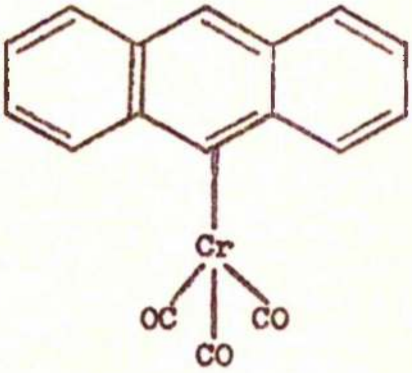
Fischer, Kreibitzsch and Fischer had reported[31] that the reaction of anthracene, phenanthrene and 9:10-dihydroanthracene with hexacarbonylchromium gave tricarbonylarenechromium complexes in yields of 0.1%, 4.5% and 5.4% respectively. Whilst the point of attachment of the $Cr(CO)_3$ group in the 9:10-dihydroanthracene complex is as in (LII) it was not possible at that time to say which ring in the anthracene or phenanthrene complexes carried the $Cr(CO)_3$ group. Thus, tricarbonylanthracenechromium could have structure (LIII) or structure (LIV). Similarly, tricarbonylphenanthrenechromium might have structure (LV) or structure (LVI)



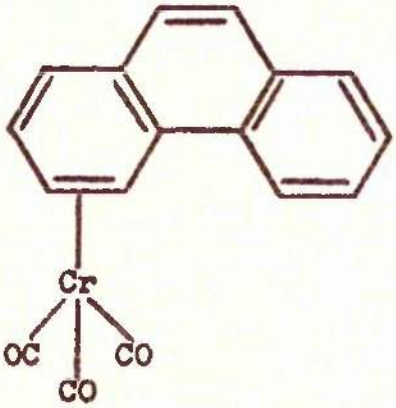
(LII)



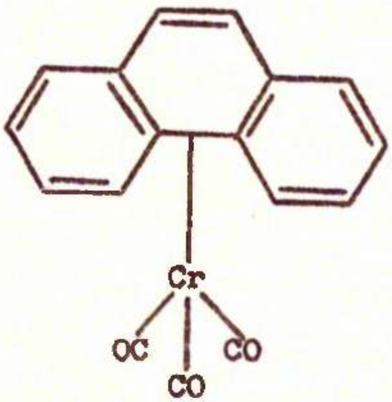
(LIII)



(LIV)



(LV)



(LVI)

While the work herein described was being undertaken, the results of King and Stone, who had reinvestigated the reactions of both anthracene and phenanthrene with hexacarbonylchromium, were published.[127] These workers had increased the yield in the phenanthrene-hexacarbonylchromium reaction to 14%, but had failed to isolate tricarbonylanthracenechromium from the reaction of anthracene with hexacarbonylchromium, although they observed an intense violet colouration in the reaction flask, which faded as the flask cooled. They reported that the phenanthrene complex was too insoluble in organic solvents to allow of its study by nuclear magnetic resonance techniques, and were unable to throw any light on the question of bonding in the compounds.

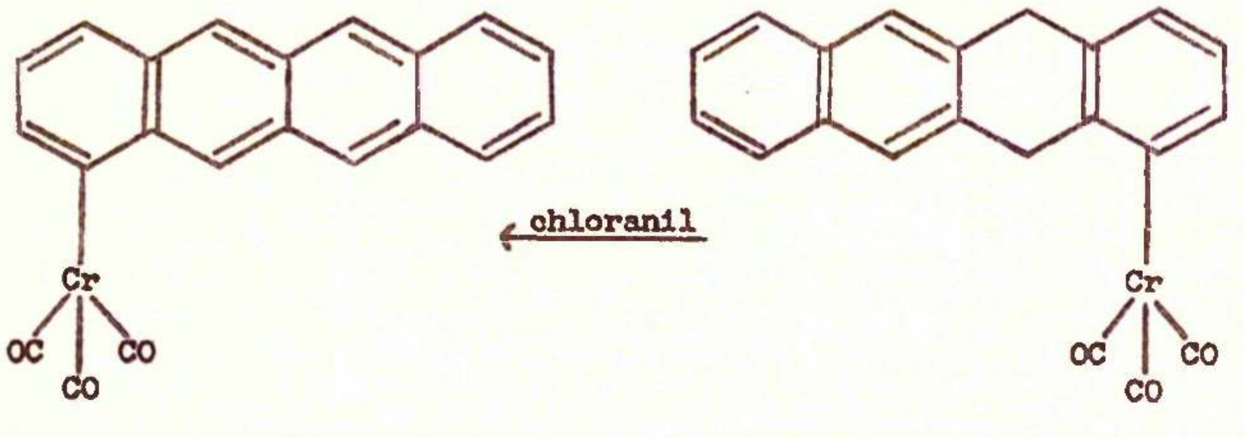
With a view to a) increase the yield of the tricarbonylanthracenechromium complex and b) prove its structure unequivocally, it was decided to try and increase the yield of tricarbonyl 9:10-dihydroanthracenechromium (LII) and then to convert it to (LIII) by dehydrogenation.

By heating 9:10-dihydroanthracene with hexacarbonylchromium in diethylene glycol dimethyl ether, a 51% yield of (LII) was obtained. An attempt to prepare (LII) by the exchange reaction,[42] of 9:10-dihydroanthracene with tricarbonylbenzenechromium, was unsuccessful.

Bonthrone and Reid had reported[129] that treatment of 9:10-dihydroanthracene with triphenylmethyl perchlorate in boiling acetic acid gave a 90% yield of anthracene. It was thought that tricarbonyl 9:10-dihydroanthracenechromium would probably not be stable to such vigorous conditions and accordingly the complex (LII) was shaken with triphenylmethyl perchlorate in benzene solution for 6 hours at room temperature. No colour change (indicating formation of the desired tricarbonylanthracenechromium) was observed and tricarbonyl 9:10-dihydroanthracenechromium was recovered unchanged in 80% yield.

In their study of hydrogen-transfer mechanisms[130] Braude and Linstead had reported on the efficaciousness of 2,3,5,6-tetrachloro-p-benzoquinone (chloranil) in promoting dehydrogenation of dihydroaromatic compounds. However, treatment of tricarbonyl 9:10-dihydroanthracenechromium with chloranil at 120°C caused complete decomposition the only isolated product being anthracene.

Nesmeyanov and Vol'kenau[34] have recently described their similarly abortive attempts to produce tricarbonyltetracenechromium (LVII) by dehydrogenation of tricarbonyl 5:12-dihydrotetracenechromium (LVIII) using chloranil, and the conditions under which the metal-free 5:12-dihydrotetracene is converted into tetracene.[132] Treating the chromium tricarbonyl derivative (LVIII) with chloranil either in glacial acetic acid or in benzene led to rapid and complete decomposition to 5:12-dihydrotetracene and transformation of the latter into tetracene.



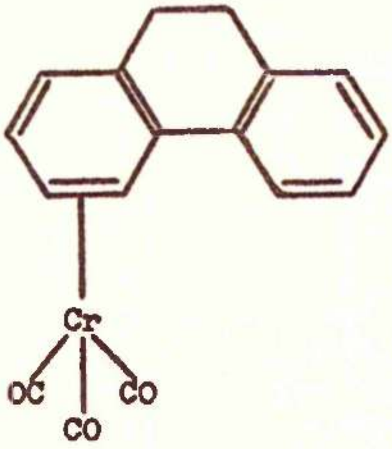
(LVII) (LVIII)

Attempts to prepare tricarbonylanthracenechromium by dehydrogenation of tricarbonyl 9:10-dihydroanthracenechromium were thus abandoned.

Attempts were made to prepare tricarbonylanthracenechromium by direct reaction of anthracene and hexacarbonylchromium. Heating these two compounds in petroleum ether (b.p. 100/120°C) produced an intense violet colouration and a small amount of gas, presumably carbon monoxide, was evolved. As the solution cooled, the violet colour disappeared, and only unreacted starting material was obtained. Addition of a small quantity of cycloheptatriene, whereby it was thought that the intermediately formed tricarbonylcycloheptatrienechromium might react with anthracene by an exchange reaction,[42] again yielded no trace of tricarbonylanthracenechromium. Finally, an attempt at direct exchange, using preformed tricarbonylcycloheptatrienechromium and anthracene gave only unreacted starting material.

It seems likely that, in view of these discouraging results, any tricarbonylanthracenechromium which forms disproportionates into the starting material at the same rate as that of the formation reaction. A similar conclusion was reached by Fischer.[31] It also seems likely that the only method available for the elucidation of the true structure of this extremely interesting compound is one based upon X-ray measurements.

Attention was next diverted to tricarbonylphenanthrenechromium. It was reasoned that if this had the structure (LV) it might be capable of hydrogenation to tricarbonyl 9:10-dihydrophenanthrenechromium (LIX). This latter compound was not known at the time, but was readily prepared



(LIX)

by direct reaction of 9:10-dihydrophenanthrene and hexacarbonylchromium.

Tricarbonylphenanthrenechromium was prepared in ca. 10% yield by refluxing phenanthrene and hexacarbonylchromium in petroleum ether at 120°C. Use of a lower temperature resulted in negligible reaction whilst use of a higher temperature (King and Stone report[127] having used a temperature of 170°C) caused irreversible decomposition into phenanthrene, carbon monoxide and pyrophoric chromium.

Attempts to hydrogenate tricarbonylphenanthrenechromium were completely unsuccessful. Use of palladium on charcoal, platinum on charcoal or Adams' platinum oxide catalyst, in diethyl ether, tetrahydrofuran, ethyl acetate and glacial acetic acid led to the isolation of unreacted tricarbonylphenanthrenechromium in yields of 80 - 95%.

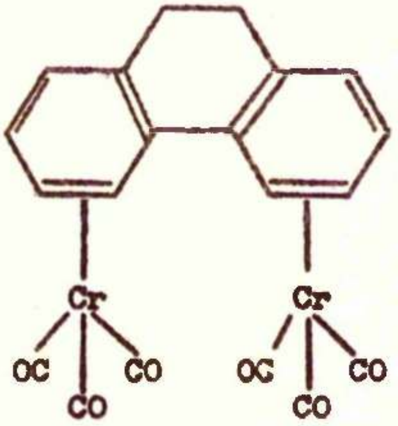
An attempt to hydrogenate the complex using copper chromite catalyst[124] at elevated pressure and temperature resulted in rupture of the metal-ring bond, and subsequently a mixture of phenanthrene and 9:10-dihydrophenanthrene was isolated in 94% yield.

Following a recent publication of Boer and Duinker[128] who report that calcium hexammine is an efficient agent for the hydrogenation of phenanthrene, by the following overall reaction:-

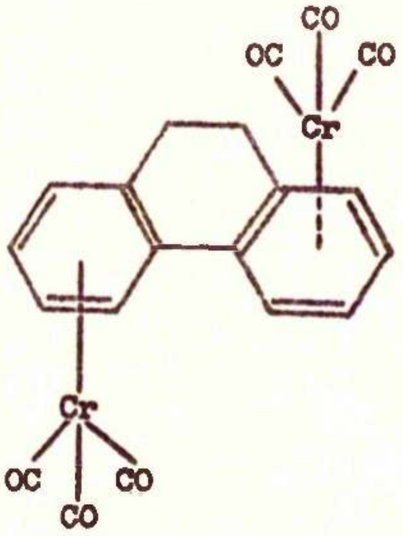
$$\text{Phenanthrene} + Ca(NH_3)_6 \longrightarrow Ca(NH_2)_2 + 4NH_3 + \text{Dihydrophenanthrene}$$

it was decided to adopt this method in a final effort to hydrogenate tricarbonylphenanthrenechromium. Treatment of tricarbonylphenanthrenechromium with a solution of calcium hexammine in liquid ammonia caused much decomposition of the chromium complex to occur. The only isolable product was unreacted tricarbonylphenanthrenechromium in 10% yield. Attempts to hydrogenate tricarbonylphenanthrenechromium were abandoned and it was decided to try and dehydrogenate tricarbonyl 9:10-dihydrophenanthrenechromium to tricarbonylphenanthrenechromium, which experiment, if successful, would have proved conclusively that tricarbonylphenanthrenechromium had structure (LV)

By heating a mixture of 9:10-dihydrophenanthrene, hexacarbonylchromium and ethylene glycol diethyl ether under pressure at 200-220°C, tricarbonyl 9:10-dihydrophenanthrenechromium (LIX) was obtained in 65% yield. From the same reaction mixture was also obtained a low yield of a compound whose properties suggest it was a hexacarbonyl 9:10-dihydrophenanthrenedichromium (LX) although it has not been possible to say whether it is the cis isomer (LX) or the trans isomer (LXI).



