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T H E S I S

submitted to

THE UNIVERSITY OF GLASGOW

in fulfilment of the

requirements for the

DEGREE OF DOCTOR OF PHILOSOPHY

by

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JULY, 1966

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DERIVATIVES OF
TRICARBONYLCYCLOHEPTATRIENECHROMIUM

A C K N O W L E D G E M E N T S

The author wishes to express his sincere gratitude to Professor P. L. Pauson, under whose guidance this work was carried out, for his invaluable advice and encouragement, and for facilities provided in his department at the University of Strathclyde, Glasgow. He also wishes to thank Drs. G. R. Knox and W. E. Watts for helpful discussions, and the Ethyl Corporation for a Research Fellowship which made this study possible.

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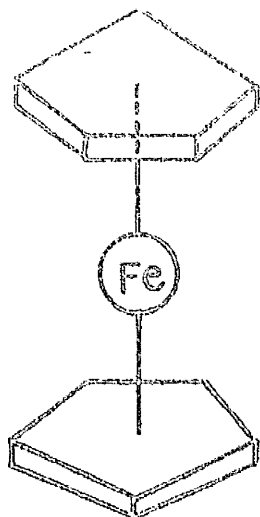
I N T R O D U C T I O N
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The discovery of ferrocene in 1951 marks the beginning of a period of intense activity and tremendous growth in the field of organo-transition metal chemistry. This is best demonstrated by the number of excellent reviews¹⁻¹⁴ on the subject, which have been published in recent years. The availability of these has greatly facilitated the task of writing this introduction, and has provided the author with an excellent coverage of references to earlier work in the field.

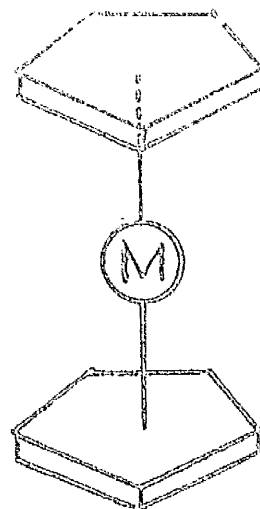
Bis-cyclopentadienylmetal Complexes.

Soon after the discovery of ferrocene^{15,16} the now well-known 'sandwich' structure was proposed^{17,18} to account for the high stability and peculiar properties of the compound. A number of x-ray studies² of the iron group metallocenes confirm the 'sandwich' structure, and indicate that in ferrocene (I) the two rings are 'staggered', such that the molecule is a pentagonal antiprism, while the analogous bis-cyclopentadienyl ruthenium (II, M = Ru) and bis-cyclopentadienylosmium (II, M = Os) have been shown to have the opposed conformation (II).

Neutral bis-cyclopentadienylmetal complexes have been obtained¹⁹ for metals of the first transition series (from titanium to nickel inclusive) except manganese, whose complex is ionic in character. These complexes do not exhibit the

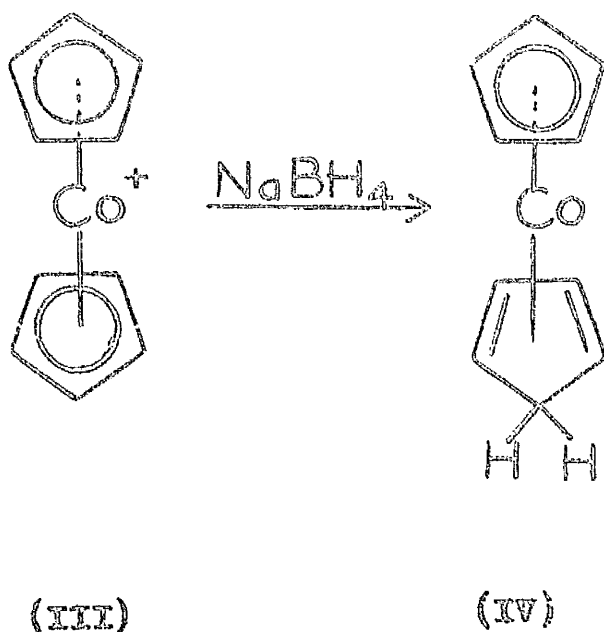


(I)



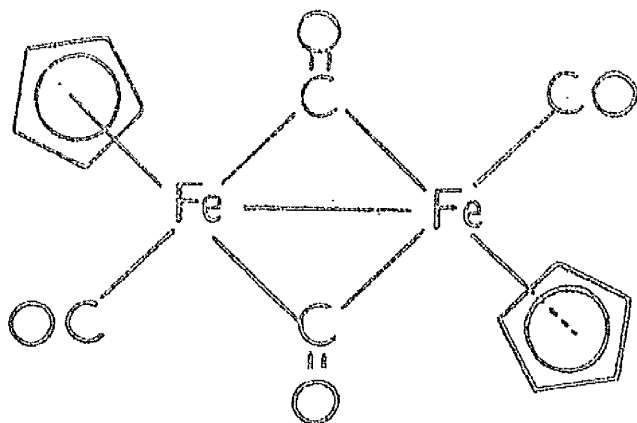
(II)

chemical and thermal stability of the iron group metallocenes but most of the metals show a tendency to acquire a closed shell of electrons in the formation of more stable complexes in other valency states, e.g. $(C_5H_5)_2Co$ is readily oxidised to the cobalticinium ion ^{20,21} $(C_5H_5)_2Co^+$ (III) which is isoelectronic with ferrocene, and is at least as stable. The tendency of the metal to remain in this state is shown by the attempted reduction of the cation $(C_5H_5)_2Co^+$ with sodium borohydride which leads, not to the neutral complex $(C_5H_5)_2Co$ but to the complex ²² $C_5H_5CoC_5H_5$ (IV) in which the E.A.N. of krypton is retained.

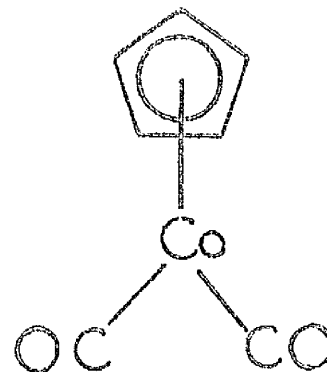


Carbonylcyclopentadienylmetal Complexes

The first examples to be described were the complexes²² $(C_5H_5)_2M_2(CO)_6$ ($M = Mo$ or W) obtained by heating the mixed vapours of cyclopentadiene and $Mo(CO)_6$ or $W(CO)_6$, in a tube at 250-300°C, in an attempt to prepare the corresponding bis-cyclopentadienylmetal complexes. Under these conditions $Cr(CO)_6$ yields $(C_5H_5)_2Cr$ but, at lower temperatures, the binuclear complex²⁴ $(C_5H_5)_2Cr_2(CO)_6$ is obtained. Cyclopentadiene reacts with all of the iron carbonyls at 135°C to form the binuclear complex^{25,26} $(C_5H_5)_2Fe_2(CO)_4$ (V) while reaction with $Co_2(CO)_8$ occurs at room temperature, with formation of dicarbonylcyclopentadienylcobalt²⁵ (VI). The complexes (V) and (VI) undergo further displacement of carbon monoxide by cyclopentadiene at elevated temperatures, to give ferrocene and cobaltocene respectively.



(v)



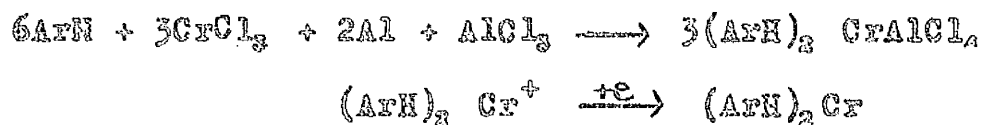
(vi)

The reverse displacement of cyclopentadiene by carbon monoxide has been employed in the preparation of the carbonyl-cyclopentadienyl complexes of chromium,^{27'28} cobalt,^{29'30} manganese^{35'29} and vanadium,³¹ from the corresponding dicyclopentadienylmetal complexes.

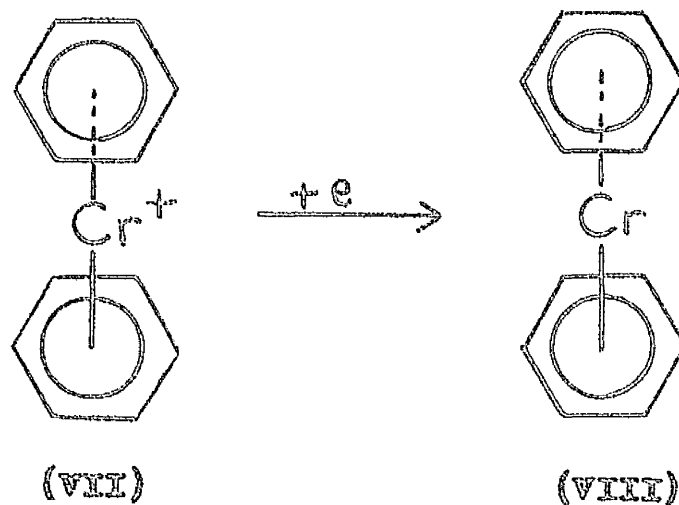
Bis-Arene Metal Complexes.

Closely analogous to the dicyclopentadienylmetal compounds are the complexes formed between transition metals and uncharged aromatic systems. In 1919, Hein³² reported the isolation of a series of 'polyphenylchromium' compounds from the reaction of phenylmagnesium bromide and chromic chloride. Many years later, on the basis of a critical reinvestigation of Hein's work, Zeiss and coworkers³ suggested that these compounds were metal π -complexes. This was supported by an independent

synthesis^{38 '54} of bis-benzenechromium, involving reaction of benzene with chromic chloride in the presence of anhydrous aluminium chloride and aluminium powder at 150°C.



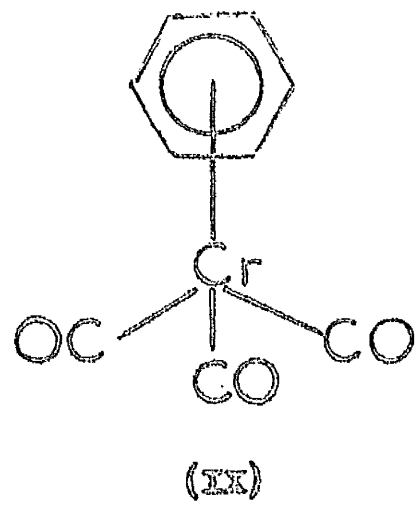
The bis-benzenechromium cation (VII) was isolated as the picrate or reineckate, which, on reduction with sodium dithionite yielded the neutral bis-benzenechromium (VIII).



This reaction has been extended to other transition metals and a number of aromatic hydrocarbons. Detailed physical studies on the complexes (VII) and (VIII) have confirmed the 'sandwich' structure.⁵

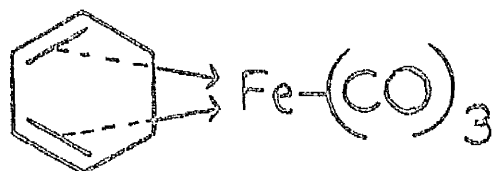
Tricarbonylaronometal Complexes

Reaction between bis-benzenechromium and hexacarbonylchromium in benzene, in a sealed system at 220°C., yielded the first complex in this series, tricarbonylbenzenechromium²⁸ (IX) the structure of which has been confirmed by x-ray analysis.³⁰



A more general method of preparation⁹ is to heat the aromatic compound with hexacarbonylchromium under reflux, or in a sealed system, in a solvent such as diethylene glycol dimethyl ether. This general method has been extended to the preparation of a wide range of tricarbonylaronometal complexes from substituted benzene derivatives and polycyclic aromatic systems. Limitations to the method have been encountered with benzene derivatives having certain substituents, e.g. CHO, COOH, CN, and NO₂.

butadiene moiety is planar and bound in the cis-form, and they supported this formulation by the isolation of the analogous tricarbonylcyclohexa-1,3-dieneiron (XIII).



(XIII)

Determination of the structure of tricarbonylbutadieneiron by x-ray analysis,⁴¹ shows that the butadiene is, in fact, planar and 'cisoid', with the iron atom roughly equidistant from all four carbon atoms of the butadiene. The suggestion of delocalised bonding is supported by the C-C bond lengths being almost equal and of the order expected for a bond between two sp^2 hybridised carbon atoms. Structure (XI) is further supported by an x-ray study⁴² of π -cyclopentadienyl-tetramethylcyclopentadienonecobalt, which shows that, in the cyclopentadienone ring, all of the carbon-carbon bond distances are equal, thus indicating complete delocalisation of the four π -electrons of the ring. However, on the basis of

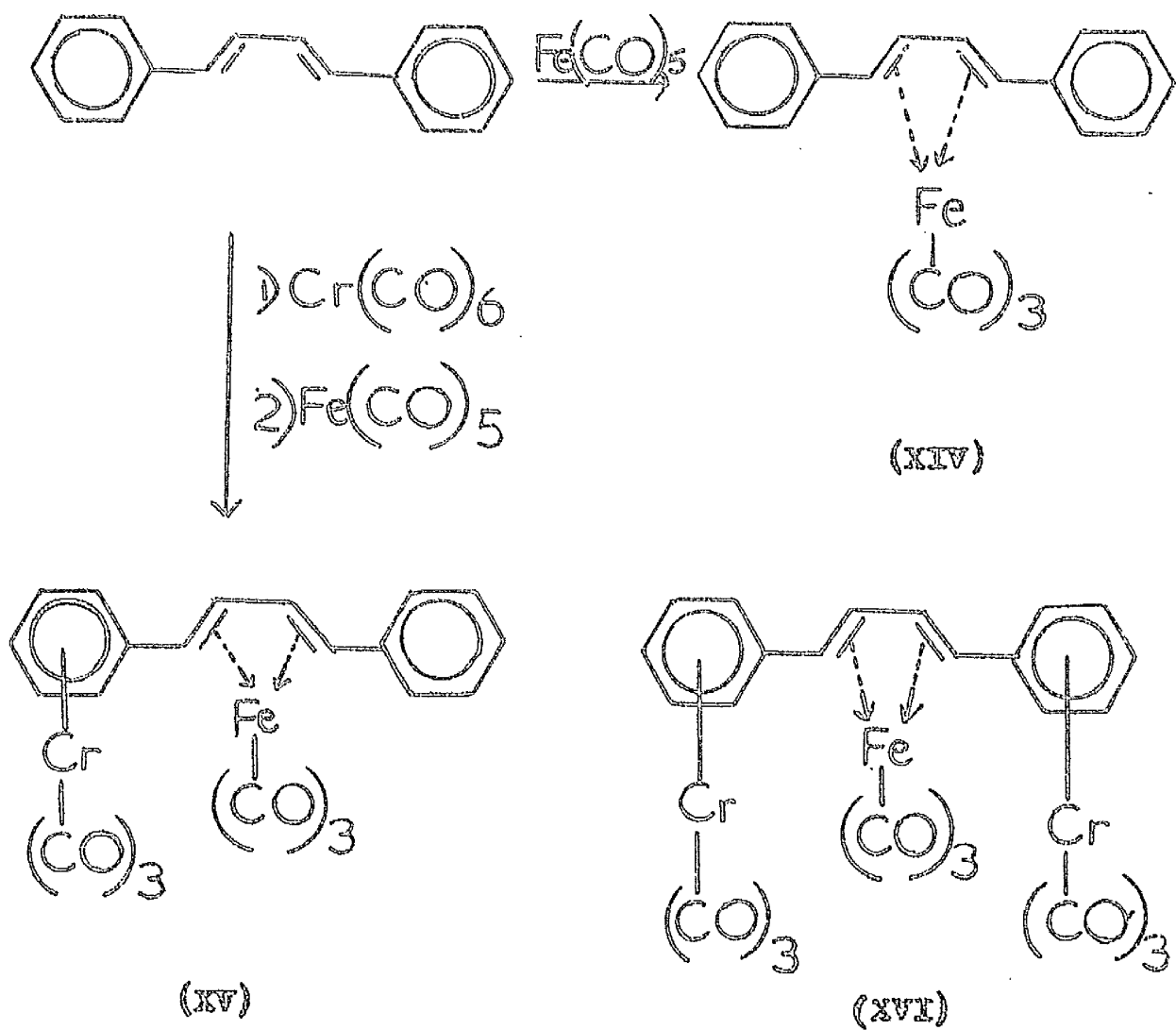
N.M.R. data on tricarbonylbutadieneiron and tricarbonyl-1,2,4,6-tetraphenylbutadieneiron, Wilkinson and coworkers³² have suggested the possibility of structure (XII) for tricarbonylbutadieneiron. This latter description of the bonding, which would lead to an approximately octahedrally coordinated iron atom, as opposed to the square pyramidal coordination of structure (XI) is preferred by Smith and Dahl⁴³ on the basis of an x-ray study of tricarbonyl-2,4,6-triphenyltroponeiron. Recent x-ray studies by Mason and coworkers have shown that this type of bonding, involving both π - and σ - bonds, is present in the complexes η -cyclopentadienyltetrakis(trifluoromethyl)cyclopentadienonecobalt,⁴⁴ tricarbonyltetrakis(trifluoromethyl)cyclopentadieneiron,⁴⁵ η -cyclopentadienyl-1-phenylcyclopentadienecobalt,⁴⁶ and η -cyclopentadienylhexakis(trifluoromethyl)benzenerhodium.⁴⁷ It would appear, therefore, that the structures (XI) and (XII) represent two extremes, and while the trifluoromethyl compounds favour the latter type of bonding, it is probable that the correct structure of tricarbonylbutadieneiron is intermediate between these extremes.

Further investigation⁴⁸ of results reported by Reihlen and coworkers³⁹ has shown very clearly the importance of conjugation to the stability of tricarbonyldiolefin-iron complexes. Reaction between cycloocta-1,5-diene and $\text{Fe}_3(\text{CO})_{12}$ yields the

complex⁴⁸ tricarbonylcycloocta-1,5-dieneiron, which is extremely unstable, whereas the unconjugated diolefins, penta-1,4-diene and 1,3,5-trimethylcyclohexa-2,5-diene react with $\text{Fe}_3(\text{CO})_{12}$ to give tricarbonyliron complexes of the isomeric conjugated dienes, penta-1,3-diene, and 1,3,5-trimethylcyclohexa-2,4-diene.⁴⁸

An interesting type of complex is obtained^{49,50} from 1,4-diphenylbutadiene, which reacts with $\text{Fe}(\text{CO})_5$ as a diene giving $\text{C}_6\text{H}_5(\text{C}_6\text{H}_5)_2\text{Fe}(\text{CO})_3$ (XIV), but in reactions with $\text{Cr}(\text{CO})_6$ functions as a benzene derivative forming the substituted aromatic tricarbonylchromium complexes $\text{C}_6\text{H}_5(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3$ and $\text{C}_6\text{H}_5(\text{C}_6\text{H}_5)_2[\text{Cr}(\text{CO})_3]_2$. The presence of a free butadiene grouping in the latter compounds is demonstrated by their further reaction with $\text{Fe}(\text{CO})_5$ to form the mixed carbonylchromium carbonyliron 1,4-diphenylbutadiene complexes (XV) and (XVI).

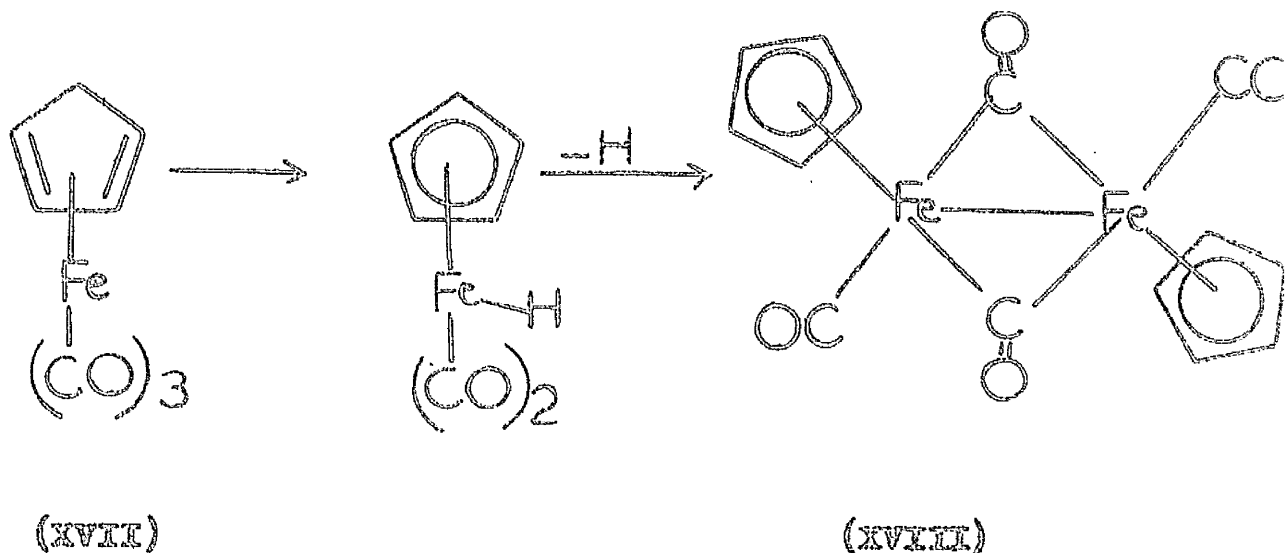
Stone and coworkers⁵⁰ have also reported the reactions between m- or p-divinylbenzene and $\text{Fe}_3(\text{CO})_{12}$ to give the hexacarbonyl m- or p-divinylbenzenediiron complexes respectively. The data available do not permit conclusive assignment of structure to these compounds particularly in view of the reported isolation⁵¹ of the complexes tetracarbonylbutadieneiron and octacarbonylbutadienediiron, in which it is suggested⁵¹



that the tetracarbonyliron moiety is bonded to only one of the two pairs of π -electrons available for coordination.

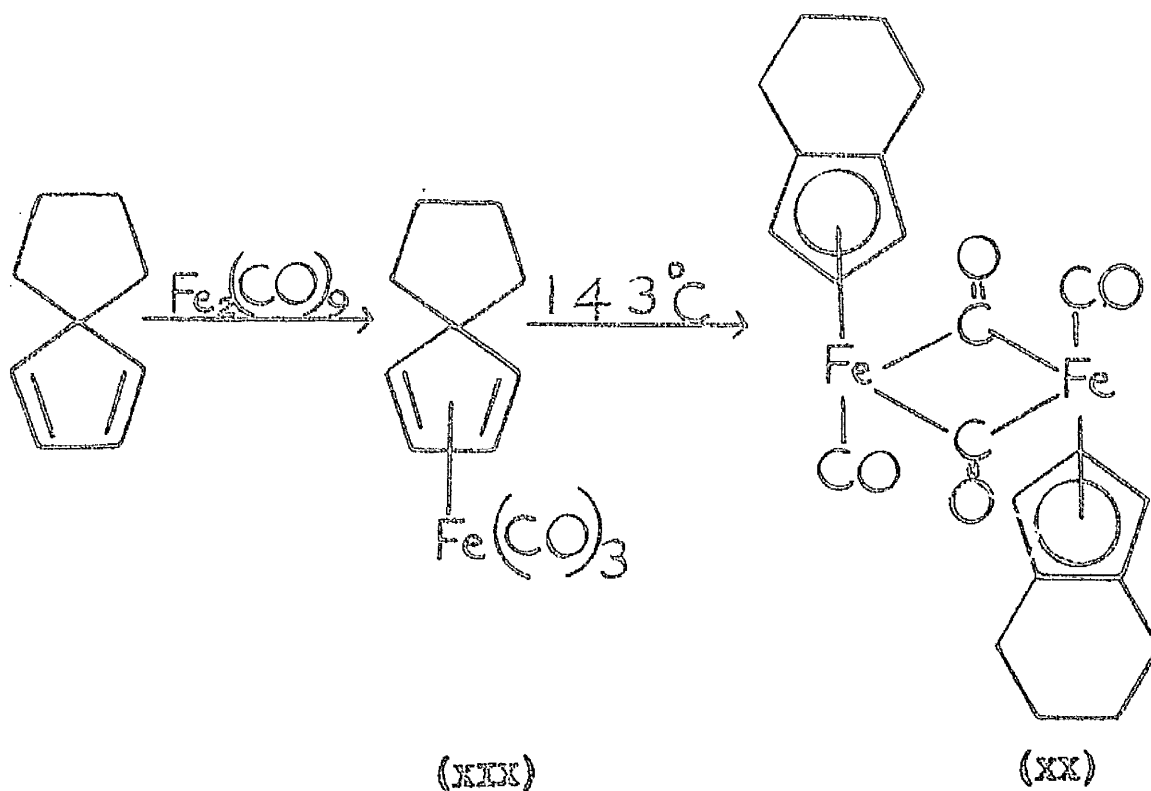
Metal η -Complexes of Cyclic Dienes

In view of the stability of tricarbonyliron complexes of conjugated dienes, it is perhaps surprising that cyclopentadiene reacts with $\text{Fe}(\text{CO})_5$ to form the binuclear complex $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ (XVIII) rather than tricarbonylcyclopentadienyliron. It has been postulated⁵³ that this reaction proceeds via the initial formation of the intermediate $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3$ (XVII) which, in subsequent steps, loses hydrogen to another molecule of unreacted cyclopentadiene giving cyclopentene, cyclopentane and the binuclear complex (XVIII).