(LX)



(LXI)

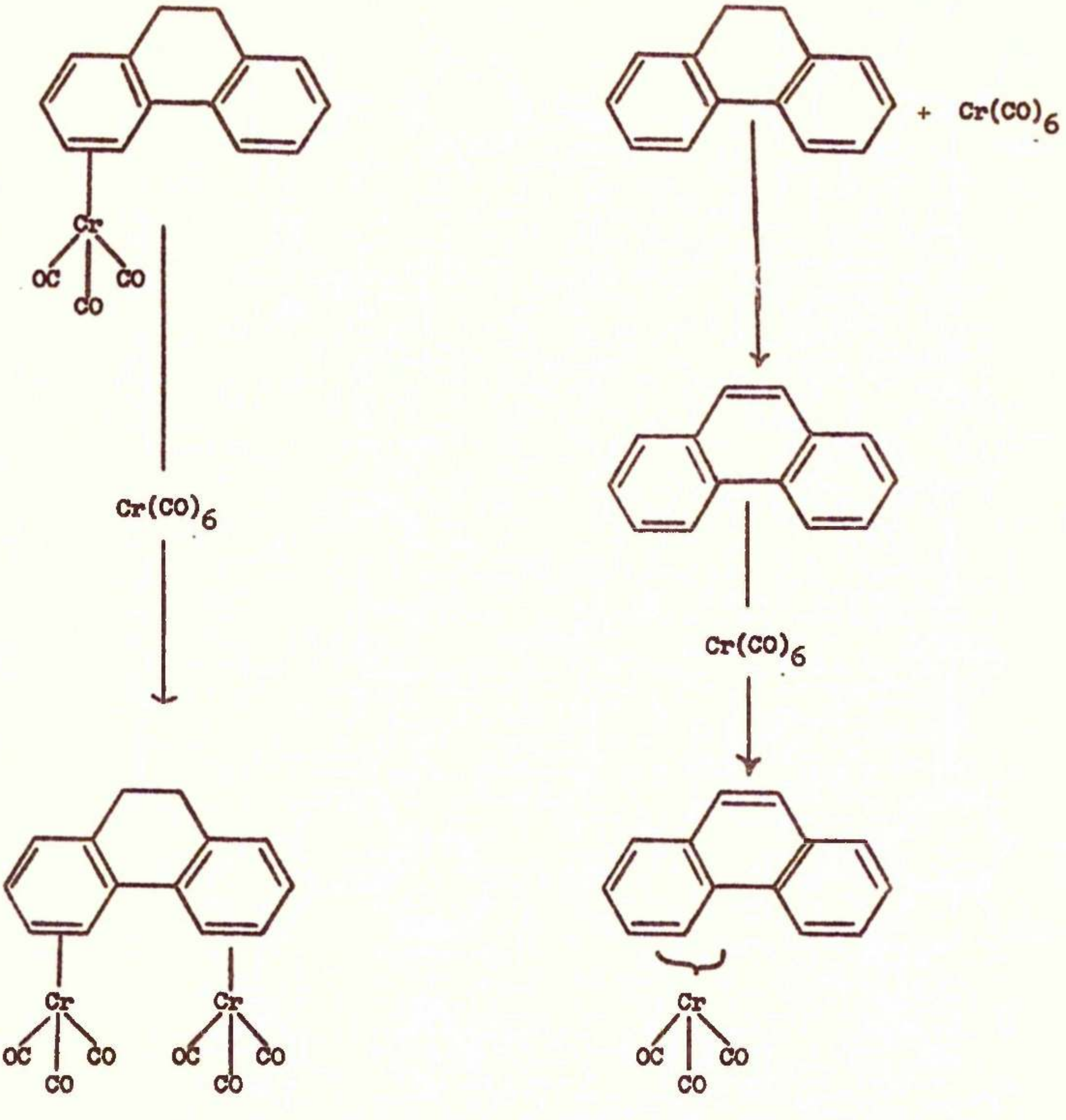
This is believed to be the first time that two $Cr(CO)_3$ groups have been introduced into a fused polynuclear aromatic compound. Indeed, the Russian workers specifically stated[34] that they were unable to introduce more than one atom of chromium into similar compounds.

Treatment of tricarbonyl 9:10-dihydrophenanthrenechromium with triphenylmethyl perchlorate under reflux in glacial acetic acid led to complete decomposition of the organometallic complex. The only product isolated from the reaction being a pale amber oil which showed no absorption in the metal carbonyl stretching frequency region of the infrared and which was almost certainly a mixture of phenanthrene and 9:10-dihydrophenanthrene.

Treatment of tricarbonyl 9:10-dihydrophenanthrenechromium with 1,2,3,4-tetrabromo-o-benzoquinone[134] (the latter reagent being some 2000 times as strong a dehydrogenating agent as chloranil) caused total decomposition of the organometallic compound.

Treatment of tricarbonyl 9:10-dihydrophenanthrenechromium with 2,3-dichloro,5,6-dicyano-p-benzoquinone resulted in rapid decomposition of the organometallic compound. After ten minutes the reaction was stopped and only unreacted tricarbonyl 9:10-dihydrophenanthrenechromium (11%) was recovered from the reaction mixture.

It was then decided to attempt to effect the required dehydrogenation using palladium on charcoal at an elevated temperature. Accordingly, tricarbonyl 9:10-dihydrophenanthrenechromium was heated at 200°C for two hours in the presence of 10% palladium on charcoal. After cooling the mixture was extracted with benzene and chromatographed on alumina. Elution gave a) Phenanthrene (78%), b) unreacted tricarbonyl 9:10-dihydrophenanthrenechromium (6%), c) tricarbonylphenanthrenechromium (1%) and d) a compound thought to be hexacarbonyl 9:10-dihydrophenanthrenedichromium (1%). It was initially thought that the dehydrogenation of tricarbonyl 9:10-dihydrophenanthrenechromium to tricarbonylphenanthrenechromium had been accomplished. However, it also seemed possible, in view of the formation of the hexacarbonyl 9:10-dihydrophenanthrenedichromium compound, that the reaction might have taken the following alternative course:-

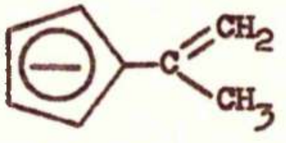


In an attempt to clarify this point, the experiment was repeated, at a slightly lower temperature, and for a much shorter period. The products this time were a) a mixture of phenanthrene and dihydrophenanthrene (26%) b) unreacted tricarbonyl 9:10-dihydrophenanthrenechromium (62%) and c) hexacarbonyl 9:10-dihydrophenanthrenedichromium (1%). No trace of tricarbonylphenanthrenechromium was obtained and it therefore seemed probable that the tricarbonylphenanthrenechromium formed in the first dehydrogenation attempt with palladium on charcoal was formed by recombination of hexacarbonylchromium and phenanthrene, the latter having been formed by dehydrogenation of 9:10-dihydrophenanthrene, which in turn had been formed by decomposition of tricarbonyl 9:10-dihydrophenanthrenechromium.

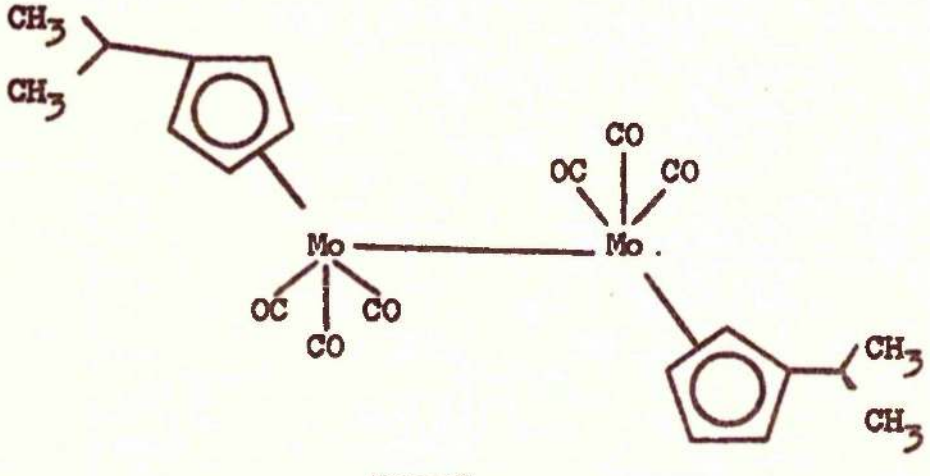
It has thus not been possible to show, by chemical methods, whether tricarbonylphenanthrenechromium has structure (LV) or structure (LVI). However, Fischer has recently reported[135] that preliminary X-ray results have proved that the structure of this compound is (LVI). Whilst (LVI) is, then, the preferred structure, it seems not unreasonable to predict the existence of a compound with structure (LV).

Additional experiments.

After it had been shown[136,137] that reaction of 6:6'-dimethylfulvene with sodamide in liquid ammonia yielded the isopropenylcyclopentadienide anion (LXIII), the possibility of achieving the same double-bond shift with metal carbonyls was investigated by Munro and Pauson.[56] It was found that when 6:6'-dimethylfulvene was allowed to react with hexacarbonylmolybdenum using the fulvene as solvent, a complex reaction mixture was obtained. The product of the same reaction, done using 1,2-dimethoxyethane as solvent, has recently been shown[138] by Abel, Singh and Wilkinson to be (LXIV).

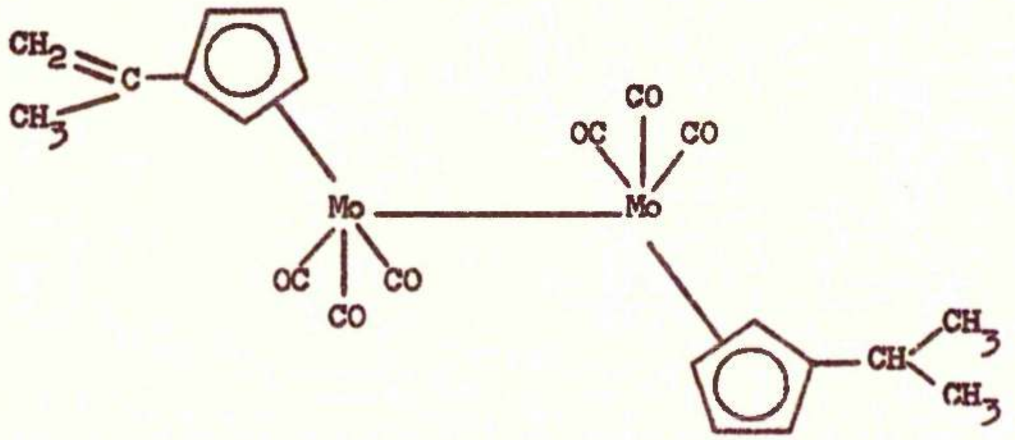


(LXIII)



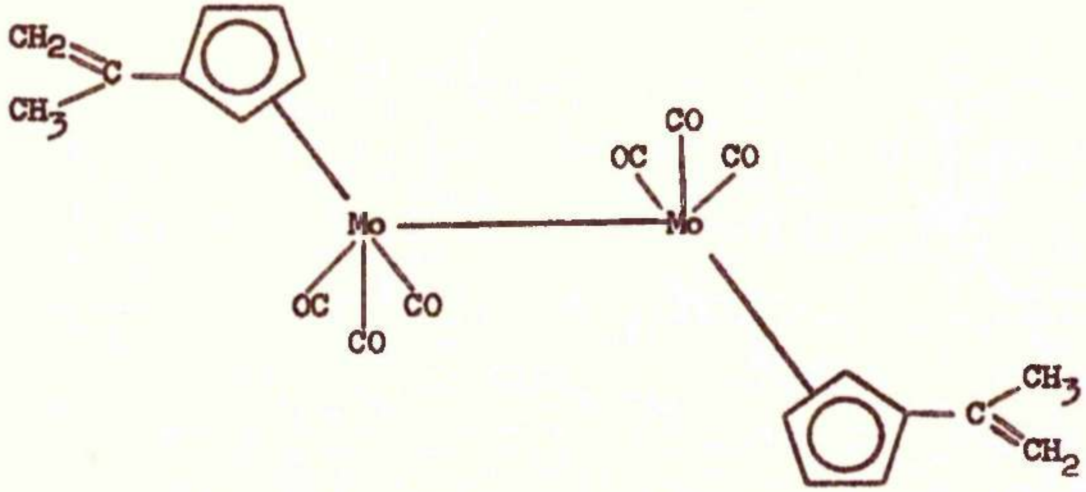
(LXIV)

Munro and Pauson had shown[56] that their complex reaction mixture was separable, by chromatography on alumina, into eight distinct compounds. These were all crimson solids having very similar infrared spectra. The fist of these has been shown to be (LXIV) by direct comparison with a sample made by the literature[138] method. The second fraction was shown to be the unsymmetrical monounsaturated product (LXV) by analysis, molecular weight determination,[139] and quantitative hydrogenation to the saturated product (LXIV). Although the other fractions have not been examined in detail it appears reasonable to assume that the third is the diene (LXVI) and that the later fractions are polymers derived from this and the above unsymmetrical product.