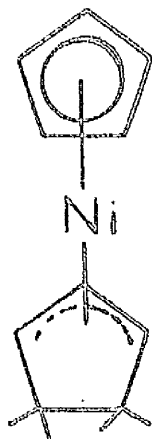
In support of the above mechanism, it has recently been shown that whereas reaction of spirocyclopentadiene with $\text{Fe}(\text{CO})_5$ at elevated temperatures gives dicarbonyltetrahydroindenyliron dimer⁵⁵ (XX) reaction with $\text{Fe}_2(\text{CO})_9$ at lower temperatures yields

tricarbonylspiro[nonadiene]iron⁶⁸ (XIX) which can be converted to the dimer (XX) by sublimation at 143°C

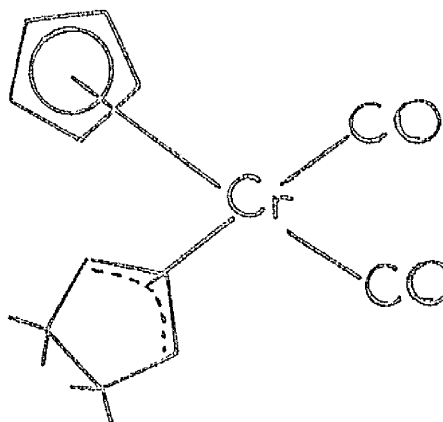


The tendency of cyclopentadiene to form the symmetrical cyclopentadienyl grouping is again exhibited in the preparation of such complexes as $C_{10}H_{12}Ni$ ⁶⁷ and $C_{10}H_{12}Cr(CO)_2$ ⁶⁸ in both of which it was postulated that two diene ligands were coordinated to the central metal atom. However, on the basis of N.M.R. studies and an alternative synthesis of $C_{10}H_{12}Ni$ several groups have independently established the structures $C_5H_5NiC_5H_7$ ⁶⁹⁻⁶¹ (XXI) and $C_5H_5CrC_5H_7(CO)_2$ ⁶⁸ (XXII) involving coordination of one dienyl

and one enyl ligand to the metal atom.

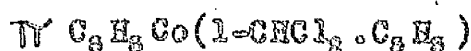
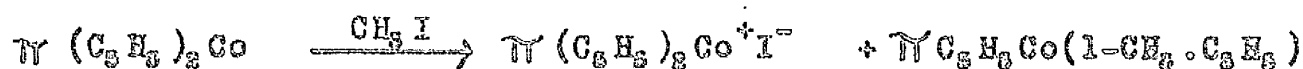


(XXI)



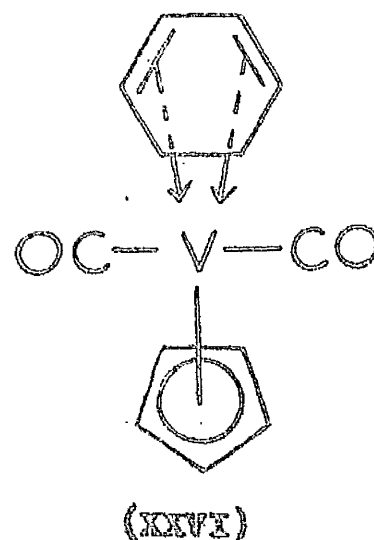
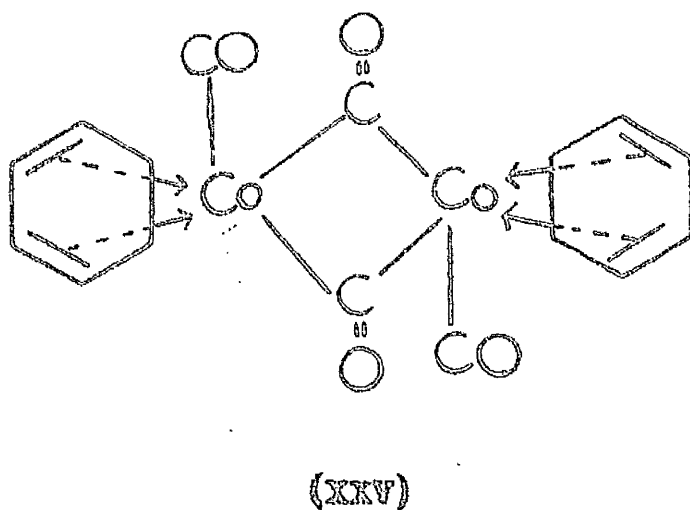
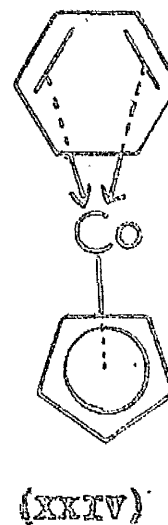
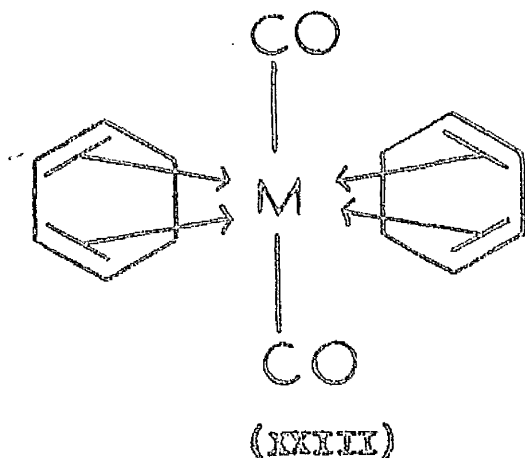
(XXII)

Mixed cyclopentadiene-cyclopentadienyl derivatives of rhodium,⁶⁸ iridium,⁶⁸ and cobalt,²² have been reported. These are obtained in poor yield⁶⁸ by the reaction of RhCl_3 or IrCl_3 with KC_5H_5 and excess cyclopentadiene in a high-boiling ether, and in high yield²² by reduction of the anhydrous cobalticinium and rhodicinium cations with NaBH_3 or LiAlH_4 . In addition to the parent compounds a number of substituted cyclopentadiene-cyclopentadienylcobalt complexes have been prepared²² from cobaltocene by reactions of the type.

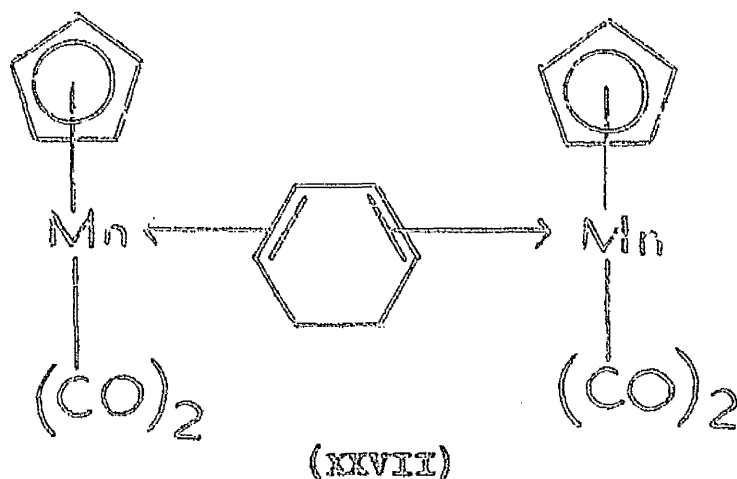


These complexes have been the subject of extensive infrared and N.M.R. studies,²² which are discussed later in this thesis.

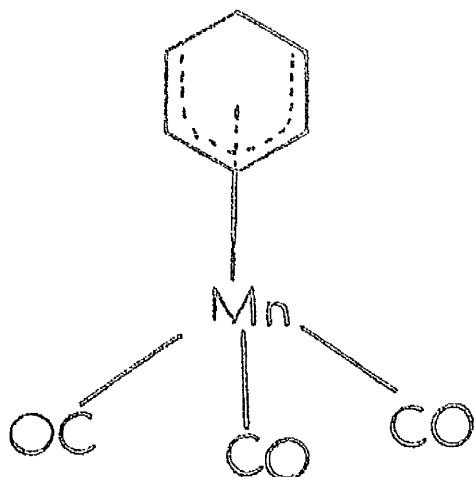
The first successful preparation of a carbonylmetal complex of a cyclic diolefin $C_6H_8Fe(CO)_3$ ⁶⁰ (XIII) was followed by the preparation of $(C_6H_8)_2M(CO)_2$ ⁶⁴ (XXIII) where M = Cr or Mo, $C_6H_8CoC_6H_8$ ⁶⁵ (XXIV) $[C_6H_8Co(CO)_2]_n$ ^{12,66} (XXV) where n = 1 or 2, and $C_6H_8VC_6H_8(CO)_2$ ⁶⁷ (XXVI).



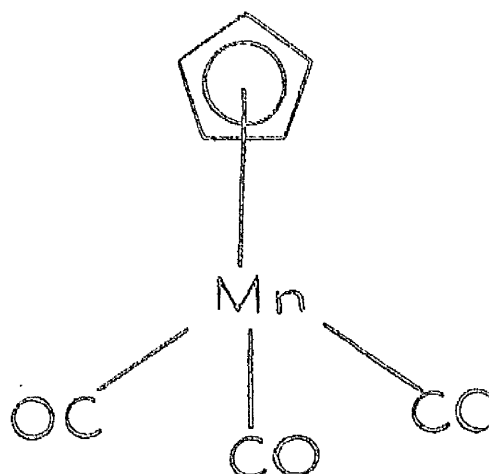
Reaction of tricarbonylcyclopentadienylmanganese with cyclohexa-1,3-diene, under ultraviolet irradiation yields the unexpected products ⁶⁹ $C_6H_8MnC_5H_3(CO)_2$ and $C_6H_9[C_5H_4Mn(CO)_2]_2$ (XXVII). The latter compound appears to be the first reported example of a metal Π -complex in which the cyclohexadiene molecule is incorporated as a bridge between two metal atoms.



N.M.R. studies ¹¹ indicate that all of the above complexes contain the cyclohexa-1,3-diene moiety, in the unchanged diene configuration. In contrast, the reaction between cyclohexa-1,3-diene and $Mn_2(CO)_{10}$ yields tricarbonylcyclohexadienylmanganese ⁶⁹ $C_6H_7Mn(CO)_3$ (XXVIII), in which the C_6H_7 group is bonded to the metal in a manner similar to the bonding in the iso- Π -electronic complex tricarbonylcyclopentadienylmanganese ^{56,84} (XXIX).



(XXVIII)

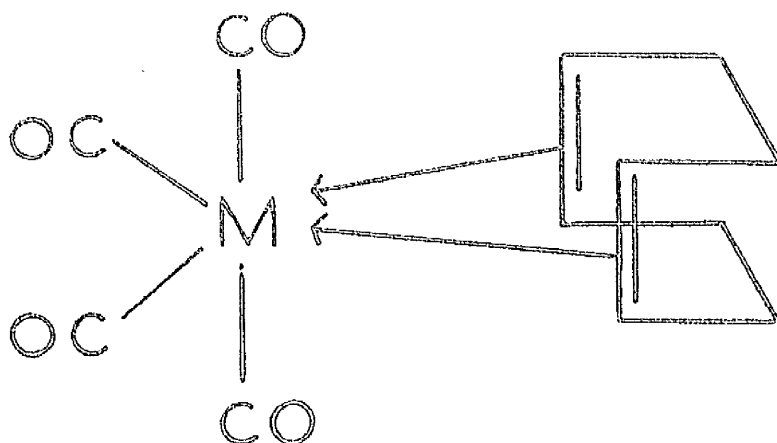


(XXIX)

The parent complex (XXVIII) and tricarbonylmanganese complexes of substituted cyclohexadienes are conveniently prepared⁷⁰ by reduction of the corresponding $[\text{ArMn}(\text{CO})_3]^+$ cations (Ar = toluene, mesitylene, hexamethylbenzene, naphthalene) with NaBH_4 or LiAlH_4 . Assignment of structures to these compounds is based on an interpretation⁷⁰ of the infrared and N.M.R. data, but in the light of a recent x-ray analysis⁴⁶ of η -cyclopentadienyl-1-phenylcyclopentadienecobalt, these assignments may have to be revised.⁷¹

The preparation of the unstable complex⁴⁸ tricarbonyl-cycloocta-1,5-dieneiron has already been mentioned.

Reaction^{72 74} of cycloocta-1,5-diene with carbonyls of group VI metals results in the formation of complexes of the general structure $\text{C}_8\text{H}_{12}\text{M}(\text{CO})_3$ (XXX) where M = Cr, Mo, or W.



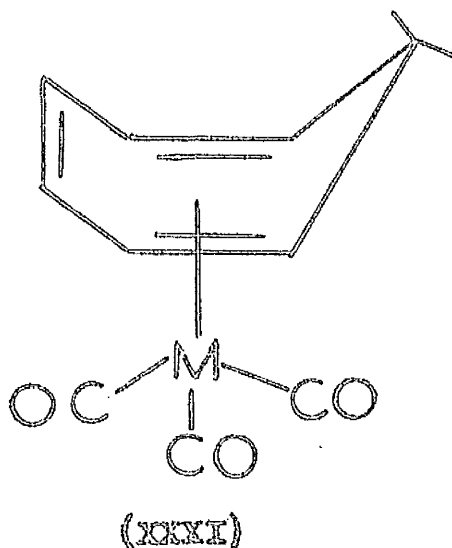
(XXX)

Comparison of the N.M.R. spectra⁷⁵ of these complexes with the spectrum of the parent diene, shows relatively slight changes, indicating that there is very little or no delocalisation between the double bonds and that they are not greatly changed by coordination.