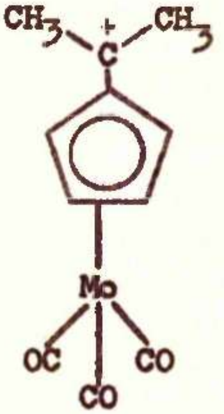
(LXV)

Although the mechanism of the reaction is not known, the formation of these products may be understood by considering the hypothetical first intermediate (LXVII) which would be expected to isomerise to the hydride (LXVIII). Such hydrides are known to decompose[65] below the

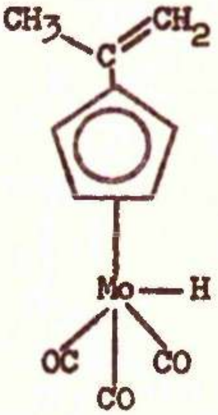


(LXVI)

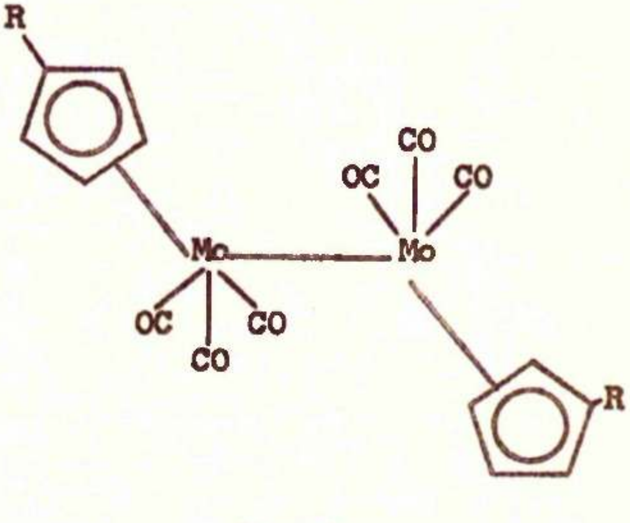
reaction temperature used here, giving the dimers (LXIX). The hydridic hydrogen is not liberated[140] as molecular hydrogen in the presence of olefins, and in the present case just sufficient hydrogen is available from this source to produce the unsymmetrical product (LXV), or equal amounts of the saturated (LXIV) and diunsaturated (LXVI) analogues.



(LXVII)

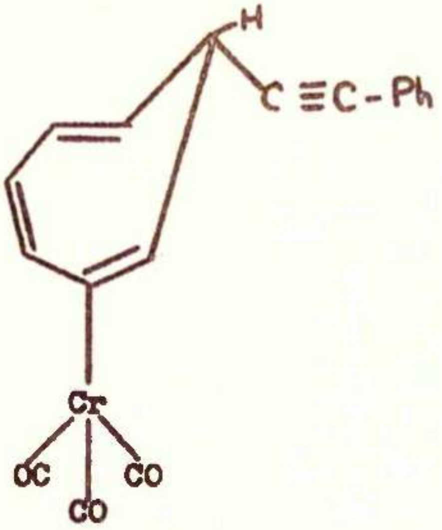


(LXVIII)

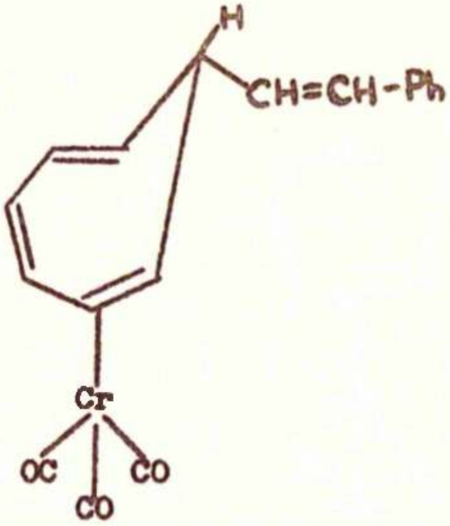


(LXIX)

Reaction of phenylethynyllithium[141] with tricarbonyltropyliumchromium fluoroborate has given tricarbonyl-7-endo-phenylethynylcyclohepta(1,3,5)-trienechromium (LXX) in 52% yield. The compound shows some similar



(LXX)

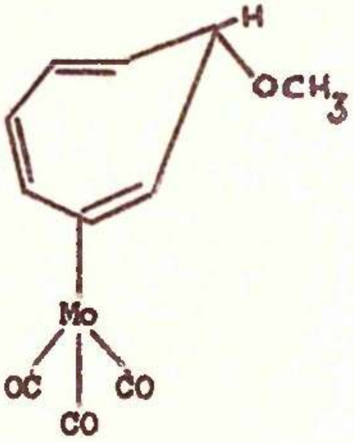


(LXXI)

properties to tricarbonyldi(cycloheptatrienyl)chromium (XXXIV), and structure (LXX) was proved by analysis, molecular weight determination and by oxidation with permanganate to yield benzoic acid.

Reduction of (LXX) over platinum oxide gave a compound with very similar properties, which is probably (LXXI). Unfortunately, a satisfactory analysis has not been obtained, and indeed it would be difficult to differentiate between (LXX) and (LXXI) by this means.

Reaction of sodium methoxide with tricarbonyltropyliummolybdenum fluoroborate gave tricarbonyl-7-endo-methoxycyclohepta(1,3,5)triene-molybdenum (LXXII) in 98% yield. The compound is extremely unstable and could not be analysed satisfactorily.



(LXXII)

EXPERIMENTAL

All reactions were carried out in an atmosphere of oxygen-free (White-Spot) nitrogen.

Spence's "Grade H" alumina was used for chromatography and was partially deactivated by exposure to the atmosphere for 6 hours.

Neutralized alumina was prepared by storing "Grade H" alumina over ethyl acetate for 1 - 2 days, filtering, washing with methanol and water and finally drying at 160°C., for 4 hours.

Molecular Weights were determined by the cryoscopic method in benzene solution.

All melting points are uncorrected and were determined in sealed, evacuated capillary tubes.

Unless otherwise indicated, all infrared spectra were recorded as potassium chloride discs.

Ultraviolet spectra were determined in $CHCl_3$.

Reaction solvents were rigorously dried unless otherwise stated.

All chromatography columns were protected from light.

Petrol or ligroin refers to that fraction of petroleum ether of b.p. 60-80°C.

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Tricarbonylcyclohepta(1,3,5)trienechromium.[56]

Freshly sublimed hexacarbonylchromium (30g., 0.13 mole) and redistilled cycloheptatriene (25 ml., excess) were refluxed in pure diglyme[142] (60 ml.) for 12 hrs. Hexacarbonylchromium which sublimed out of the reaction mixture was mechanically returned at 10 minute intervals. The mixture was cooled overnight, filtered into air-free water, extracted with ether (4 x 200 ml.) and the ether extract washed with water. After filtration through Celite, the ethereal solution was dried (Na_2SO_4) for ½ hr., out of contact with light. Evaporation to ca. 100 ml. was followed by addition of ligroin, further evaporation to 150 ml, and chilling to -78°C. Deep-red crystals [16.0g., 91% based on non-recovered $Cr(CO)_6$] m.p. 129-130°C (lit[56] m.p. 128-130°C) appeared and were filtered off.

Note. It is essential to use rigorously purified diglyme in this preparation, for traces of peroxides can lead to complete decomposition.

Tricarbonyltropyliumchromium fluoroborate.

Treatment of a solution of tricarbonylcycloheptatrienechromium in methylene chloride with a slight excess of freshly prepared triphenylmethyl fluoroborate[143] in the same solvent gave a quantitative yield of tricarbonyltropyliumchromium fluoroborate as an orange flocculent precipitate. The compound can be recrystallised from acetone as deep red needles. m.p. > 300°C.

Tricarbonyl-7-exo-methylcyclohepta(1,3,5)trienechromium.[54]

7-methylcycloheptatriene[54] (2.86 g., 0.03 mole) and hexacarbonylchromium (6.9 g., 0.03 mole) were refluxed in ethylene glycol diethyl ether (50 ml.) for 45 hrs. Then, excess unreacted material was removed in vacuo, leaving a red oil. The oil was crystallised from ether/pentane to yield red needles (3.99 g., 65%) m.p. 72-73°C lit[54] m.p. 72-73°C of tricarbonyl-7-exo-methylcyclohepta(1,3,5)trienechromium, soluble in common organic solvents. The compound sublimes at 60°C/0.01 mm.

Tricarbonylmethyltropyliumchromium fluoroborate.

To a solution of tricarbonyl-7-exo-methylcyclohepta(1,3,5)triene chromium (1.59 g., 0.0066 mole) in methylene chloride (30 ml.) was added a solution of triphenylmethyl fluoroborate (2.50 g., 0.0076 mole) in methylene chloride (100 ml.). The flocculent orange precipitate which appeared was filtered, washed with methylene chloride and ether (to remove triphenylmethane) and then recrystallised from acetone to yield deep red needles (1.85 g., 86%) m.p. > 300°C., soluble in acetone, alcohol and water. Tricarbonylmethyltropyliumchromium fluoroborate is insoluble in other common organic solvents.

Found : C, 39.9; H, 2.4; Cr, 16.2;

$C_{11}H_9BCrF_4O_3$ requires : C, 40.3; H, 2.8; Cr, 15.9%

Reaction of tricarbonylmethyltropyliumchromium fluoroborate with sodium borohydride.

A stirred suspension of tricarbonylmethyltropyliumchromium fluoroborate (1.11 g., 0.0034 mole) in air-free water (25 ml.) was treated with a solution of sodium borohydride (0.24 g., 0.0068 mole) in water (50 ml.). Gas evolution occurred, with the rapid separation of an oily red solid. After stirring the reaction mixture for 10 mins., the solid was filtered off and well washed with water to remove entrained unreacted tricarbonylmethyltropyliumchromium fluoroborate.

The oily solid (0.56 g.) was dissolved in pentane and chromatographed on alumina (60 g., deactivated 2 hrs.) to yield one broad band. Three fractions were taken using pentane as eluent. The first two fractions yielded oily red crystals melting below room temperature. From the third fraction, deep red crystals (0.166 g., 21%) m.p. 96-97°C were obtained. Repeated recrystallisation from pentane raised the m.p. to 103-104°C. Tricarbonyl-1-methylcyclohepta(1,3,5)trienechromium shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 2004, 1930 and 1908 cm^{-1} (CCl_4). It is very soluble in common organic solvents.

Found : C, 54.6; H, 4.4; Cr, 21.5;

$C_{11}H_{10}CrO_3$ requires : C, 54.55; H, 4.2; Cr, 21.5%

Zinc dust reduction of tricarbonylmethyltropyliumchromium fluoroborate.

Tricarbonylmethyltropyliumchromium fluoroborate (0.5 g., 0.0015 mole) in water (20 ml.) was treated with zinc dust (0.3 g., 0.0046 mole) and the mixture was shaken in vacuo for 6 hrs. Then, the mixture was extracted with ether (4 x 6 ml.), the extract filtered and dried (Na_2SO_4). Further filtration, followed by evaporation and cooling to -70°C gave orange needles (0.31 g., 85%) which were recrystallised from ether/pentane to yield deep orange needles of hexacarbonyldi[methylcyclohepta-(1,3,5)trienylchromium] m.p. 168-169°C. The compound is soluble in benzene, ether, chloroform and methylene chloride, but only sparingly soluble in paraffins and carbon tetrachloride. It shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 2000, 1942 and 1916 cm.$^{-1}$

Found : C, 54.9; H, 3.6; Cr, 21.6;

$C_{22}H_{18}Cr_2O_6$ requires : C, 54.8; H, 3.8; Cr, 21.6%

Reaction of tricarbonyltropyliumchromium fluoroborate with methyllithium.

To a solution of methyllithium [from lithium (0.1 g., 0.014 g.atom) and methyl iodide (3.0 g., 0.02 mole)] in ether (5 ml.) was added a suspension of tricarbonyltropyliumchromium fluoroborate (1.0 g., 0.003 mole) in ether (25 ml.). The solution was vigorously shaken for 1 hr., then left overnight, at room temperature. The solid residue remaining after removal of ether, was extracted with hot ligroin (3 x 10 ml.). This extract was chromatographed on alumina (30 g.). The single orange band which formed gave orange needles (0.073 g., 15%) m.p. 146-147°C identified as tricarbonyldi[cyclohepta(1,3,5)trienyl] chromium on the basis of m.p., mixed m.p., and infrared spectral comparison with an authentic sample.[56]

The petrol-insoluble residue was next extracted with benzene, and upon cooling this extract deep red needles (0.126 g., 18%) m.p. 224-225°C were obtained, identified as hexacarbonyldi[cyclohepta(1,3,5)-trienylchromium] on the basis of their m.p., mixed m.p. with an authentic sample[56] and infrared spectrum.

Tricarbonyl-7-endo-methylcyclohepta(1,3,5)trienechromium.

a) To a suspension of methylmagnesium iodide [from magnesium (0.24 g., 0.01 g.atom) and methyl iodide (1.42 g., 0.01 mole)] in ether (10 ml.) was added a solution of tricarbonyl-7-endo-methoxycycloheptatrienechromium[56] (1.0 g., 0.004 mole) in ether (20 ml.). The resulting orange solution was stirred for 1½ hrs., by the end of which time the solution had turned deep red-orange. The solution was evaporated to dryness in vacuo at room temperature. The red crystalline residue was extracted with hot benzene (25 ml.) and chromatographed on alumina (60 g.). Three bands developed. Elution with ligroin/benzene (10/1) gave the main red-orange band, from which was obtained tricarbonyl-7-endo-methylcyclohepta(1,3,5)trienechromium (0.614 g., 80%) m.p. 85-85.5°C, as fine red needles, soluble in common organic solvents. The compound shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 1980, 1908 and 1876 $cm.^{-1}$

Found : C, 54.70; H, 4.3; Cr, 21.0;

$C_{11}H_{10}CrO_3$ requires : C, 54.55; H, 4.2; Cr, 21.5%

Further elution of the column with ligroin/benzene (1/1) gave orange crystals of tricarbonyldi(cycloheptatrienyl)chromium (0.007 g.) m.p. 140-142°C., and elution with benzene gave red crystalline hexacarbonyldi(cycloheptatrienylchromium) (0.002 g.) m.p. 200-210°C

b) To a suspension of methylmagnesium iodide [from magnesium (0.24 g., 0.01 g.atom) and methyl iodide (1.42 g., 0.01 mole)] in ether (10 ml.) was added a suspension of tricarbonyltropyliumchromium fluoroborate (1.56 g., 0.005 mole) in ether (20 ml.). The mixture soon turned dark brown and was stirred ½ hr. Filtration was followed by evaporation to dryness in vacuo at room temperature. The residue was extracted with benzene (20 ml.) and chromatographed on alumina (20 g.) giving one main band, together with a trace of two others.

The main band was eluted with ligroin/benzene (10/1) and afforded orange needles (0.091 g., 13%) m.p. 86-87°C., of tricarbonyl-7-endo-methylcycloheptatrienechromium. Identity was established by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

The filtered residues from the reaction mixture were dissolved in hot water and to this solution was added excess of a solution of sodium borohydride in water. The resulting solution was stirred for 2 hrs., and then extracted with ether. From the dried ether extract was obtained tricarbonylcycloheptatrienechromium (0.46 g., 41%).

Attempted reaction of triphenylmethyl fluoroborate with tricarbonyl-7-endo-methylcycloheptatrienechromium.

A solution of freshly prepared triphenylmethyl fluoroborate (0.269 g., 0.0008 mole) in dry methylene chloride (7 ml.) was added to a solution of tricarbonyl-7-endo-methylcycloheptatrienechromium (0.198 g., 0.0008 mole) in methylene chloride (0.5 ml.). No precipitate had formed after 10 mins. The solution was poured into water (50 ml.), shaken and the methylene chloride layer separated and dried ($CaCl_2$). It was then evaporated to dryness in vacuo, extracted with ligroin and chromatographed on alumina (20 g.) to yield unreacted tricarbonyl-7-endo-methylcycloheptatrienechromium (0.154 g., 78%) m.p. 84-85°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample. No trace of triphenylmethane was found.

Attempted preparation of tricarbonyl-7-exo-methoxycyclohepta(1,3,5)-trienechromium.

a) By direct reaction of 7-methoxycycloheptatriene with hexacarbonylchromium.

7- methoxycycloheptatriene[116] (1.14 g., 0.01 mole) and hexacarbonylchromium (3.2 g., 0.014 mole) were refluxed in a mixture of petroleum ether (b.p. 100/120°C) (20 ml.) and n-hexane (10 ml.) in an apparatus designed[144] to automatically return subliming hexacarbonylchromium into the reaction zone (hereinafter referred to as the Strohmeier apparatus) for 12½ hrs. Carbon monoxide (170 ml.) was evolved. Then, the mixture was filtered to leave unreacted hexacarbonylchromium (2.6 g., 81%). The filtrate was evaporated to dryness and extracted with ligroin. Chromatography of the pale-pink extract caused a trace of a pink band to decompose on the column.

b) By exchange with tricarbonylcycloheptatrienechromium.

Tricarbonylcycloheptatrienechromium (1.14 g., 0.005 mole) and 7-methoxycycloheptatriene (6.1 g., 0.05 mole) were refluxed in ethylene glycol diethyl ether (b.p. 125°C., 30 ml.) for 24 hrs., using an air condenser so positioned that the cycloheptatriene which might have been liberated could distil (b.p. 114°C.) out of the reaction zone. Then, the deep red solution was evaporated to dryness and extracted with ligroin (3 x 20 ml.). Concentration of this extract and chromatography on alumina (60 g.) gave only unreacted tricarbonylcycloheptatrienechromium, (0.11 g., 10%) as red needles m.p. 126-129°C.

Tricarbonyl-7-endo-phenylcyclohepta(1,3,5)trienechromium.

a) To a solution of phenylmagnesium bromide [from magnesium (0.24 g., 0.01 g. atom) and bromobenzene (1.57 g., 0.01 mole)] in ether (5 ml.) was added a solution of tricarbonyl-7-endo-methoxycycloheptatrienechromium (0.516 g., 0.002 mole) in ether (20 ml.). The mixture was stirred 1½ hrs. Then, after filtration, the filtrate was evaporated to dryness at room temperature in vacuo. The dried extract was triturated with hot ligroin (3 x 20 ml.) and this solution after filtration and concentration was chromatographed on alumina (20 g.) to yield one band. Elution with ligroin/benzene (9/1) gave red needles (0.573 g., 95%) m.p. 134-135°C., soluble in common organic solvents. Tricarbonyl-7-endo-phenylcyclohepta(1,3,5)trienechromium shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 1976, 1905 and 1862 $cm.^{-1}$

Found : C, 62.80; H, 3.9; Cr, 17.0;

$C_{16}H_{12}CrO_3$ requires : C, 63.15; H, 4.0; Cr, 17.1%

b) To a solution of phenylmagnesium bromide [from magnesium (0.24 g., 0.01 g.atom) and bromobenzene (2.0 g., 0.013 mole)] in ether (5 ml.) was added a suspension of tricarbonyltropyliumchromium fluoroborate (1.57 g., 0.005 mole) in tetrahydrofuran (25 ml.). An immediate exothermic reaction occurred with gas (CO) evolution. The mixture was stirred 1½ hrs., at room temperature. Then, after filtration, the solution was evaporated to dryness in vacuo. The resultant gum was triturated with hot ligroin (20 ml.), and this extract was filtered and concentrated. Chromatography on alumina (20 g.) gave a single orange-red band from which orange crystals (0.020 g., 1%) m.p. 132-135°C were obtained. The compound was identified as tricarbonyl-7-endo-phenylcycloheptatrienechromium on the basis of its m.p., mixed m.p. with an authentic sample, and infrared spectrum. The petrol-insoluble material was extracted with benzene and from this extract, by chromatography on alumina (20 g.) was obtained a further (0.080 g.), total (0.100 g., 7%) of the same compound.

Tricarbonyl-7-exo-(ethyoxycarbonyl)methylcyclohepta(1,3,5)trienechromium.

Hexacarbonylchromium (3.0 g., 0.013 mole) and 7-(ethyoxycarbonyl)-methylcycloheptatriene[121] (2.44 g., 0.013 mole) were refluxed in a mixture of ethylene glycol diethyl ether (20 ml.) and n-hexane (20 ml.) in the Strohmeier apparatus[144] for 40 hrs. The flask was cooled, and unreacted hexacarbonylchromium (1.0 g., 33%) was removed by filtration. The filtrate and ligroin washings were evaporated to dryness *in vacuo* leaving a deep red oil. The oil was dissolved in benzene/ligroin (4/1, 20 ml.) and chromatographed on neutralized (1 hr. deactivated) alumina (60 g.). Elution with ligroin gave a single red band which afforded red leaflets (1.91 g., 67%) m.p. 49-50°C., very soluble in common organic solvents. Tricarbonyl-7-exo-(ethyoxycarbonyl)methylcyclohepta(1,3,5)trienechromium shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 2000, 1934, 1905 and 1862 cm^{-1} and at 1730 cm^{-1} in the 'ester' region.

Found : C, 53.2; H, 4.7; Cr, 16.70;

$C_{14}H_{14}CrO_5$ requires : C, 53.5; H, 4.5; Cr, 16.55%

Tricarbonyl-7-exo-(ethoxycarbonyl)methylcyclohepta(1,3,5)trienemolybdenum.

Hexacarbonylmolybdenum (5.8 g., 0.02 mole) and 7-(ethoxycarbonyl)-methylcycloheptatriene[121] (3.5 g., 0.02 mole) were refluxed 10 hrs. in ethylene glycol diethyl ether (20 ml.). The solution was filtered hot, under nitrogen, and unreacted material was removed *in vacuo*, leaving a deep red oil (5.0 g.). Initial attempts to crystallise this oil by chromatography, action of the usual solvents and sublimation were without success. The oil was kept in a refrigerator for 10 weeks. Then, the partly decomposed mass was triturated with ether (3 x 6 ml.) filtered and cooled to -78°C. Bright orange crystals (1.40 g., 20%) m.p.114-115°C., separated and were recrystallised from ether/pentane to give bright orange needles, soluble in common organic solvents, but sparingly soluble in paraffins. Tricarbonyl-7-exo-(ethoxycarbonyl)methylcyclohepta(1,3,5)trienemolybdenum has absorption in the metal carbonyl stretching frequency region of the infrared at 1992, 1916 and 1869 cm^{-1} and in the 'ester' carbonyl region at 1736 $cm.^{-1}$

Found : C, 46.9; H, 4.1;

$C_{14}H_{14}MoO_5$ requires : C, 46.8; H, 3.9%

Tricarbonyl-7-endo-(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium.

To a suspension of zinc (freshly prepared turnings, 1.30 g., 0.02 g. atom) in tetrahydrofuran (2 ml.) was added a crystal of iodine and 5 ml of a solution of ethyl bromoacetate (1.7 ml., 0.02 mole) together with tricarbonyl-7-endo-methoxycycloheptatrienechromium (2.54 g., 0.01 mole) in tetrahydrofuran (20 ml.).

A vigorously exothermic reaction began after a few minutes and the remainder of the solution was added dropwise over a 20 min. period. Towards the end of the reaction, a hot water bath was used to maintain a gentle refluxing of the solution. After cooling, the solution was poured into water (200 ml.) and extracted with ligroin (6 x 20 ml.). This extract was washed with water (2 x 200 ml.) and dried (Na_2SO_4). The solution was concentrated and chromatographed on neutralized alumina (60 g., deactivated for 2 hrs.). Elution with ligroin afforded two bands. The first, orange, band afforded tricarbonyldi(cycloheptatrienyl)chromium (0.002 g.) identified by m.p., and infrared spectral comparison with an authentic sample.

The second, red, band afforded deep red needles (2.76 g., 88%) m.p. 100-101°C., soluble in common organic solvents. Tricarbonyl-7-endo-(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 1980, 1905 and 1859 cm^{-1} and at 1730 cm^{-1} in the 'ester' carbonyl region.

Found : C, 53.3; H, 4.6; Cr, 17.00;
$C_{14}H_{14}CrO_5$ requires : C, 53.5; H, 4.5; Cr, 16.55%

A trace of a third, orange, band which stuck to the column was not examined further.