Metal η^5 -Complexes of Cyclic Trienes.

In 1958, three groups⁵ independently discovered that Group VI metal carbonyls react thermally with a number of aromatic compounds to give tricarbonylarene-metal complexes. This discovery stimulated an investigation of the reaction of these carbonyls with cyclic olefinic systems. On the premise that the tropylium cation, being η^7 -isoelectronic with both the cyclopentadienyl anion and the neutral benzene nucleus,

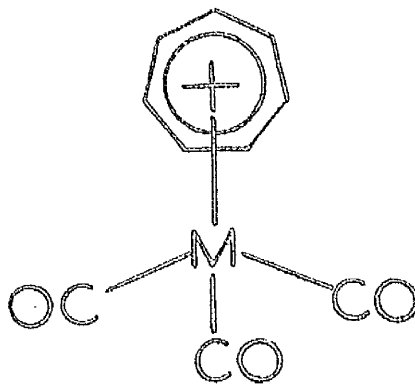
should be able to form a 'sandwich' type bond with a transition metal, Wilkinson and coworkers⁷⁵ attempted the preparation of tricarbonyltropyliummetal complexes. However, reactions involving the tropylium cation led to the formation of bicycloheptatrienyl, and reaction between hexacarbonylmolybdenum and refluxing cycloheptatriene yielded the red diamagnetic product⁷⁶ $C_7H_6M(CO)_3$ (XXXI) where $M = Mo$ i.e. a compound with a triene instead of the expected symmetrical cycloheptatrienyl.



The latter reaction has subsequently been extended to chromium and tungsten and to a large number of substituted cycloheptatrienes.⁷⁵⁻⁷⁸ An x-ray analysis⁷⁹ of tricarbonylcycloheptatrienemolybdenum shows that the six sp^2 hybridised carbon atoms of the ring lie practically in one plane, while the methylene group projects outwards away from the metal. The three CO groups have approximately trigonal symmetry with

respect to an axis through the metal atom, and one of them lies almost in a mirror plane of the ring. The distances between the planar sp^2 hybridised carbon atoms are approximately those expected for alternate single and double bonds in a conjugated triene. The N.M.R. spectrum of tricarbonylcycloheptatriene-molybdenum has been interpreted⁷⁶ to agree with the x-ray data and the proposed structure (XXXI).

The true tropylium complexes of composition $[C_7H_7M(CO)_3]^+$ (XXXII) where M = Mo or Cr, are obtained^{80,81} in almost quantitative yield from $C_7H_8M(CO)_3$ (XXXI) where M = Mo or Cr, by abstraction of hydride ion with trityl salts.



(XXXII)

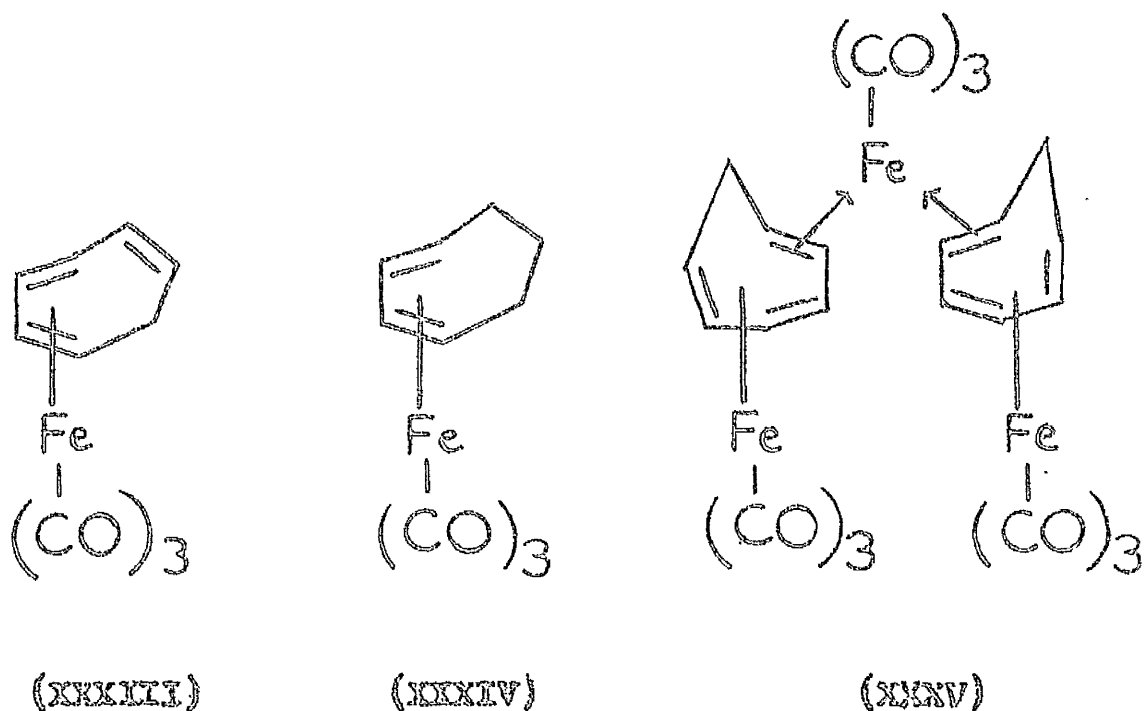
The existence of a symmetrical C_7 ring is indicated by the presence of a single proton resonance in the N.M.R. spectrum⁸⁰ of its solution in D_2SO_4 . Treatment of the tropylium salt complexes with numerous anions provides a

convenient route^{77,78,81} to 7-substituted cycloheptatriene tricarbonylmetal complexes, which are discussed in detail later in this thesis.

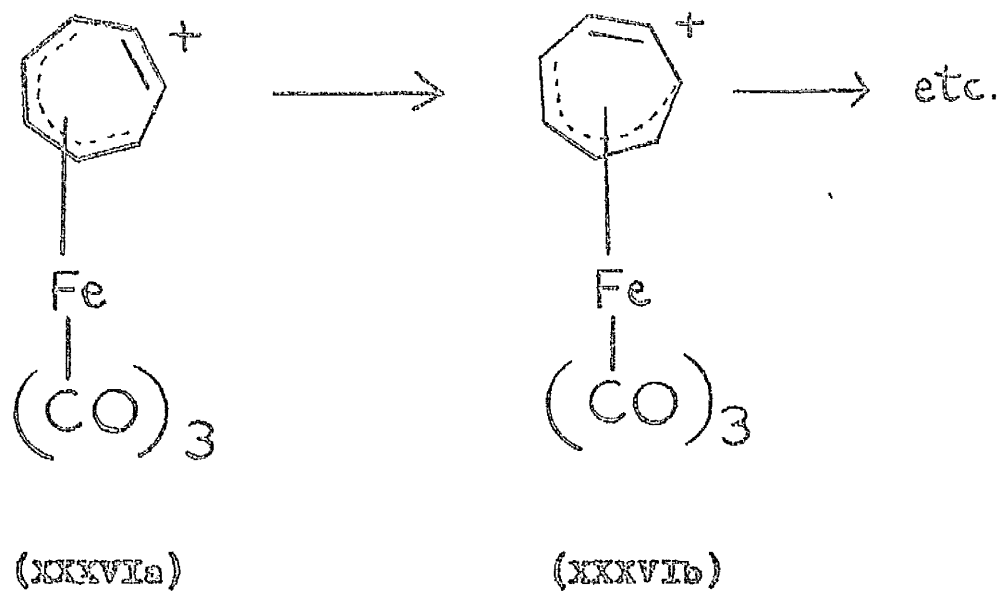
The cycloheptatrienyl compounds of vanadium, of formulae $C_7H_7VC_8H_8$ ⁸² and $C_7H_7V(CO)_3$ are obtainable from cycloheptatriene and $C_8H_8V(CO)_4$ and $V(CO)_6$ respectively. The preparation of $C_8H_8CrC_7H_7$ ^{84,85} and $C_8H_8Mo(CO)_2C_7H_7$ ⁸⁵ have also been reported, and, although the N.M.R. spectrum of the latter compound shows only two proton resonance signals, of relative intensity 5:7 characteristic of cyclopentadienyl and cycloheptatrienyl proton resonances there is doubt⁸⁶ as to its correct structure.

In contrast to the reaction of cycloheptatriene with carbonyls of group VI metals, reaction with $Fe(CO)_5$ yields,^{86,87} not the expected $C_7H_7Fe(CO)_3$ but a mixture of $C_7H_9Fe(CO)_3$ (XXXIII), $C_7H_{10}Fe(CO)_3$ (XXXIV) and the trinuclear complex $C_{23}H_{16}Fe_3O_9$ which has been speculatively formulated⁸⁸ as having structure (XXXV).

The tricarbonylcycloheptadienyliron cation $[C_7H_9Fe(CO)_3]^+$ is formed^{88,87} from $C_7H_9Fe(CO)_3$ (XXXIII) by addition of a proton and from $C_7H_{10}Fe(CO)_3$ (XXXIV) by hydride abstraction with trityl tetrafluoroborate.

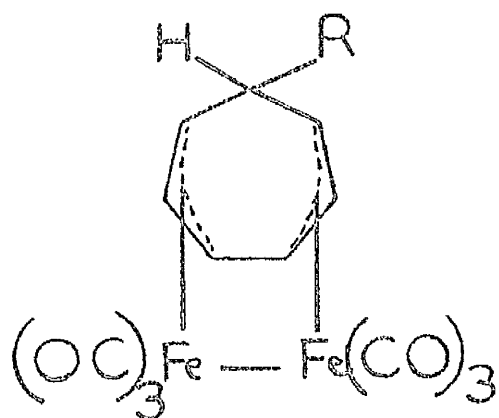


Pettit and coworkers⁸⁸ have reported the preparation of the tricarbonylcycloheptatrienyliron cation $[\text{C}_7\text{H}_7\text{Fe}(\text{CO})_3]^+$ by treatment of tricarbonyl-7-methoxycycloheptatrieneiron with tetrafluoroboric acid. The N.M.R. spectrum of this salt shows a single sharp absorption, but the infrared spectrum indicates the presence of a 'cis' double bond. To account for this anomaly the authors⁸⁸ propose structure (XXXVIa) and suggest that, in solution, the system undergoes rapid valence tautomerism to the equivalent structures (XXXVIb etc) which would eventually lead to rotation of the tricarbonyliron group around the C_7H_7 ring and thus result in equivalence of the ring protons.



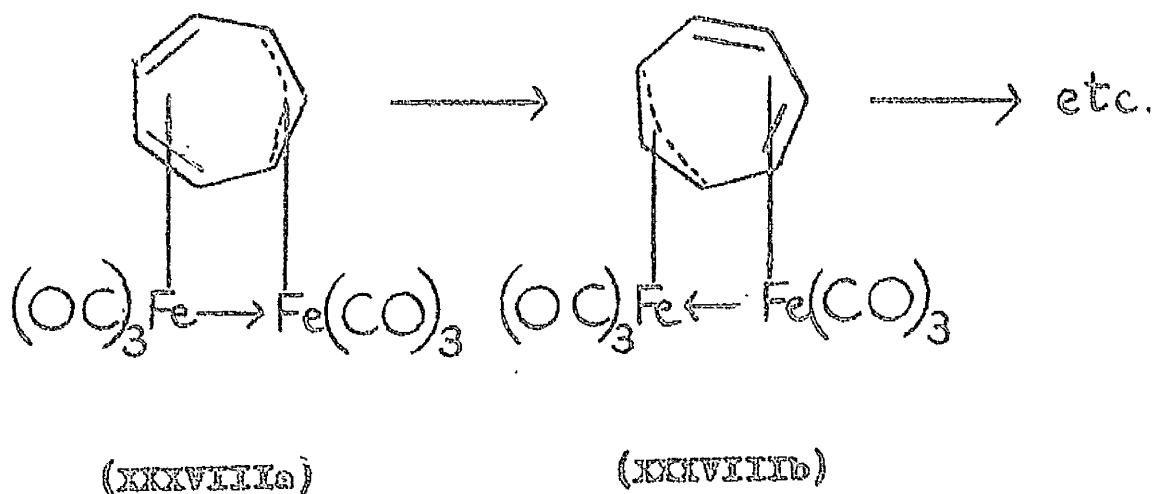
These workers also report²⁹ the preparation of compounds of the general type triene - $\text{Fe}_2(\text{CO})_6$, which, they suggest, are essentially carbonyl bis- π -allyliron complexes.

(XXXVII, R = H or OCH_3).



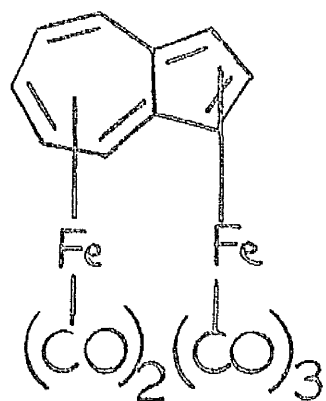
(XXXVII)

On the basis of the non-equivalence of the methylene protons ($R = H$) in the N.M.R. spectrum, and the high dipole moment of the complexes, the two iron atoms are considered⁸⁹ to be situated on the same side of the cycloheptatriene ring. Treatment of the complexes (XXXVII; $R = H$ or OCH_3) with trityl fluoroborate yields the fluoroborate salt of a $C_7H_7Fe_2(CO)_6$ cation which exhibits a single N.M.R. absorption. This is again explained⁸⁹ on the basis of a rapid valence tautomerism between structures (XXXVIIIa; XXXVIIIb; etc.) resulting in the equivalence of the seven ring protons in the N.M.R. spectrum.

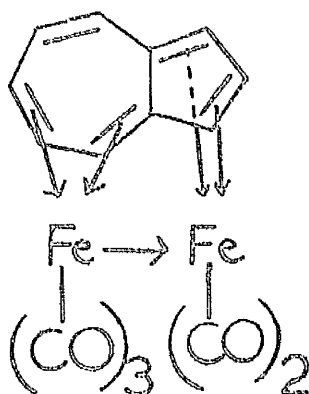


A number of metal complexes of azulene and substituted azulenes have been reported.⁹⁰ Reaction between azulene and $Fe(CO)_5$ or $Fe_2(CO)_9$ yields the diamagnetic complex $C_{10}H_8Fe_2(CO)_8$. It is not clearly known whether the iron atoms

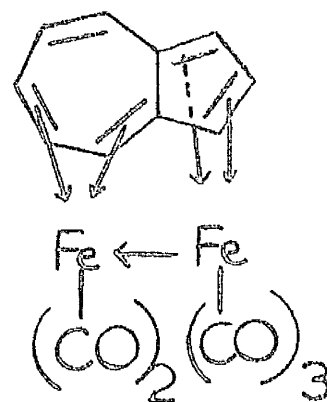
lie on the same side of the ring system (cis) or on opposite sides (trans), but the relatively high dipole moment of the compound is believed⁹⁰ to favour the 'cis' configuration. The distribution of $\text{Fe}(\text{CO})_3$ and $\text{Fe}(\text{CO})_2$ groups between each part of the azulene nucleus is uncertain, and three different structures (XXXIXa, b, and c), which satisfy the requirements of diamagnetism have been proposed.⁹⁰



(XXXIXa)



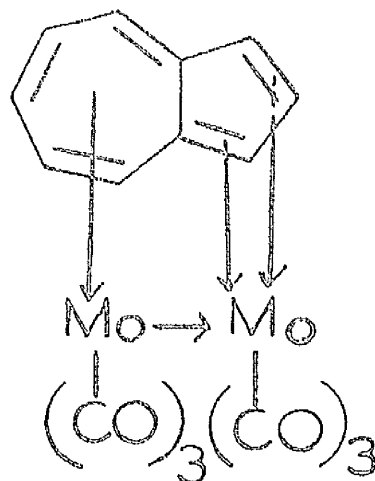
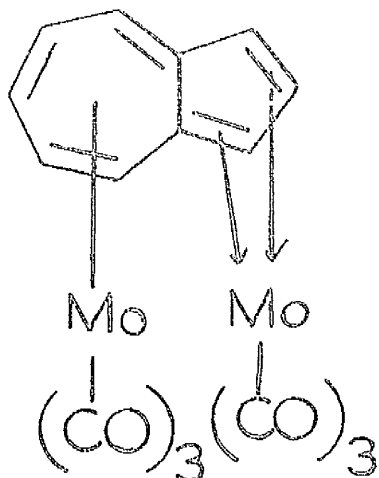
(XXXIXb)



(XXXIXc)

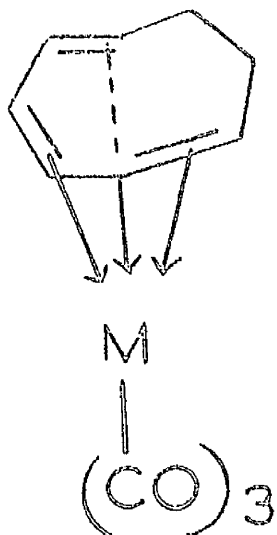
Prolonged reaction of azulenes with $\text{Mo}(\text{CO})_6$ yields black diamagnetic complexes of general formula (azulene)- $\text{Mo}_2(\text{CO})_8$ for which the structures (XLa and XLb) have been suggested.⁹⁰

Reaction of a mixture of cycloocta-1,3,5-triene and cycloocta-1,3,6-triene with the carbonyls of group VI metals results in the formation of two complexes to which the structures

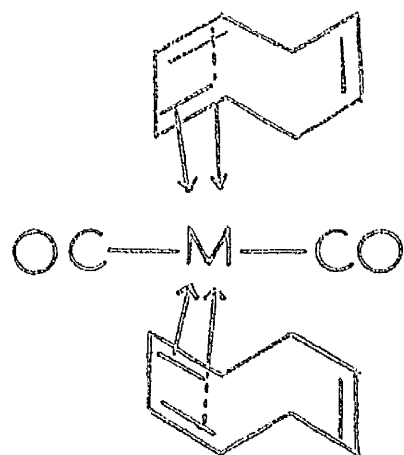


(XLI where M = Cr or Mo) and (XLII where M = Mo, or W) have been assigned.⁹¹ An x-ray study⁹² of tricarbonylcycloocta-1,3,5-trienechromium (XLI; M = Cr) shows that the conjugated system of the hydrocarbon is approximately planar with the methylene groups projecting outwards away from the metal, i.e. a structure similar to that observed for tricarbonylcycloheptatrienemolybdenum.⁷⁹

Interaction of the same mixture of isomeric cyclooctatrienes with $\text{Fe}(\text{CO})_5$ yields a complex^{91,93} $\text{C}_8\text{H}_{10}\text{Fe}(\text{CO})_3$ while interaction with $\text{Fe}_2(\text{CO})_{12}$ and $\text{Fe}_3(\text{CO})_9$ yields two different complexes^{94,95} of composition $\text{C}_8\text{H}_{10}\text{Fe}(\text{CO})_5$ and a complex^{99,96} of composition $\text{C}_8\text{H}_{10}\text{Fe}_2(\text{CO})_6$. The structures of these compounds have not been fully elucidated.



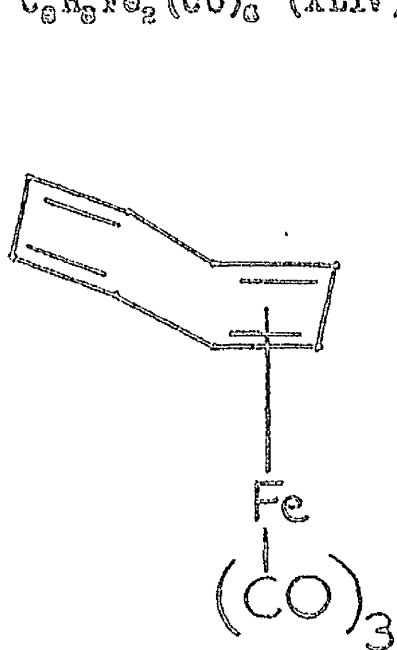
(XLI)



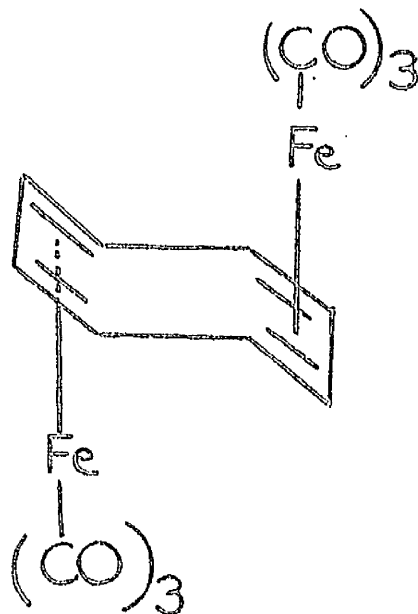
(XLII)

Metal π -Complexes of Cyclooctatetraene

Reaction of cyclooctatetraene with $\text{Fe}(\text{CO})_5$ affords ^{93 96 99} a monoiron complex $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ (XLIII) and a diiron complex $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$ (XLIV).



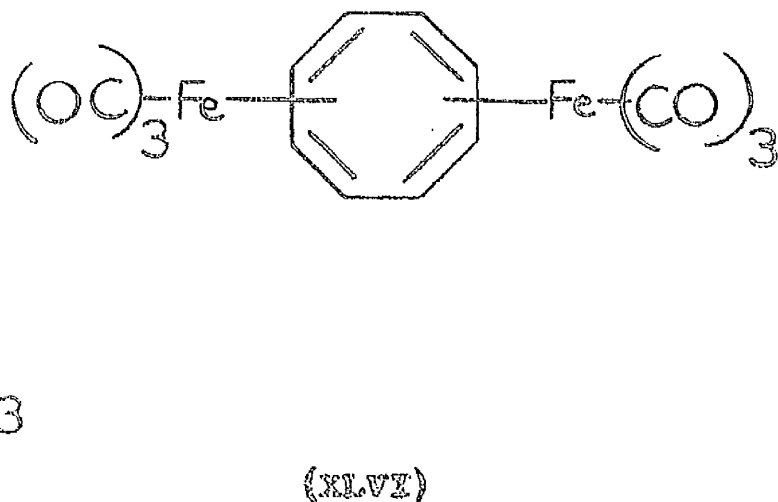
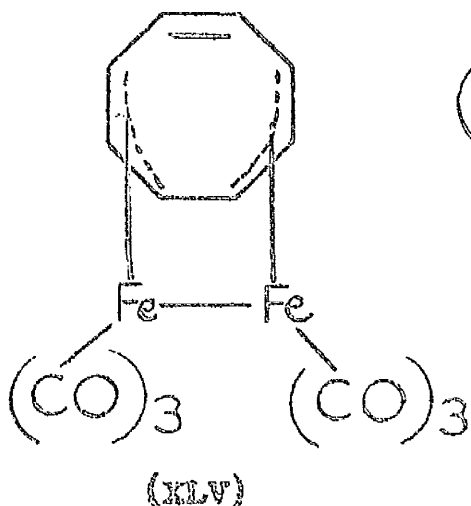
(XLIII)



(XLIV)

Various structures were suggested⁹⁵⁻⁹⁶⁻¹⁰¹ for these complexes on the basis of spectral evidence and chemical considerations but x-ray studies¹⁰²⁻¹⁰⁵ have shown that these formulations are incorrect, and the structures are as shown above (XLIII) and (XLIV). Pettit and coworkers have suggested¹⁰⁶ that the presence of a single absorption in the N.M.R. spectrum of $C_9H_9Fe(CO)_3$ can be explained on the basis of a tricarbonylmetal-diene formulation with rapid rotation of the $Fe(CO)_3$ group about the ring to produce equivalent valence-tautomeric structures similar to that suggested for the tricarbonyltropyliumiron complex.⁶⁸

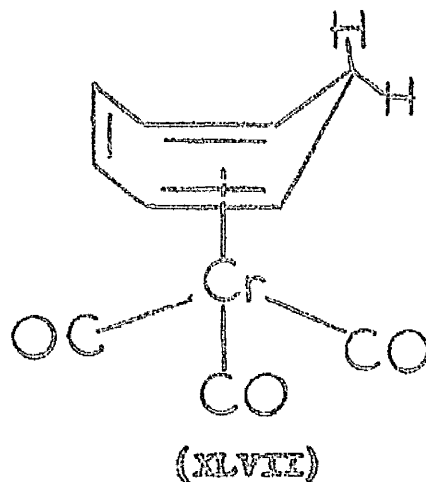
It has recently been reported¹⁰⁴ that reaction between cyclooctatetraene and $Fe_2(CO)_9$ yields, in addition to the complexes (XLIII) and (XLIV), two other complexes of composition $C_8H_8Fe_2(CO)_6$, to which the structures (XLV) and (XLVI) have been assigned on the basis of infrared, N.M.R., and Mossbauer spectra and dipole moment measurements.