Tricarbonyl-7-exo-di(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium.

7-di(ethoxycarbonyl)methylcycloheptatriene[121] (2.0 g., 0.008 mole) and hexacarbonylchromium (2.0 g., 0.009 mole) were refluxed in petroleum ether (b.p. 100/120°C., 20 ml.) and n-hexane (15 ml) in the

Strohmeier apparatus[144] for 14½ hrs. The mixture was then cooled, filtered and evaporated to dryness in vacuo, leaving a deep red oil. This was chromatographed on neutralized alumina (25 g., deactivated 2 hrs.) to give one red band. Elution with ligroin/benzene (4/1) afforded red needles (1.54 g., 50%) m.p. 77-78°C., soluble in common organic solvents. Tricarbonyl-7-exo-di(ethoxycarbonyl)methylcyclohepta(1,3,5)-trienechromium shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 1996, 1905 and 1887 cm^{-1} and in the 'ester' carbonyl region at 1751 and 1715 $cm.^{-1}$

Found : C, 53.20; H, 4.9; Cr, 13.4;

$C_{17}H_{18}CrO_7$ requires : C, 52.85; H, 4.7; Cr, 13.5%

Tricarbonyl-7-endo-di(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium.[56]

Diethyl malonate (1.28 g., 0.008 mole) was added to a solution of sodium ethoxide [from sodium (0.138 g., 0.006 g. atom)] in ethanol (5 ml.) and the mixture was stirred 30 mins. Tetrahydrofuran (20 ml.) was then added together with tricarbonyltropyliumchromium perchlorate (1.5 g., 0.0046 mole) and the resulting mixture was stirred overnight. The solvents were removed in vacuo., and the red residue was extracted with ligroin. Evaporation of this extract to dryness yielded a red crystalline residue (0.81 g.), which was chromatographed on neutral alumina (90 g.) to give two major bands with traces of two others. Elution with ligroin gave a trace of a red solid and also yellow needles of tricarbonylbenzenechromium (0.236 g., 24%) m.p. 162-163°C., the identity being established by mixed m.p. and infrared spectral comparison with an authentic sample.

Elution with ligroin/benzene (1/1) gave orange-red crystals of tricarbonyl-7-endo-di(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium (0.552 g., 31%). Recrystallisation from ligroin gave orange-red plates m.p. 122-123°C., soluble in common organic solvents. The compound shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 1999, 1932 and 1905 cm^{-1} and at 1753 and 1738 cm^{-1} in the 'ester' carbonyl region.

Found : C, 52.8; H, 4.8;

$C_{17}H_{18}CrO_7$ requires : C, 52.8; H, 4.7%

Elution with benzene gave a small amount of a green gum (0.011 g.) which did not show absorption in the carbonyl region of the infrared and was not examined further.

Tricarbonyl-7-endo-di(ethoxycarbonyl)methylcyclohepta(1,3,5)trienemolybdenum.

A solution of sodium ethoxide [from sodium (0.12 g., 0.005 g. atom)] in ethanol (5 ml.) was added to a solution of diethyl malonate (5 ml.) in tetrahydrofuran (25 ml.). The resulting solution was shaken 30 mins., then tricarbonyltropyliummolybdenum fluoroborate (1.83 g., 0.005 mole) was added and the resulting solution was shaken a further 30 mins. Unreacted material was then removed *in vacuo*., and the solid red-brown residue was extracted with pentane (25 ml.). After filtration, the extract was concentrated and cooled to -78°C. Red needles (0.725 g., 33%) m.p. 92-93°C., were obtained. Tricarbonyl-7-endo-di(ethoxycarbonyl)methylcyclohepta(1,3,5)trienemolybdenum shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 2000, 1923 and 1880 cm^{-1} and in the 'ester' region at 1733 and 1721 $cm.^{-1}$ The compound is soluble in common organic solvents with the exception of the paraffins.

Found : C, 47.60; H, 4.4;

$C_{17}H_{18}MoO_7$ requires : C, 47.45; H, 4.2%

Alkaline hydrolysis of tricarbonyl-7-endo-(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium.

To a solution of sodium hydroxide (0.08 g., 0.002 mole) in aqueous methanol (45 ml.) was added tricarbonyl-7-endo-(ethoxycarbonyl)methylcycloheptatrienechromium (0.314 g., 0.001 mole). The resulting mixture was stirred 22 hrs. Then, the solution was evaporated to dryness in vacuo., at room temperature leaving a red oily residue. This was extracted with benzene, to remove any unchanged ester, and then dissolved in water. Acidification in the presence of chloroform was followed by shaking after which the chloroform layer was separated and dried ($CaCl_2$). Evaporation to dryness left a deep red crystalline solid (0.251 g., 93%) m.p. 148-150°C. Recrystallisation of the compound from methylene chloride/ligroin, gave red needles, m.p. 151-152°C, soluble in common organic solvents with the exception of the paraffins. Tricarbonyl-7-endo-(carboxy)methylcyclohepta(1,3,5)trienechromium shows absorption in the metal carbonyl stretching frequency region of the infrared at 1976, 1901 and 1873 cm^{-1} and in the 'acid' carbonyl region at 1698 $cm.^{-1}$

Found : C, 50.3; H, 3.8; Cr, 17.8;

$C_{12}H_{10}CrO_5$ requires : C,50.35; H, 3.5; Cr, 18.2%

Rearrangement of tricarbonyl-7-endo-di(ethoxycarbonyl)methylcyclohepta-(1,3,5)trienechromium with diethylsodiomalonate.[56]

Tricarbonyl-7-endo-di(ethoxycarbonyl)methylcycloheptatrienechromium (0.18 g., 0.0005 mole) and diethylsodiomalonate [from sodium (0.076 g., 0.0033 g. atom) and diethyl malonate (1.0 g., 0.0062 mole)] were allowed to react in ethanol at room temperature overnight. The solvent was then removed in vacuo., and the orange residue was extracted with ligroin. Chromatography of the orange extract on alumina (50 g.) and elution with ligroin gave yellow crystals (0.038 g., 38%) m.p. 162-163°C. Mixed m.p. and infrared spectral comparison with an authentic specimen showed the compound to be tricarbonylbenzenechromium.

Elution with benzene gave unreacted tricarbonyl-7-endo-di(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium (0.007 g.) as red plates m.p. and mixed m.p. 122-123°C.

Rearrangement of tricarbonyl-7-exo-di(ethoxycarbonyl)methylcyclohepta-(1,3,5)trienechromium with sodium methoxide.

To a solution of sodium methoxide [from sodium (0.258 g., 0.01 g. atom)] in methanol (10 ml.) was added tricarbonyl-7-exo-di(ethoxycarbonyl)methylcycloheptatrienechromium (0.267 g., 0.0008 mole). The mixture was stirred at room temperature overnight. Then, the solvent was removed in vacuo., at room temperature to leave a red viscous residue. This was triturated with ligroin (4 x 5 ml.) and the filtered extract was concentrated and chromatographed on alumina (20 g.) to give one yellow band from which tricarbonylbenzenechromium (0.010 g., 6 %) m.p. 162-163°C was obtained by elution with benzene/ligroin (1/1) and subsequent sublimation. Identity was established by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

Attempted rearrangement of tricarbonyl-7-exo-di(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium using potassium t-butoxide in t-butanol.

To a solution of tricarbonyl-7-exo-di(ethoxycarbonyl)methylcycloheptatrienechromium (0.193 g., 0.0005 mole) in tetrahydrofuran (40 ml.) was added 1 ml. of a solution of potassium t-butoxide [from potassium (0.181 g., 0.005 g. atom)] in t-butanol (40 ml.). The resulting solution contained 0.2 molar equivalents of potassium t-butoxide. The solution was stirred 67 hrs. Then, the solution was evaporated to dryness at room temperature *in vacuo*. Extraction of the residue with ligroin was followed by chromatography of the extract on neutralized alumina (20 g., deactivated 2 hrs.). The single red band gave only unreacted tricarbonyl-7-exo-di(ethoxycarbonyl)methylcycloheptatrienechromium (0.124 g., 65%) m.p. 76-77° C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

No trace of tricarbonylbenzenechromium was found.

Attempted rearrangement of tricarbonyl-7-exo-(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium with sodium methoxide.

To a solution of sodium methoxide [from sodium, (0.10 g., 0.004 g. atom)] in methanol (10 ml.) was added tricarbonyl-7-exo-(ethoxycarbonyl)methylcycloheptatrienechromium (0.57 g., 0.002 mole). The resulting mixture was stirred 45 hrs at room temperature. The solvent was removed *in vacuo*., at room temperature and the red residue was extracted with ligroin (3 x 20 ml.). After concentration to about 5 ml., the extract was chromatographedon neutralized alumina (20 g., deactivated 2 hrs.) and from the single red band eluted with ligroin was obtained unchanged tricarbonyl-7-exo-(ethoxycarbonyl)methylcycloheptatrienechromium (0.46 g., 80 %) m.p. 48-49°C., identified by m.p., mixed m.p. and infrared spectral comparison with anauthentic sample.

No trace of tricarbonylbenzenechromium was found.

Attempted rearrangement of tricarbonyl-7-endo-(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium with sodium methoxide.

To a solution of tricarbonyl-7-endo-(ethoxycarbonyl)methylcycloheptatrienechromium (0.314 g., 0.001 mole) in dry methanol (40 ml.) was added 1 ml of a solution of sodium methoxide [from sodium (0.015 g., 0.00065 g.atom)] in methanol (45 ml.). The resulting solution, which contained 0.01 molar equivalents of sodium methoxide, was stirred 24 hrs. Then, the solvent was removed *in vacuo*., and the residue was extracted with ligroin and chromatographed on neutralized alumina (20 g., deactivated 2 hrs.). Elution with ligroin afforded only unreacted tricarbonyl-7-endo-(ethoxycarbonyl)methylcycloheptatrienechromium (0.281 g., 90 %) m.p. 100-101°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample. No trace of tricarbonylbenzenechromium was found.

Attempted rearrangement of tricarbonyl-7-endo-(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium with potassium t-butoxide in t-butanol.

To a solution of tricarbonyl-7-endo-(ethoxycarbonyl)methylcycloheptatrienechromium (0.314 g., 0.001 mole) in tetrahydrofuran (20 ml.) was added 1 ml. of a solution of potassium t-butoxide [from potassium (0.87 g., 0.025 g.atom)] in t-butanol (40 ml.). The resulting solution which contained 0.5 molar equivalents of potassium t-butoxide, was stirred for 13 hrs at room temperature. Then, the solvent was removed in vacuo., at room temperature and the brown residue was extracted with ligroin (2 x 20 ml.). Chromatography of this extract on alumina afforded only unreacted tricarbonyl-7-endo-(ethoxycarbonyl)methylcycloheptatrienechromium (0.13 g., 42%) m.p.100-101°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample. No trace of tricarbonylbenzenechromium was found.

Attempted rearrangement of tricarbonyl-7-endo-(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium with sodium hydride.

To sodium hydride (supplied as a 50 % dispersion in oil, by L. Light and Co., 0.159 g., 0.003 mole) in tetrahydrofuran (20 ml.) was added tricarbonyl-7-endo-(ethoxycarbonyl)methylcycloheptatrienechromium (0.516 g., 0.0016 mole). The resulting mixture was stirred 20 hrs., at room temperature. Then, excess sodium hydride was destroyed with aqueous ethanol and the solution was evaporated to dryness at room temperature in vacuo. The resulting pink gum was triturated with ligroin (4 x 10 ml.) and this extract was chromatographed on alumina (10 g.) but no trace of tricarbonylbenzenechromium was found.

The ligroin-insoluble material was dissolved in water and this solution was acidified using dilute hydrochloric acid. The reddish suspension was extracted with chloroform and the chloroform layer was then separated and dried ($CaCl_2$). Filtration and evaporation to dryness at room temperature in vacuo., gave tricarbonyl-7-endo-(carboxy)methylcycloheptatrienechromium (0.286 g., 60 %) m.p. 149-150°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

Attempted rearrangement of tricarbonyl-7-endo-(ethoxycarbonyl)methylcyclohepta(1,3,5)trienechromium with triphenylmethylsodium.

A solution of triphenylmethylsodium[146] [from triphenylmethylchloride, freshly prepared (2.78 g., 0.01 mole) and 1 % sodium amalgam (51 g.)] in ether (66 ml.) was added to a solution of tricarbonyl-7-endo-(ethoxycarbonyl)methylcycloheptatrienechromium (0.335 g., 0.001 mole) in ether (50 ml.). The resulting solution was stirred for 19 hrs. Then, dry methanol (13 ml.) was added to decompose the excess triphenylmethylsodium.

The resulting yellow solution was chromatographed on neutralized alumina (deactivated 2 hrs.) to give one yellow band from which yellow crystals (1.40 g.) m.p.88-90°C., were obtained. Rechromatographing this yellow compound gave pure triphenylmethane (1.35 g., 57%) and a bright yellow crystalline compound (0.030 g.) m.p. 218-220°C.

Found ; C, 93.35; H, 6.3%. M. 130.

No trace was found of any compound having absorption in the metal carbonyl stretching frequency region of the infrared.

Repetition of the reaction using an excess of tricarbonyl-7-endo-(ethoxycarbonyl)methylcycloheptatrienechromium resulted in recovery of the compound in 94% yield.

Tricarbonyl-7-endo-(2',3',4',5'-tetraphenylcyclopentadienyl)cyclohepta(1,3,5)-trienechromium.

To a solution of phenyllithium [from lithium (0.12 g., 0.017 g. atom) and bromobenzene (1.3 g., 0.0083 mole)] in ether (10 ml.) was added a solution of 2,3,4,5-tetraphenylcyclopentadiene[147] (2.76 g., 0.0075 mole) in benzene (50 ml.). The resulting milky suspension was refluxed 2 hrs., and then cooled. Tricarbonyltropyliumchromium fluoroborate (2.36 g., 0.0075 mole) was then added and the resulting mixture was stirred 13½ hrs.

Evaporation of the solvents was followed by extraction with ligroin (5 x 20 ml.). Filtration gave an orange filtrate and a pink residue.

The orange filtrate was evaporated to dryness and extracted with ligroin (4 x 3 ml.). Chromatography of this extract on alumina (60 g.) gave one band, which afforded tricarbonyldi(cycloheptatrienyl)chromium (0.050 g., 4%) m.p. 147-148°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

The pink solid was sublimed at 140°C/0.1 mm., for 40 hrs., and yielded tetraphenylcyclopentadiene (0.100 g., 4%). The remaining solid was extracted with hot benzene (5 x 20 ml.) and concentrated. This extract was chromatographed on alumina (600 g.). Washing with ligroin (1200 ml.) to remove tetraphenylcyclopentadiene was followed by elution with benzene/ligroin (1/9) which gave a red solid (0.030 g., 2 %) m.p.

222-224°C., identified as hexacarbonyldi(cycloheptatrienylchromium) on the basis of its m.p., mixed m.p. with an authentic sample and infrared spectrum.

Elution with benzene/ligroin (1/1) afforded a deep-orange compound which gave orange-red needles (1.94 g., 43 %) m.p. 198-198.5°C from benzene/ligroin, soluble in benzene, chloroform and methylene chloride, but only slightly soluble in other common organic solvents. Tricarbonyl-7-endo-(2',3',4',5'-tetraphenylcyclopentadienyl)cyclohepta(1,3,5)trienechromium shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 2000, 1927 and 1887 cm.$^{-1}$

Found : C, 78.0; H, 5.0; Cr, 8.7;

$C_{39}H_{28}CrO_3$ requires : C, 78.5; H, 4.7; Cr, 8.7%

Attempted rearrangement of tricarbonyl-7-endo-(2',3',4',5'-tetraphenylcyclopentadienyl)cyclohepta(1,3,5)trienechromium with sodium methoxide.

Tricarbonyl-7-endo-(2',3',4',5'-tetraphenylcyclopentadienyl)cycloheptatrienechromium (0.576 g., 0.001 mole) was added to a solution of sodium methoxide [from sodium (0.042 g., 0.0018 g. atom)] in benzene (100 ml.) and methanol (1 ml.). The resulting mixture was stirred at room temperature for 21 hrs. After filtration, the filtrate was evaporated to dryness at room temperature in vacuo. The dried extract was sublimed at 100°C/0.1 mm for 2 hrs. No trace of tricarbonylbenzenechromium was found.

The solid was then extracted with hot ligroin (12 ml.) and filtered, washed with water and dried leaving a deep pink solid (0.404 g., 70%)

m.p. 196-198°C., identified as tricarbonyl-7-endo-(2',3',4',5'-tetraphenylcyclopentadienyl)cycloheptatrienechromium on the basis of its m.p., mixed m.p. with an authentic sample and infrared spectrum.

The filtrate was chromatographed on alumina (60 g.). Elution with benzene/ligroin (1/20) gave tetraphenylcylopentadiene (0.024 g., 5 %) m.p. 162-164°C., (lit^{147} m.p. 164-165°C).

Attempted rearrangement of tricarbonyl-7-endo-(2',3',4',5'-tetraphenylcyclopentadienyl)cyclohepta(1,3,5)trienechromium with potassium t-butoxide in t-butanol.

Tricarbonyl-7-endo-(2',3',4',5'-tetraphenylcyclopentadienyl)cycloheptatrienechromium (0.337 g., 0.0006 mole) was added to a solution of potassium t-butoxide [from potassium (0.012 g., 0.0003 g. atom)] in t-butanol (7 ml.). The resulting mixture was refluxed 6 hrs. Then, ethanol (10 ml.) was added and the solution was filtered. The solid was extracted with hot benzene (10 ml.) and the resulting filtrate was evaporated to dryness in vacuo. Sublimation of this dry residue at 100°C/0.1 mm., gave no tricarbonylbenzenechromium.

The residue was dissolved in benzene and chromatographed on alumina (30 g.). Only unreacted tricarbonyl-7-endo-(2',3',4',5'-tetraphenylcyclopentadienyl)cycloheptatrienechromium (0.20 g., 60 %) was obtained

Tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)cyclohepta(1,3,5)-trienechromium.

To a solution of 2,3,4-triphenylcyclopentadiene^{125} (5.88 g., 0.02 mole) in benzene (150 ml.) was added 18.7 ml. of a solution of phenyllithium [from lithium (3.0 g., 0.4 g. atom) and bromobenzene (32 g., 0.2 mole)] in ether (100 ml.). A white precipitate formed immediately and the suspension was refluxed 2 hrs., and then cooled to room temperature. Tricarbonyltropyliumchromium fluoroborate (3.14 g., 0.01 mole) was then added, together with benzene (10 ml.). The resulting suspension was stirred for 20 hrs. Then, after addition of ethanol (10 ml.) the mixture was filtered and the solid residue was well washed with hot benzene, giving a total volume of filtrate of 250 ml. This was evaporated to dryness leaving a red oil. The oil was dissolved in benzene (20 ml) and chromatographed on alumina (3 hr. deactivated, 400 g.) in ligroin/ benzene (5/1). Elution with the same solvent mixture gave first a yellow band which afforded unreacted triphenylcyclopentadiene (2.6 g., 45 %) and then bright red needles (3.62 g., 70 %) m.p. 165-167.5°C., soluble in common organic solvents with the exception of the paraffins. Recrystallisation from methylene chloride/ligroin raised the m.p. to 167-167.5°C. Tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)-cyclohepta(1,3,5)trienechromium shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 2000, 1934 and 1901 cm^{-1} (CCl_4) and 1984, 1923 and 1866 cm^{-1}(KCl).

Found : C, 76.2; H, 4.7; Cr, 9.8;
$C_{33}H_{24}CrO_3$ requires : C, 76.1; H, 4.6; Cr, 10.0%

The ultraviolet absorption consists of two peaks; at 242 mμ ($\log\epsilon = 4.6$) and at 356 mμ ($\log\epsilon = 4.1$).

Reaction of 2,3,4-triphenylcyclopentadienyllithium with tricarbonyltropyliumchromium fluoroborate in the presence of tetrahydrofuran.

To a suspension of phenyllithium [from lithium (0.70 g., 0.1 g. atom) and bromobenzene (7.85 g., 0.05 mole)] in ether (20 ml.) was added a solution of 2,3,4-triphenylcyclopentadiene (14.6 g., 0.05 mole) in benzene (150 ml.). The mixture, in which a white precipitate quickly formed, was refluxed for 2 hrs. After cooling, tricarbonyltropyliumchromium fluoroborate (9.57 g., 0.03 mole) and tetrahydrofuran (15 ml.) were added, and the resulting mixture was stirred for 16 hrs. After filtration, the solution was taken to dryness *in vacuo.* The resultant solid was dissolved in benzene/ligroin and filtered through alumina to remove copious quantities of a green decomposition product. The filtrate was taken to small volume and chromatographed on alumina (250 g.). Elution with benzene/ligroin (1/1) gave red needles of tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)cycloheptatrienechromium (1.8 g., 11 %) m.p. 165-167°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample. Further elution with pure benzene gave red needles (0.100 g., 1 %) m.p. 165-167°C. The compound is soluble in common organic solvents with the exception of the paraffins. *Tricarbonyl-7-endo-(1',2',3'-triphenylcyclopentadienyl)cyclohepta(1,3,5)trienechromium* shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 1984, 1916 and 1887 cm.$^{-1}$ The ultraviolet spectrum shows two peaks; at 242 mμ (log ε = 4.5) and at 320 mμ (log ε = 4.1)

Found : C, 75.3; H, 4.8;

$C_{33}H_{24}CrO_3$ requires : C, 76.1; H, 4.6%

Ozonolysis of tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)-cyclohepta(1,3,5)trienechromium.

Tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)cycloheptatrienechromium (0.27 g., 0.0005 mole) in methylene chloride (14 ml.) was treated (at -14°C.) with a slight excess of ozonized oxygen. The resulting mixture of ozonides was decomposed by shaking with ferrous sulphate solution. The dried methylene chloride layer was chromatographed on alumina (5 g.). Elution withbenzene/ether (1/1) gave a trace of a yellow gum whose infrared spectrum was identical with that of benzil.

Attempted rearrangement of tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)cyclohepta(1,3,5)trienechromium with sodium methoxide.

Tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)cycloheptatrienechromium (0.67 g., 0.0013 mole) was added to a solution of sodium methoxide from sodium (0.016 g., 0.0007 g. atom) in methanol (40 ml.), to which had been added benzene (20 ml.). The mixture was stirred 48 hrs. The mixture was then evaporated to dryness at room temperature in vacuo. The residue was extracted with benzene (4 x 2 ml.) and this extract was chromatographed on alumina (70 g.) in ligroin to give unchanged tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)cycloheptatrienechromium (0.332 g., 50 %) m.p. 164-165°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

Traces of two other bands were eluted with ether/methanol, but showed no absorption in the metal carbonyl region of the infrared.

Rearrangement of tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)-cyclohepta(1,3,5)trienechromium with triphenylmethylsodium.

A solution of triphenylmethylsodium[146] [from triphenylmethyl chloride (4.0 g., 0.014 mole)] in ether (200 ml.) was added to tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)cycloheptatrienechromium (1.5 g., 0.003 mole). The resulting mixture, which rapidly turned black-brown, was stirred for 22 hrs. Then, methanol (20 ml.) was added to destroy excess triphenylmethylsodium. At this stage the mixture was pale red. Solvents were removed in vacuo., leaving a yellow residue. This was extracted with ligroin and the extract was chromatographed on alumina (60 g.). Elution with ligroin gave:-

a) White needles (1.55 g., 45 %) m.p.90-92°C., identified as triphenylmethane on the basis of m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

b) Pale yellow crystals (1.01 g.) m.p.200-210°C., which m.p. was raised to 224-226°C., by repeated recrystallisation from ligroin.

c) A red-brown gum (0.190 g.) which was sublimed at 100°C/0.1 mm., to yield tricarbonylbenzenechromium (0.150 g.).

The petrol-insoluble material was sublimed at 100°C/0.1 mm., to yield tricarbonylbenzenechromium (0.020 g., total 0.170 g., 28 %).

Reaction of triphenylmethylsodium and 2,3,4-triphenylfulvene.

To a solution of 2,3,4-triphenylfulvene[125] (0.43 g., 0.0014 mole) in ether (25 ml.) was added 25 ml. of a solution of triphenylmethylsodium[146] [from triphenylmethyl chloride (3.54 g., 0.013 mole) and 1 % sodium amalgam (60 g., 0.026 g. atom)] in ether (200 ml.). The fulvene solution was instantly decolourised. The mixture was allowed to stand overnight. Then, the solvent was removed at room temperature in vacuo. The residue was extracted with ligroin and chromatographed on alumina. Elution with ligroin gave:-

a) White needles (0.140 g., 4.7%) of triphenylmethane, m.p. 90-92°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

b) A trace of a yellow-orange gum.

c) White crystals (0.0123 g., 1 %) of triphenylmethyl peroxide, m.p. 180-184°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

d) White prisms (0.152 g., 4 %) m.p. 224-226°C. (lit[148] m.p.218°C) thought to be hexaphenylpropane.