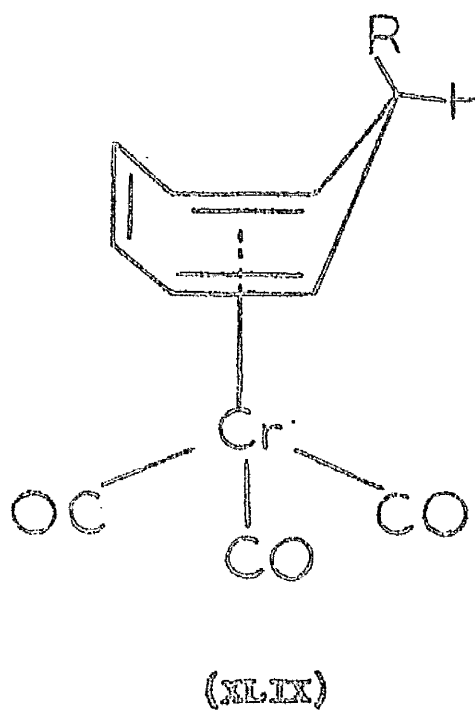
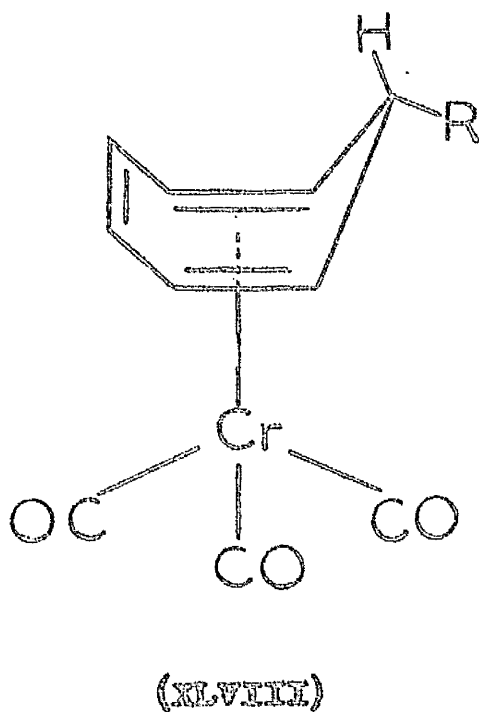
DISCUSSION OF RESULTS
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PART I

Tricarbonylcycloheptatrienechromium⁷⁸ may be assumed to have the structure (XLVII) analogous to that established⁷⁹ for the corresponding molybdenum compound (XXXI, M = Mo).

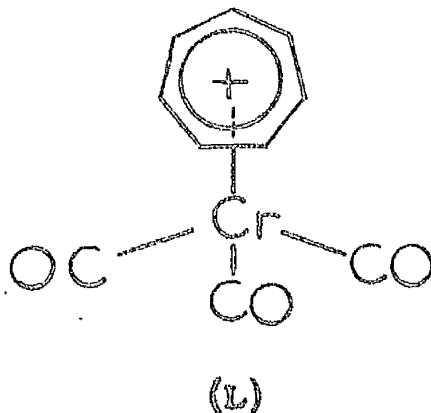


Mono-7-substituted derivatives may therefore exist in two stereoisomeric forms (XLVIII) and (XLIX).



Previous work in this field by Munro¹¹⁰ and Smith⁷⁰ has shown that a variety of derivatives of tricarbonylcycloheptatrienechromium can be obtained by three routes:

- (a) by heating hexacarbonylchromium with a 7-substituted cycloheptatriene, C_7H_7R , under reflux or in a suitable solvent.
- (b) by addition of anions R^- to the tricarbonylcycloheptatrienylchromium cation (L).



- (c) by replacement of the methoxyl group from tricarbonyl-7-exomethoxycycloheptatrienechromium (XLIX; $R = OCH_3$) by anions R^- . Smith⁷⁰ has further shown that reaction (a) produces predominantly or exclusively one stereoisomer, while reactions (b) and (c) proceed stereospecifically to afford the other isomer. Tentative assignment⁷⁰ of structure to these compounds was based largely on an interpretation of N.M.R. data. This interpretation is invalidated by work to be described later in this thesis,

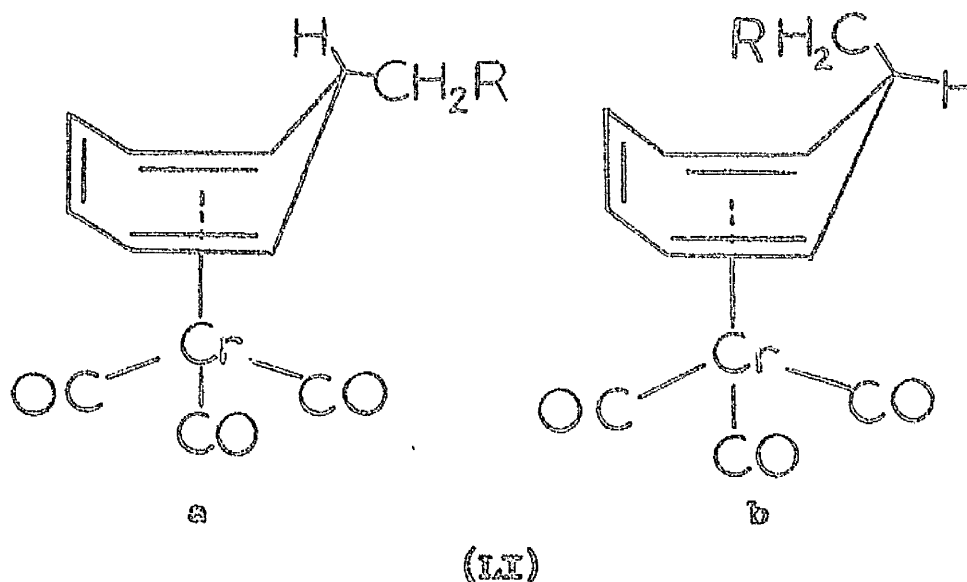
and it has now been shown that the endo-stereoisomer (XLVIII) is produced by reaction (a) while reactions (b) and (c) afford the exo-stereoisomer (XLIX).

One object of the present work was to seek chemical evidence for or against these structural assignments. Other objects were:

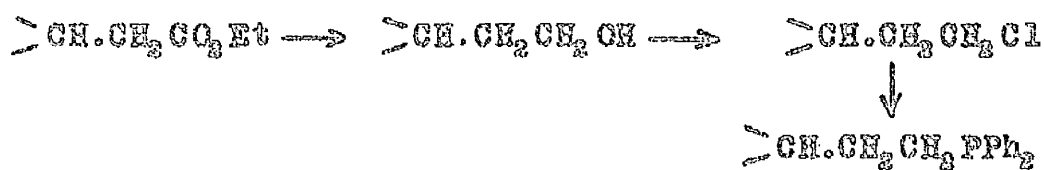
- (i) to extend the usefulness of the above routes for the introduction of new types of substituents, including the preparation of those isomers of the endo-series which are not accessible by route (a),
- (ii) to investigate to what extent the reaction (c) is an example of a more general reaction pattern for replacement of one substituent R by another R', and if so, to study the order of preferred replacement,
- (iii) to study the possible displacement of cycloheptatriene, C_7H_8 from (XLVII) by C_7H_7R , and the identity of the isomer so produced.

In order to verify chemically the stereochemistry of 7-substituted derivatives of tricarbonylcycloheptatriene-chromium, it was desired to introduce in a side-chain a functional grouping such as $-CH=CH_2$, $-C\equiv CR$, or $-PPh_2$ which might displace one CO group from the metal, and so to adjust the length of the side-chain as to make such displacement possible in the case of the endo-isomer (XLVIII) but not of

the exo-isomer (XLIX). Possible methods for introducing such side-chains were therefore investigated. In view of the ready availability of the ester, tricarbonyl-7-ethoxycarbonylmethyl-cycloheptatrienechromium,⁷⁸ (LI; R = CO₂Et) (see footnote) modification of its side chain was first attempted.



The following reaction scheme was envisaged:



However, attempted reduction of this ester (exo- or endo-) by the Bouveault-Blanc method¹¹⁸ (using sodium/ethanol or sodium/isopropyl alcohol, with or without toluene as co-solvent¹¹⁹

Footnote:- The endo-isomer obtained by the method of Smith⁷⁸ has m.p. 78-79°C and not 49-50°C as reported.

or with lithium aluminium hydride or lithium borohydride led in each case to complete decomposition, whereas lithium tri-tert-butoxyaluminumhydride left the ester largely unchanged.

To obtain the alcohol expected from such reduction of the endo-ester in another way, method (a) was attempted with 2-(7-cycloheptatrienyl)ethanol,¹⁰⁷ $C_7H_7CH_2CH_2OH$. However, at moderate temperatures, this gave a poor yield of a red gummy product, believed to be a mixture of isomers of the desired alcohol (LI; $R = CH_2OH$). Attempts to obtain a crystalline product by acetylation of the starting alcohol, or the gummy product, were unsuccessful. Use of higher reaction temperatures led to the formation of an insoluble high-melting solid as the main product. This has not been identified.

As an alternative route to the desired derivatives tricarboxyl-7-exomethoxycycloheptatrienechromium¹¹⁰ (XLIX; $R = OCH_3$) was treated with zinc turnings and propargyl bromide in tetrahydrofuran to give tricarboxyl-7-exopropargylcycloheptatrienechromium (LI(b); $R = C \equiv CH$), in excellent yield. This reaction resembles the 'pseudo-Reformatsky' reaction by which the methoxy compound was previously converted to the ester⁷⁶ (LI(b); $R = CO_2Et$). Hydrogenation over Lindlar¹⁰⁸ catalyst smoothly converts the acetylenic derivative (LI(b); $R = C \equiv CH$) to the corresponding olefin (LI(b); $R = CH = CH_2$). Neither of

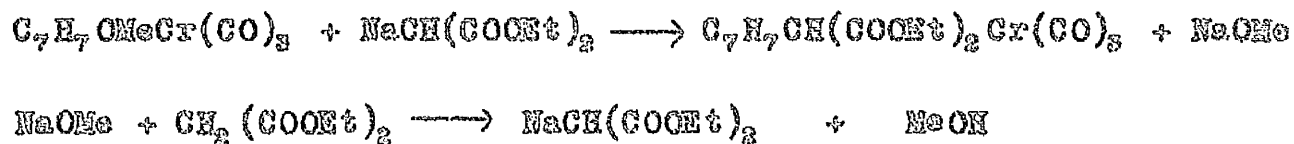
these substituents displaced CO from the metal- either during preparation of the compounds or on their subsequent irradiation with U.V. light or by heating in refluxing toluene. However, both substituents offer opportunities for further modification of the side-chain.

Smith⁷⁹ suggested that interaction of the carboxyl group of tricarbonyl-7-endocarboxymethylcycloheptatrienechromium (LI(a); R = COOH) with the metal might occur to a sufficient extent to result in a significantly different dissociation constant from that of its exo-isomer (LI(b); R = COOH) and that this might help in establishing the relative configurations. The two acids have been prepared in pure form by alkaline hydrolyses of the corresponding esters⁷⁹ (LI; R = CO₂Et). Their dissociation constants and that of the parent 7-carboxymethylcycloheptatriene,¹⁰⁷ C₇H₇CH₂COOH, have been measured by potentiometric titration in 50% aqueous ethanol (see appendix).

The values obtained are:	pK _a
7-carboxymethylcycloheptatriene	6.5
tricarbonyl-7- <u>endo</u> carboxymethylcycloheptatriene-chromium	6.4
tricarbonyl-7- <u>exo</u> carboxymethylcycloheptatriene-chromium	6.35

The differences between these values are clearly too small to permit useful deductions.

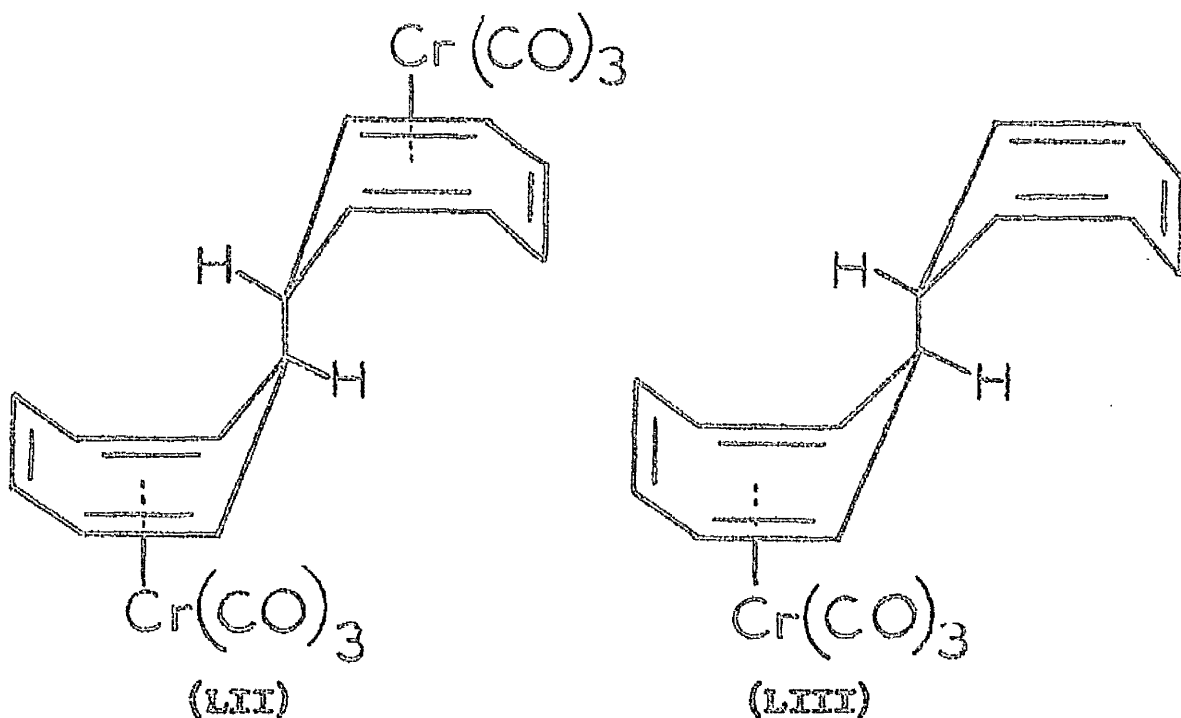
In previous work tricarbonyl-7--exomethoxycycloheptatriene-chromium (XLIX; R = OCH₃) was shown⁷⁹ to react smoothly with alkyl- or aryl- lithium, with zinc and ethyl bromoacetate, and, as mentioned above, with zinc and propargyl bromide. Zinc and diethyl bromomalonate react similarly to give the exo-malonyl derivative (XLIX; R = CH(CO₂Et)₂) in excellent yield. Even simpler is the preparation of this product using diethyl sodiomalonate. Only a trace of base is required as it is regenerated by the sequence:



This avoids the rearrangement¹¹⁰ promoted by excess base, which lowers the yield in the older method (b) for preparing this ester. Hydrolysis of this ester led readily to an aqueous solution of the sodium salt of the corresponding acid, but the free acid could not be extracted after acidification.

In contrast to the above mentioned halides, chloro- and bromo-acetal did not prove sufficiently reactive to undergo similar reactions with zinc and tricarbonyl-7--exomethoxycycloheptatrienechromium. Instead the latter (XLIX; R = OMe) was largely reduced to hexacarbonyl(bicycloheptatrienyl)bis-chromium (LII). This, and tricarbonyl(bicycloheptatrienyl)chromium (LIII) also resulted as the only products when

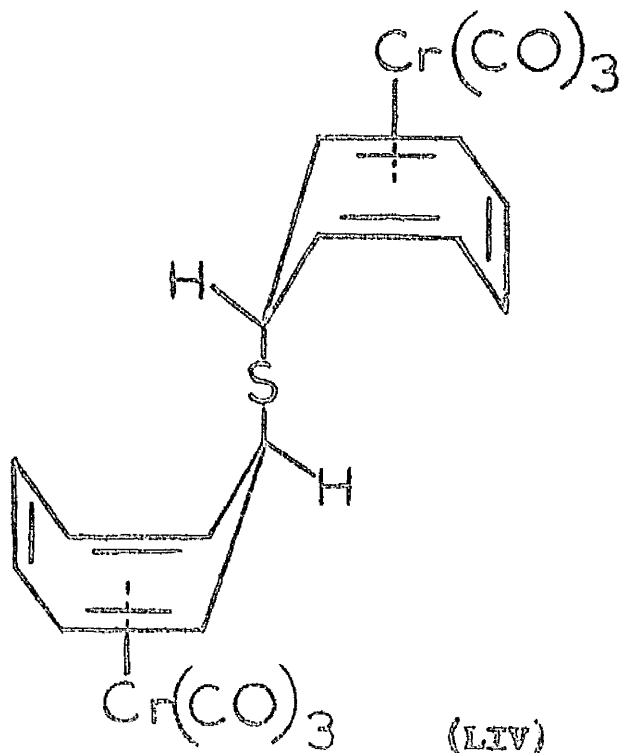
replacement of the methoxyl group by $-CN$ or $-NMePh$, was attempted under a variety of conditions. Replacement by $p-SC_6H_4CH_3$ was however readily achieved, using the sodium salt of toluene-*p*-thiol in tetrahydrofuran at room temperature to give the expected tricarbonyl-7-exo-*p*-tolylthiocycloheptatrienechromium (XLIX; $R = SC_6H_4CH_3-p$).



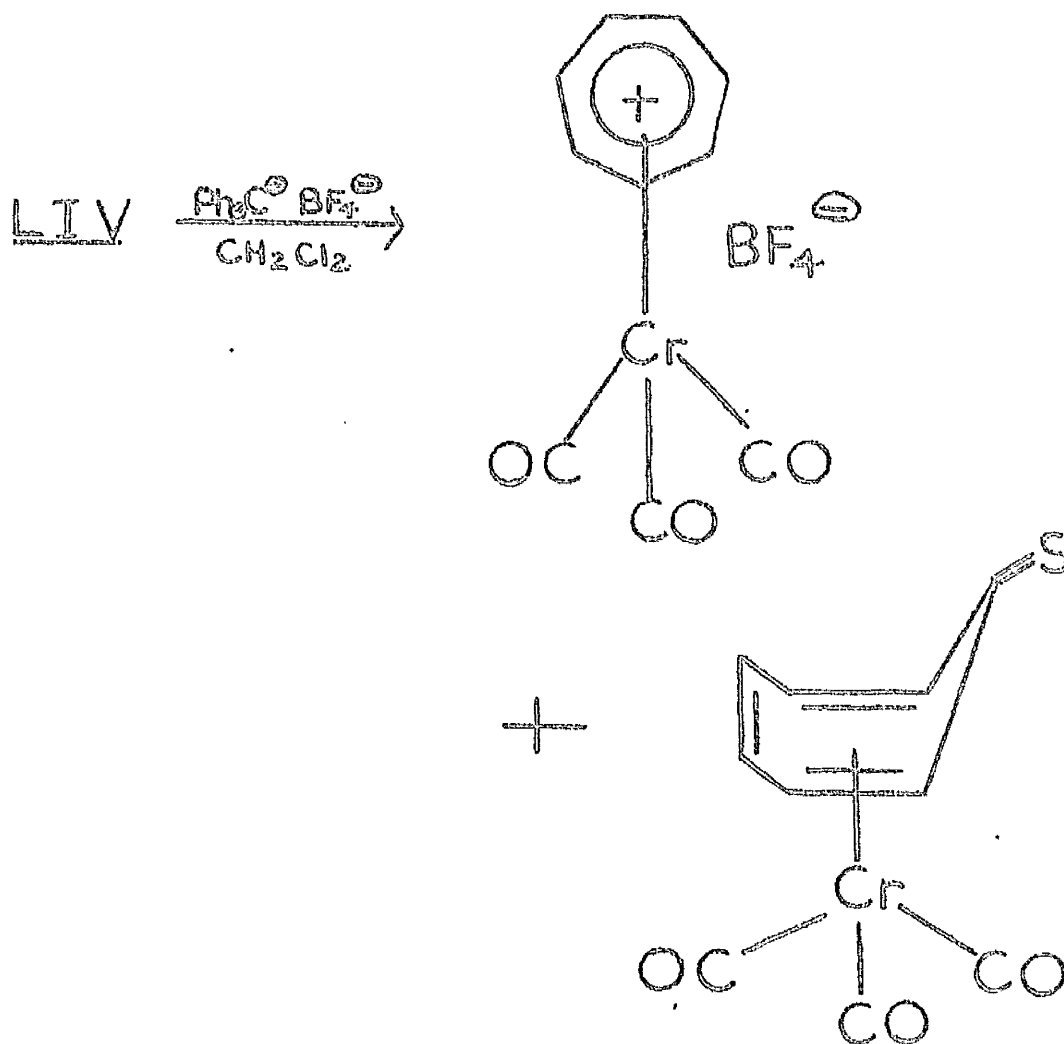
Munro¹¹⁰ has reported that treatment of tricarbonyl-cycloheptatrienylchromium perchlorate with potassium cyanide in aqueous solution, results in the formation of tricarbonyl-7-exocyanocycloheptatrienechromium (XLIII; $R = CN$) in only 18% yield, the main products being the dimeric species (LII) and (LIII). However, reaction between the corresponding fluoroborate and 'analar' potassium cyanide has afforded the desired

oxocyanide-complex in 92% yield. This increased yield is attributed to the superior quality of the potassium cyanide used and not to the difference of the anion.

Treatment of tricarbonylcycloheptatrienylchromium fluoroborate (L) with aqueous dimethylamine, resulted in the quantitative formation of tricarbonyl-7-oxodimethylaminocycloheptatrienylchromium (XLIX; $R = NMe_2$). The extreme instability of this complex has prevented its complete characterization. Consistent analyses could not be obtained and all attempts to record the N.H.R. spectrum caused rapid and complete decomposition. Treatment of the amino-complex (XLIX; $R = NMe_2$) with the sodium salt of toluene-p-thiol in tetrahydrofuran afforded the above mentioned thio-ether (XLIX; $R = SC_6H_4CH_3-p$), whereas treatment with potassium cyanide resulted in decomposition.



Bis-exo-(tricarbonylcycloheptatrienylchromium)sulphide (LIV) has been obtained in almost quantitative yield from the reaction of tricarbonylcycloheptatrienylchromium fluoroborate (L) and sodium sulphide in aqueous solution. The possibility that the above thio-ether (LIV) might react with triphenylmethyl tetrafluoroborate¹¹⁹ to form a thio-tropone complex as follows was investigated.



The expected tricarbonylcycloheptatrienylchromium fluoreborate was precipitated quantitatively but the red solution afforded only yields of the starting thio-ether (LIV) and triphenylmethanol, and no thio-tropone complex was obtained.

Analogous behaviour to this has been noted⁷⁸ in the case of tricarbonyl-7-exomethylcycloheptatrienylchromium (XLIX; R = Me) which fails to react with triphenylmethyl tetrafluoroborate, in contrast to the corresponding 7-endo isomer⁷⁷ (XLVIII; R = Me). It would therefore appear that this reaction is stereospecific involving removal of hydride from the exo-position.

It has been reported¹¹⁸ that reaction between 7-methoxycycloheptatriene¹⁰⁹ and phenol results in the formation of *o'* and *p'*-tropyli-phenols. Accordingly tricarbonyl-7-exo-methoxycycloheptatrienylchromium (XLIX; R = OCH₃) was treated with phenol in tetrahydrofuran. A red gum, believed to be a mixture of isomeric tropyli-phenol complexes, was obtained. Attempted chromatography or crystallisation of this material led rapidly to complete decomposition. Since ferrocene exhibits

reactivity similar to that of phenol, tricarbonyl-7-oxomethoxy-cycloheptatrienechromium (XLIX; R = OCH₃) was treated with ferrocene in tetrahydrofuran in an attempt to obtain a mixed-metal complex. However, at room temperature both starting materials were recovered unchanged, and at reflux temperature ferrocene was recovered quantitatively along with yields of the dimeric complexes (LII) and (LIII).

Tricarbonyl-7-endodimethylaminocycloheptatrienechromium (XLVIII; R = NMe₂) is the only stereoisomer produced either by reaction of 7-dimethylaminocycloheptatriene with hexacarbonylchromium in a refluxing mixture of diglyme and petroleum ether, b.p. 80-100°C, or by displacement of cycloheptatriene from tricarbonylcycloheptatrienechromium (XLVII) by 7-dimethylaminocycloheptatriene in refluxing petroleum ether, b.p. 100-120°. Since the complex (XLVIII; R = NMe₂) is insoluble in dilute hydrochloric acid, and has a nuclear magnetic resonance spectrum (N.M.R. 14 page 70) not fully consistent with the spectra of other tricarbonylcycloheptatrienechromium complexes attempts were made to recover the organic moiety for investigation. Reductive degradation of the complex with sodium borohydride afforded a pale yellow oil, the N.M.R. spectrum of which shows strong N-methyl proton absorption but no signal pattern characteristic of cycloheptatriene ring protons. The oil forms a picrate;

(m.p. 151-152°C) which, on admixture with an authentic sample of 7-dimethylaminocycloheptatriene picrate (m.p. 159-160°C) shows a marked depression of the melting point. It is therefore probable that some rearrangement of the organic moiety has occurred during this reaction, but the identity of this complex here designated tricarbonyl-7-endodimethylaminocycloheptatrienechromium has not yet been fully elucidated.

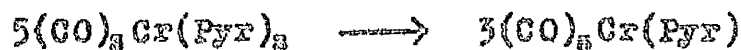
It has been shown¹¹⁸ that treatment of tricarbonyltripyridinechromium with certain monohalo-benzenes and boron trifluoride dimethyl etherate in ether, results in the formation of tricarbonylmonohalo-benzenechromium complexes. The feasibility of employing this technique in the preparation of tricarbonyl-7-substituted-cycloheptatrienechromium complexes hitherto inaccessible by reaction of 7-substituted-cycloheptatrienes with hexacarbonylchromium in refluxing diglyme was therefore investigated.

Tricarbonyltripyridinechromium has been obtained in very good yields by the modified process of heating hexacarbonylchromium in a refluxing mixture of pyridine and aromatic-free petroleum ether, b.p. 80-100°C, in a 'Strohmaier apparatus'¹⁰⁸ for 40 hr.

In order to assess the usefulness of the above technique the preparation of known tricarbonylcycloheptatrienechromium complexes was first attempted and the following results obtained.