Found : C, 94.1; H, 6.3; M. 493;

$C_{39}H_{32}$ requires : C, 93.6; H, 6.4; M. 501.

Elution with increasing proportions of benzene gave low yields of a further seven compounds, obtained in insufficient quantity for identification.

Rearrangement oftricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)-cyclohepta(1,3,5)trienechromium with potassium t-butoxide in dimethyl sulphoxide.

Freshly sublimed potassium t-butoxide (0.724 g., 0.006 mole) was added to a solution of tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)cycloheptatrienechromium (1.00 g., 0.002 mole) in pure dry dimethyl sulphoxide[126] (40 ml.). The mixture was stirred 17 hrs. at room temperature. It was then poured into water (300 ml.) and extracted with ether (4 x 100 ml.). The ethereal extract was concentrated, dried (Na_2SO_4) and evaporated to dryness in vacuo. The residue was dissolved in ligroin and filtered through alumina. The solution was evaporated to dryness and sublimed to give tricarbonylbenzenechromium (0.115 g., 28 %) m.p. 161-2°C.

The aqueous solution was continuously extracted with ether for 4 hrs. in an extractor. This extract yielded only uncrystallisable gums (0.20 g.) having no absorption in the metal carbonyl stretching frequency region of the infrared.

The aqueous layer was acidified (dilute HCl) and extracted with ether. Concentration, drying and evaporation to dryness gave an orange gum (0.124 g.) having absorption in the metal carbonyl stretching frequency region of the infrared at 1985 and 1910 cm^{-1}. Attempts to crystallise this gum were unsuccessful.

Rearrangement of tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)-cyclohepta(1,3,5)trienechromium with sodium hydride.

To a suspension of sodium hydride [0.130 g., 0.0055 mole, as a 50 % dispersion in oil (0.26 g.)] in tetrahydrofuran (20 ml.) was added a solution of tricarbonyl-7-endo-(2',3',4'-triphenylcyclopentadienyl)cycloheptatrienechromium (0.329 g., 0.0006 mole) in tetrahydrofuran (10 ml.). The resulting mixture, which rapidly turned deep purple, was stirred for 1 hr. Methanol (4 ml.) was then added to destroy the remaining sodium hydride and the solvents were then removed at room temperature in vacuo. A ligroin extract was chromatographed on alumina (20 g.) and from the main yellow band was obtained tricarbonylbenzenechromium (0.007 g., 5 %) m.p. 161-162°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample. Only trace amounts of two other bands were eluted from the column.

The ligroin-insoluble residue (0.400 g.) was a deep purple crystalline solid and proved to be quite sensitive to oxygen. A sample (0.297 g.) was dissolved in ethanol (10 ml.)/water (150 ml.). Acidification (dilute HCl) was followed by extraction into methylene chloride (2 x 50 ml.). The deep-orange oil which resulted from this dried ($CaCl_2$) extract upon evaporation, showed absorption in the metal carbonyl stretching frequency region of the infrared at 1975 and 1910cm.$^{-1}$

Attempted rearrangement of 7-di(ethoxycarbonyl)methylcyclohepta(1,3,5)-triene [121] with sodium methoxide.

To a solution of sodium methoxide [from sodium (0.51 g., 0.022 g. atom)] in dry methanol (10 ml.) was added a solution of 7-di(ethoxycarbonyl)-methylcycloheptatriene[121] (2.37 g., 0.0095 mole) in methanol (10 ml.). The mixture was left for 16 hrs. Then, the mixture was heated and the volatile distillate (b.p. 62-64°C.) was collected and examined on a V.P.C. column. Only unreacted methanol was present in the distillate. No trace of benzene was found.

Tricarbonyl 9:10-dihydroanthracenechromium.

9:10-dihydroanthracene (5.4 g., 0.03 mole) and hexacarbonylchromium (6.6 g., 0.03 mole) were refluxed in diglyme (50 ml.) for 4 hrs. By this time the theoretical amount of carbon monoxide had been evolved. Unreacted material was removed in vacuo. The residue was recrystallised from diglyme and then benzene/ligroin to give lemon-yellow needles (3.9 g., 51 %) m.p. 143-144°C (lit[31] 143-144°C.) of tricarbonyl 9:10-dihydroanthracenechromium.

Attempted reaction of tricarbonylbenzenechromium with 9:10-dihydroanthracene.

Tricarbonylbenzenechromium (1.04 g., 0.005 mole) and 9:10-dihydroanthracene (0.225 g., 0.0012 mole) were heated at 160°C. for 8 hrs. Then, some unreacted tricarbonylbenzenechromium (0.55 g.) was removed by sublimation. The dark-brown residue was extracted with hot benzene (25 ml.) allowed to cool and filtered through alumina, (30 g.). The yellow solution was evaporated to yield tricarbonylbenzenechromium (0.48 g., total 1.00 g., 99%).

Attempted dehydrogenation of tricarbonyl 9:10-dihydroanthracenechromium using triphenylmethyl perchlorate.

To a solution of tricarbonyl 9:10-dihydroanthracenechromium (0.25 g., 0.0008 mole) in benzene (25 ml.) was added a suspension of triphenylmethyl perchlorate[143] (0.35 g., 0.001 mole) in benzene (25 ml.). The mixture was shaken for 6 hrs. No colour change was apparent at this stage. The mixture was poured into water (500 ml.), the benzene layer separated and dried (Na_2SO_4). Concentration and chromatography on alumina (60 g.) gave unreacted tricarbonyl 9:10-dihydroanthracenechromium

(0.20 g., 80 %) m.p. 143-144°C., identified by m.p., mixed m.p and infrared spectral comparison with an authentic sample.

Attempted dehydrogenation of tricarbonyl 9:10-dihydroanthracenechromium with chloranil.

A solution of tricarbonyl 9:10-dihydroanthracenechromium (0.77 g., 0.0025 mole) and chloranil (1.39 g., 0.005 mole) in ethylene glycol diethyl ether (50 ml.) was refluxed for 20 hrs. The excess solvent was removed *in vacuo*., and the solid residue was extracted with hot benzene (4 x 10 ml.). This extract was filtered hot, to yield a colourless solution which afforded anthracene (0.27 g., 63 %) m.p.211-212°C.

The red residue had no absorption in the carbonyl region of the infrared and turned green upon exposure to moist air.

Attempted preparation of tricarbonylanthracenechromium.

a) Anthracene (3.6 g., 0.02 mole) and hexacarbonylchromium (4.4 g., 0.02 mole) were refluxed in petroleum ether (b.p. 100/120°C., 27 ml.) for 3½ hrs. At this stage, the solution had developed an intense violet colour and half the theoretical amount of gas had been evolved. The solution was allowed to cool, whence it turned yellow. Only starting materials were recovered.

b) Anthracene (4.0 g., 0.022 mole), hexacarbonylchromium (4.0 g., 0.018 mole) and cycloheptatriene (0.7 g., 0.007 mole) were refluxed in petroleum ether (b.p. 100/120°C.) for 10½ hrs., by which time the theoretical amount of gas had been evolved. Excess solvent and unreacted material was removed *in vacuo* whilst the mixture was still hot, leaving a pink solid. On sublimation this yielded only anthracene, hexacarbonylchromium and tricarbonylcycloheptatrienechromium.

c) Anthracene (4.06 g., 0.023 mole) and tricarbonylcycloheptatrienechromium (1.2 g., 0.005 mole) were refluxed in ethylene glycol diethyl ether (22 ml.) for 19 hrs Then, the dark red mixture was filtered and evaporated to dryness, <u>in vacuo</u>., at room temperature. The red residue was extracted with ligroin and chromatographed on alumina (60 g.) to yield one red band which afforded tricarbonylcycloheptatrienechromium (1.01 g., 88 %) m.p. 128-129°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

Attempted catalytic hydrogenation of tricarbonylphenanthrenechromium at atmospheric pressure.

The general method was as follows:- Tricarbonylphenanthrenechromium 127 (A g.) dissolved in solvent S was added to a pre-reduced suspension of the catalyst (B g.) in the same solvent. After 'apparent' hydrogen uptake had ceased, the mixture was filtered and the catalyst well washed with the solvent. The filtrate was taken to dryness in a weighed flask. The percentage recovery of tricarbonylphenanthrenechromium is given (D) together with the catalyst/complex ratio (C).

Run No	A	B	C	D	S
1	0.492	2.750 Pd/C	1 : 2	95	diethyl ether
2	0.746	0.347 Pd/C	20 : 1	90	T.H.F.
3	0.500	0.280 Pt/C	20 : 1	90	T.H.F.
4	0.438	0.034 RhO_2	20 : 1	95	T.H.F.
5	0.581	0.137 PtO_2	5 : 1	95	T.H.F.
6	0.720	0.160 PtO_2	5 : 1	80	ethyl acetate
7	0.602	0.140 PtO_2	5 : 1	80	glacial acetic acid

Attempted hydrogenation of tricarbonylphenanthrenechromium using copper chromite catalyst.

Tricarbonylphenanthrenechromium (0.564 g., 0.002 mole) and copper chromite catalyst[124] (0.19 g.) in ethanol (50 ml.) were heated at 150°C for 3 hrs. under a hydrogen pressure of 109 atmospheres. After cooling and venting, the products were washed out of the autoclave with ethanol (100 ml.) and after filtration were evaporated to dryness at room temperature in vacuo. The only isolated product was phenanthrene (0.302 g., 94 %), contaminated to a slight degree with 9:10-dihydrophenanthrene.

Attempted reduction of tricarbonylphenanthrenechromium with calcium hexammine[128] in liquid ammonia.

Calcium turnings (0.26 g., 0.0065 g. atom) were added to liquid ammonia (10 ml.) which had been dried over sodium. This, bronze-coloured solution was slowly added to a stirred solution of tricarbonylphenanthrenechromium (0.28 g., 0.0009 mole) in dry ether (50 ml.). The resulting mixture, which was initially orange, turned deep-brown after 20 minutes. Stirring was then continued a further 40 mins. Then, the mixture was filtered under nitrogen [$Ca(NH_3)_6$ is pyrophoric], without suction, and the brown slimy deposit was washed with ether (5 - 10 ml.). The orange filtrate was evaporated to dryness leaving tricarbonylphenanthrenechromium (0.029 g., 10 %) m.p. 157-159°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

Reaction of hexacarbonylchromium with 9:10-dihydrophenanthrene.

Hexacarbonylchromium (8.06 g., 0.04 mole) and 9:10-dihydrophenanthrene (6.96 g., 0.04 mole) together with ethylene glycol diethyl ether (100 ml.) were heated together at 200-220°C., in an oscillating autoclave (1 litre.) for 2 x 4 hr., periods with intermediate cooling and venting of carbon monoxide. Then, the autoclave was opened and the contents washed out with ether (100 ml.). After filtration, to remove unreacted hexacarbonylchromium (4.37 g., 54 %) the solution was taken to dryness at room temperature in vacuo. The residual yellow oil was chromatographed on alumina (400 g.) in n-hexane. After thoroughly washing the column with n-hexane to remove unreacted 9:10-dihydrophenanthrene, elution with benzene/n-hexane (1/1) afforded yellow needles (3.25 g., 65 %) m.p. 106-107°C., soluble in common organic solvents. Tricarbonyl 9:10-dihydrophenanthrenechromium shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 1976, 1897 and 1873 $cm.^{-1}$ Recrystallisation from methylene chloride/n-hexane raised the m.p. to 108-109°C.

Found : C, 65.0; H, 3.8; Cr, 16.3; M. 312

$C_{17}H_{12}CrO_3$ requires : C, 64.6; H, 3.8; Cr, 16.4% M. 316.

Further elution of the column with 100 % benzene afforded a deep yellow crystalline compound (0.050 g., 1 %) m.p. 217-218°C (d from 160°C), thought to be hexacarbonyl 9:10-dihydrophenanthrenedichromium.

Found : C, 54.2; H, 3.3; M. 437

$C_{20}H_{12}Cr_2O_6$ requires : C, 53.1; H, 2.7; M. 452.

The compound is only slightly soluble in common organic solvents and shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 1957 and 1887 cm.$^{-1}$

Attempted dehydrogenation of tricarbonyl 9:10-dihydrophenanthrenechromium with triphenylmethyl perchlorate.

Tricarbonyl 9:10-dihydrophenanthrenechromium (1.27 g., 0.004 mole) and triphenylmethyl perchlorate (1.38 g., 0.004 mole) were refluxed for 4 mins. in a mixture of glacial acetic acid (100 ml.) and acetic anhydride (10 ml.). After cooling, the mixture was poured into water (1000 ml.) and this solution was extracted with ether (3 x 100 ml.). Concentration in vacuo gave a pale amber oil which showed no absorption in the metal carbonyl stretching frequency region of the infrared and which was probably a mixture of phenanthrene and 9:10-dihydrophenanthrene.

Attempted dehydrogenation of tricarbonyl 9:10-dihydrophenanthrenechromium with 1,2,3,4 -tetrabromo-o-benzoquinone.

Tricarbonyl 9:10-dihydrophenanthrenechromium (0.57 g., 0.002 mole) and 1,2,3,4-tetrabromo-o-benzoquinone (0.84 g., 0.002 mole) were refluxed in pure benzene (5 ml.) for 18½ hrs. (An exothermic reaction occurred upon mixing the two compounds in benzene and a gas, presumably carbon monoxide, was evolved.). Then, benzene (6 ml.) was added and the dark brown mixture was filtered to yield a dark brown amorphous material. This showed no absorption in the metal carbonyl region of the infrared and was discarded. The filtrate was evaporated to dryness, extracted with benzene (5 ml.) and chromatographed on alumina (10 g.). Elution with benzene gave a trace of a yellow compound which decomposed on the column.

Attempted dehydrogenation of tricarbonyl 9:10-dihydrophenanthrenechromium with 2,3-dichloro 5,6-dicyano-o-benzoquinone.

To a solution of 2,3-dichloro 5,6-dicyano-o-benzoquinone (0.21 g., 0.001 mole) in benzene (5 ml.) was added tricarbonyl 9:10-dihydrophenanthrenechromium (0.25g., 0.0008 mole). An immediate dark brown colour appeared and the mixture was stirred 10 mins. Benzene (5 ml.) was then added and the mixture was filtered. The solid residue showed no absorption in the metal carbonyl stretching frequency region of the infrared. It was washed with benzene (5 ml.) and the filtrate and washings were concentrated *in vacuo*. The solution was chromatographed on alumina (30 g.) to yield only unreacted tricarbonyl-9:10-dihydrophenanthrenechromium (0.029 g., 11 %) m.p. 108-109°C., identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

Dehydrogenation of tricarbonyl 9:10-dihydrophenanthrenechromium with palladium on charcoal.

Tricarbonyl 9:10-dihydrophenanthrenechromium (1 g.) and 10 % palladium on charcoal (0.9 g.) were heated in a stream of carbon dioxide at 120°C for 2 hrs. No gas was evolved, and the temperature was slowly raised to 200°C over 1 hr., at which temperature gas was evolved. Some hexacarbonylchromium sublimed out of the reaction zone. The temperature was kept at 200°C for 2 hrs. and then the apparatus was allowed to cool overnight.

The mixture was extracted with hot benzene (5 x 15 ml.) and this extract was evaporated to dryness at room temperature *in vacuo*. The gum so obtained was chromatographed on alumina (60 g.). Elution with ligroin afforded white needles (0.439 g., 78 %) m.p. 95-97°C., of phenanthrene.

Elution with benzene/ligroin (1/200) afforded two yellow bands. From the first was isolated a yellow crystalline compound (0.061 g., 6 %) m.p. 108-109°C., identified as tricarbonyl 9:10-dihydrophenanthrenechromium on the basis of its m.p., mixed m.p. with an authentic sample and infrared spectrum. From the second band was isolated an orange crystalline solid (0.008 g., 1 %) m.p. 158-159°C., identified as tricarbonylphenanthrenechromium on the basis of its m.p., mixed m.p. with an authentic sample and infrared spectrum.

Elution with benzene gave a third yellow band which afforded yellow crystals (0.005 g., 1 %) m.p. 225-226°C., (d from 150°C) of what is probably a hexacarbonyl 9:10-dihydrophenanthrenedichromium.

Repeated dehydrogenation of tricarbonyl 9:10-dihydrophenanthrenechromium with palladium on charcoal.

Tricarbonyl 9:10-dihydrophenanthrenechromium (0.45 g.) and palladium on charcoal (0.395 g.) were heated in a stream of carbon dioxide at 190-200°C for 27 mins. After being cooled rapidly, the mixture was extracted with hot benzene (5 x 20 ml.). After filtration and evaporation to dryness, in vacuo., the yellow gum so obtained was chromatographed on alumina (30 g.). Elution with ligroin gave a colourless compound (0.067 g., 26 %) m.p. 42-46°C., which was shown to be a mixture of phenanthrene and 9:10-dihydrophenanthrene by infrared spectral comparison.

With benzene/ligroin (1/19) a yellow band was obtained which afforded unchanged tricarbonyl 9:10-dihydrophenanthrenechromium (0.28 g., 62 %) m.p. 108-109°C. Identity was established by m.p., mixed m.p. with an authentic sample and infrared spectral comparison.

Further elution with benzene, afforded a second yellow crystalline compound (0.007 g., 1 %) m.p. 210-218°C., (d from 150°C.) which is probably hexacarbonyl 9:10-dihydrophenanthrenedichromium.

Additional experiments.

Hexacarbonyldi(isopropylcyclopentadienyl)dimolybdenum.

Redistilled 6:6'-dimethylfulvene[131] (5.4 g., 0.05 mole) and hexacarbonylmolybdenum (13.4 g., 0.05 mole) were refluxed in ethylene glycol dimethyl ether (25 ml.) for 6 hrs. Then, unreacted material was removed *in vacuo.*, at room temperature, leaving a deep red residue. This was extracted with petroleum ether (b.p. 40/60°C., 20 ml.) and the extract was chromatographed on alumina (1000 g.). The single red band which formed was eluted with ligroin and afforded purple crystals (0.724 g.) m.p. 155-156°C., lit[138] 162-163°C. of hexacarbonyldi(isopropylcyclopentadienyl)dimolybdenum, extremely soluble in common organic solvents. The compound shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 1957 and 1905 cm.$^{-1}$

Found : M. 534. Ref 139.

$C_{22}H_{24}Mo_2O_6$ requires : M. 574.

Reaction of 6:6'-dimethylfulvene with heacarbonylmolybdenum.[56(in part)]

Freshly distilled 6:6'-dimethylfulvene[131] (10 g., 0.095 mole) was heated with hexacarbonylmolybdenum (10 g., 0.038 mole) until evolution of carbon monoxide ceased (7 hrs.) Unreacted starting materials were then removed *in vacuo.*, the red residue dissolved in ligroin and chromatographed on alumina to give eight bands. Elution with ligroin afforded purple crystals (0.45 g., 4 %) m.p. 154-155°C., of hexacarbonyldi(isopropylcyclopentadienyl)dimolybdenum, identified by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

Further elution with ligroin gave the second band as purple crystals (0.34 g., 3%) m.p. 116-119°C(d)., of *hexacarbonylisopropenylcyclopentadienylisopropylcyclopentadienyldimolybdenum*.

Found : C, 46.2; H, 3.6; M. 500 Ref 139

$C_{22}H_{20}Mo_2O_6$ requires : C, 46.2; H, 3.5% M. 572.

The compound was hydrogenated in a micro-hydrogenation apparatus over 10 % palladium on charcoal.

Results.

A	B	C	D	E	F
1	8.625	0.411	0.089	0.322	0.338
2	12.384	0.749	0.128	0.621	0.485
3	38.654	1.675	0.398	1.277	1.514

A = Experiment No.,

B = Weight (mgm.) used,

C = Volume of hydrogen (ml.) absorbed, corrected to N.T.P.,

D = Correction (ml.) for Band I (see below),

E = Corrected value (ml.),

F = Theoretical uptake (ml.) required for 1 isopropenyl group.

In a similar experiment, Band I [hexacarbonyldi(isopropylcyclopentadienyl)dimolybdenum] (16.023 mgm.) absorbed 0.165 ml. of hydrogen, corrected to N.T.P.

The next four bands were also eluted with ligroin and afforded red amorphous solids with closely similar infrared spectra, all showing strong absorption at 1957 and 1905 cm^{-1} in the metal carbonyl stretching frequency region of the infrared. The compounds did not possess sharp melting points and attempts to crystallise them were unsuccessful.

Elution with benzene gave a trace of a red amorphous solid and also red crystals (0.020 g.) m.p. 69-74°C., of another unidentified product, which showed absorption maxima at 2010, 1957 and 1905 cm^{-1} in the metal carbonyl stretching frequency region of the infrared. The general spectrum was very similar to those of the other compounds.

<u>Tricarbonyl-7-endo-phenylethynylcyclohepta(1,3,5)trienechromium.</u>

To a solution of phenylethynyllithium[141] [from phenylacetylene (2.2 g., 0.02 mole) and lithium amide (0.43 g., 0.02 mole)] in dioxan (145 ml.) was added tricarbonyltropyliumchromium fluoroborate (2.21 g., 0.007 mole), with the immediate formation of a deep red colour. The mixture was stirred for 14 hrs. After filtration, the filtrate was evaporated to dryness <u>in vacuo</u>. The residue was extracted with benzene (5 ml.) and chromatographed on alumina in ligroin (250 g.). Elution with benzene yielded a single orange-red band which afforded deep red needles (1.20 g., 52 %) m.p. 143-144°C., soluble in common organic solvents, with the exception of the paraffins, upon recrystallisation from ether/pentane. <u>Tricarbonyl-7-endo-phenylethynylcyclohepta(1,3,5)trienechromium</u> shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 1980, 1914 and 1869 cm.$^{-1}$

Found : C, 65.95; H, 3.7; Cr, 15.6; M, 330;

$C_{18}H_{12}CrO_3$ requires : C, 65.85; H, 3.7; Cr, 15.8% M, 328.

<u>Permanganate oxidation of tricarbonyl-7-endo-phenylethynylcyclohepta-(1,3,5)trienechromium.</u>

Tricarbonyl-7-endo-phenylethynylcycloheptatrienechromium (0.353 g.) in acetone (15 ml.) was treated with an excess of an aqueous solution of potassium permanganate, acidified with dilute sulphuric acid. The solution was refluxed 1 hr. After cooling and filtering (to remove MnO_2) the solution was extracted with ether. This extract was dried (Na_2SO_4) and evaporated to dryness giving a yellow oil. Methanol (2 ml.) was added, giving a yellow solution, and to the solution was added water (8 ml.). A white crystalline precipitate formed and was filtered off giving white crystals (0.105 g., 80 %) m.p. 116-118°C., identified as benzoic acid by m.p., mixed m.p. and infrared spectral comparison with an authentic sample.

<u>Reduction of tricarbonyl-7-endo-phenylethynylcyclohepta(1,3,5)triene-chromium.</u>

Tricarbonyl-7-endo-phenylethynylcycloheptatrienechromium (0.15 g.) in ethyl acetate (20 ml.) was added to a pre-reduced suspension of platinum oxide catalyst (0.049 g.) in ethyl acetate (10 ml.). After 3 hrs., hydrogen uptake had ceased and the solution was filtered. The filtrate was evaporated to dryness <u>in vacuo</u>., at room temperature and the red crystalline residue was recrystallised from ether/pentane to give red needles (0.101 g., 67 %) m.p. 124-125°C., soluble in common organic solvents. The infrared spectrum of this compound was very similar to that of the starting material, but slight differences were apparent.

Tricarbonyl-7-endo-methoxycyclohepta(1,3,5)trienemolybdenum.

To a solution of sodium methoxide [from sodium (0.115 g., 0.005 g. atom)] in methanol (20 ml.) was added tricarbonyltropyliummolybdenum fluoroborate (1.79 g., 0.005 mole) and tetrahydrofuran (30 ml.). The resulting solution was stirred vigorously for 7 mins. Then, after filtration under nitrogen, the solvent was removed, at 0°C., in vacuo., to leave a yellow-orange solid. Trituration of this solid with ligroin (10 x 20 ml.) and filtration was followed by cooling to -70°C., when bright orange needles (1.39 g., 98 %) m.p. 84-85°C., were precipitated. The compound was recrystallised from pentane. Tricarbonyl-7-endo-methoxycyclohepta(1,3,5)trienemolybdenum shows intense absorption in the metal carbonyl stretching frequency region of the infrared at 2000, 1923 and 1887 cm^{-1} and at 1054 cm^{-1} due to the methoxyl group.

The compound is extremely unstable, even under high vacuum and could not be analysed satisfactorily.

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