Starting Material	Product	Yield
1. Cycloheptatriene	Tricarbonylcycloheptatriene - chromium	80
2. 7-Ethoxycarbonylmethyl-cycloheptatriene	Tricarbonyl-7- <u>endo</u> -ethoxycarbonylmethylcycloheptatrienechromium	69
3. 7-Di(ethoxycarbonyl)-methylcycloheptatriene	Tricarbonyl-7- <u>endo</u> -di(ethoxycarbonyl)-methylcycloheptatrienechromium	63

In the above examples no exo-stereoisomer was produced and the reactions therefore proceed in the same stereochemical direction as the reaction of 7-substituted-cycloheptatrienes with hexacarbonylchromium. From the reactions (2) and (3) pentacarbonylpyridinechromium was obtained in yields of 27% and 33% respectively, calculated on the basis of



The process is therefore extremely efficient in its almost quantitative use of available carbon monoxide. Treatment of tricarbonyltripyridinechromium with boron trifluoride diethyl etherate in ether also leads to the formation of the mono-pyridine complex in good yield.

Since, as previously mentioned, irradiation with U.V. light, or prolonged heating of the exo-propargyl (LI(b) R = C≡CH) or exo-allyl (LI(b); R = CH=CH₂) complexes failed

to cause displacement of CO from the metal by the terminal functional group, the possibility that the corresponding endo-isomers might undergo such reaction was investigated. Treatment of 7-methoxycycloheptatriene with propargyl bromide and zinc turnings in tetrahydrofuran afforded 7-propargylcycloheptatriene in 64% yield. Treatment of the latter compound with tricarbonyltripyridinechromium and boron trifluoride diethyl etherate afforded the expected tricarbonyl-7-endo-propargylcycloheptatrienechromium (LI(a); R = C \equiv CH). No corresponding exo-isomer was detected. The endo-propargyl complex (LI(a); R = C \equiv CH) was again the only stereoisomer produced by the reaction of 7-propargylcycloheptatriene with hexacarbonylchromium in a refluxing mixture of diglyme and petroleum ether, b.p. 60-100°C.

Hydrogenation over Lindlar¹⁰⁸ catalyst smoothly converts the above propargyl derivative (LI(a); R = C \equiv CH) to the corresponding endo-allyl derivative (LI(a); R = CH = CH₂). Irradiation with U.V. light in hexane solution, or prolonged heating in refluxing toluene of the propargyl or allyl complex, led in each case, to partial decomposition, only quantities of the starting materials being isolated.

Dreiding models of the complexes (LI(a); R = C \equiv CH) and (LI(a); R = CH = CH) have been examined, and it is now

believed that the terminal functional grouping of the side chain cannot approach closely enough to the chromium atom for interaction to occur. The inclusion of another methylene group in the side-chain would allow the functional group to lie in a more favourable position for possible displacement of one CO group from the metal.

It has previously been shown that several 7-substituted cycloheptatrienes, e.g. 7-cyanocycloheptatriene, 7-phenylcycloheptatriene, bicycloheptatrienylether, and 7-methoxycycloheptatriene, do not react smoothly, if at all, with hexacarbonylchromium. The possible reaction of a number of these compounds with tricarbonyltripyridinechromium in the presence of boron trifluoride diethyl etherate was therefore investigated. Such treatment of 7-cyanocycloheptatriene¹¹¹ led to the formation of the yellow σ -bonded pentacarbonyl-7-cyanocycloheptatriene-chromium, m.p. 96-97°C ($C_7H_7CN \rightarrow Cr(CO)_5$) and a red crystalline material, m.p. 105-110°C, the N.M.R. spectrum of which indicated a mixture of stereoisomeric tricarbonyl-7-cyanocycloheptatriene-chromium complexes. Careful chromatography of the latter material afforded tricarbonyl-7-endocyanocycloheptatrienechromium, m.p. 133-134°C (XLVIII; R = CN) followed by tricarbonyl-7-exocyanocycloheptatrienechromium, m.p. 118-119°C (XLIX; R = CN) in the

ratio endo:exo 2:9. The endo-cyano complex was found to be very much more unstable to air, heat, or light than the corresponding exo-isomer. The thermal instability of the endo-isomer may explain the rapid decomposition occurring in the treatment⁷⁸ of 7-cyanocycloheptatriene¹¹¹ with hexacarbonylchromium in refluxing diglyme.

Another case where Fischer's method¹¹⁶ leads to the predominant formation of the exo-stereoisomer is 7-phenylcycloheptatriene.¹⁰⁹ This reaction afforded a mixture of stereoisomers, from which, by repeated chromatography, tricarbonyl-7-endophenylcycloheptatrienechromium, m.p. 114-115°C (XLVIII; R = Ph) and tricarbonyl-7-exophenylcycloheptatrienechromium, m.p. 134-135°C (XLIX; R = Ph) were obtained in the ratio endo:exo 3:7.

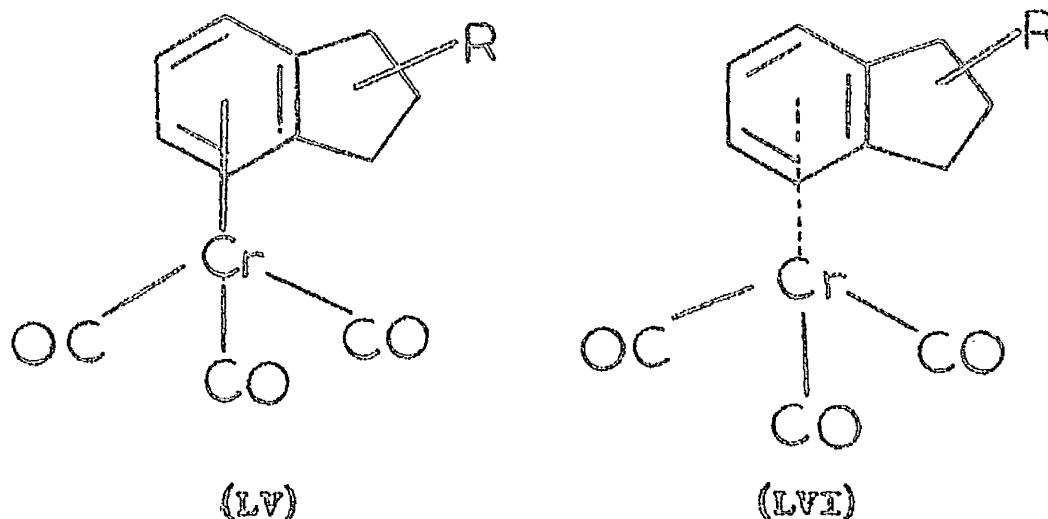
Munro¹¹⁰ has shown that reaction of hexacarbonylchromium with 7-phenylcycloheptatriene¹⁰⁹ results in the formation of a red gummy product believed to be a mixture of tricarbonyl-phenylcycloheptatrienechromium complexes. Since the 7-exo and 7-endophenyl complexes have now been isolated by the methods outlined above, this reaction was reinvestigated. Treatment of hexacarbonylchromium with 7-phenylcycloheptatriene¹⁰⁹ in a refluxing mixture of diglyme and petroleum ether, b.p. 80-100°C

again resulted in the formation of a gummy product which, on chromatography, afforded tricarbonyl-7-endophenylcycloheptatrienechromium (XLVIII; R = Ph) followed by a red amorphous solid from which a few black crystals, m.p. 73-74°C, were isolated mechanically. The very low yield of the latter material obtained from this reaction precluded its complete characterisation at this stage. However, treatment of tricarbonylcycloheptatrienechromium (XLVII) with 7-phenylcycloheptatriene¹⁰⁹ in refluxing petroleum ether, b.p. 80-100°C, followed by careful chromatography afforded tricarbonyl-7-endophenylcycloheptatrienechromium (XLVIII; R = Ph) and black crystals, m.p. 73-74°C, in 8% yield. The analysis, I.R. spectrum and N.M.R. spectrum (page 70 N.M.R. 15) indicate that this material is an isomeric tricarbonyl-7-phenylcycloheptatrienechromium for which a possible structure is suggested later in this thesis.

The boron trifluoride technique¹¹⁶ was applied to various other organic compounds (listed in the experimental section) without success. The boron trifluoride complex of a number of these compounds was immediately precipitated from solution on addition of boron trifluoride diethyl etherate, thus preventing further reaction taking place. In every case pentacarbonylpyridinechromium was formed, and with 7-methoxy-

cycloheptatriene¹⁰⁹, hexacarbonyl (bicycloheptatrienyl) bis-chromium (LII) was isolated in 5% yield.

It has been shown¹¹⁷ that reactions between hexacarbonylchromium and 1- or 2-substituted indanes in boiling cyclohexanol produce a mixture of cis- (LV) and trans (LVI) tricarbonylchromium compounds.



The cis:trans ratios obtained represent the relative thermodynamic stability of each of the pairs of isomers since it is shown¹¹⁷ in separate experiments, that when free ligand is present in solution, individual isomers (1 - CN; 2 - OH; 2 - Me; 2 - CN) come to equilibrium. When the free organic ligand is absent the individual isomers are recovered unchanged.

The possibility that individual isomers of tricarbonyl-7-substituted cycloheptatrienechromium complexes might thus

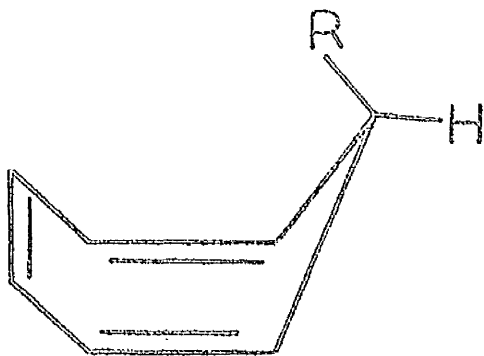
equilibrate was therefore investigated. Experiments were carried out on tricarbonyl-7-exo-(ethoxycarbonylmethyl)cycloheptatrienechromium (LIB; R = CO₂Et) and tricarbonyl-7-phenyl-cycloheptatrienechromium (exo- or endo-). These complexes were individually treated with boron trifluoride diethyl etherate in refluxing ether, in the presence of tricarbonyltripyridine chromium or the free organic ligand, or heated in a refluxing mixture of diglyme and petroleum ether, b.p. 100-120°C with or without the free organic ligand. In no case was conversion to the corresponding stereoisomer observed.

DISCUSSION OF RESULTS

PART II

Non-planarity of Cycloheptatriene

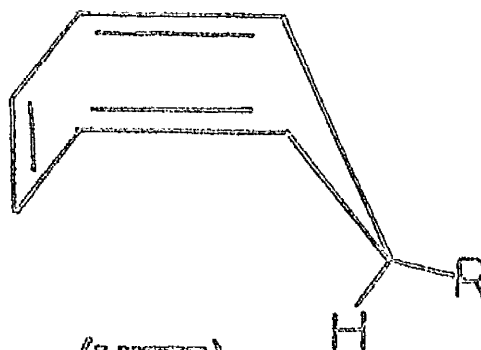
For a number of years the planarity or non-planarity of cycloheptatriene was in dispute. An x-ray determination¹¹⁸ of the structure of the p-bromophenacyl ester of 7,7-dimethylcycloheptatriene-3-carboxylic acid has shown that the seven-membered ring exists in a boat conformation with C₇ and C₃-C₄ at distances of 0.63 and 0.48 Å, respectively from the plane of C₁-C₂-C₅-C₆. The boat structure received further support from the observation¹¹⁹ that the 7,7-dimethyl groups of 2-t-butyl-3,7,7-trimethylcycloheptatriene were non-equivalent at low temperatures (e.g. -100°C), and the non-planarity of cycloheptatriene itself was indicated¹²⁰ by the observation of 1,5-transannular hydrogen shift in cycloheptatriene. Examination of N.M.R. spectra of cycloheptatriene, at very low temperatures, by Jensen and Smith,¹²¹ and Anet¹²² has shown conclusively that the molecule is non-planar, and also provides information on the barrier to inversion of the seven-membered ring. These authors^{121,122} have shown that the cycloheptatriene molecule is a mixture of the rapidly equilibrating conformers (LVII (a)) and (LVIII (a)).



(LVII)

(a) R = H

(b) R = D



(LVIII)

(a) R = H

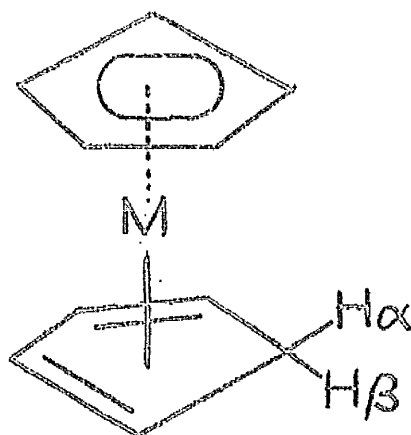
(b) R = D

The N.M.R. spectrum of cycloheptatriene does not change between room temperature and -120°C , but below this temperature the methylene triplet begins to broaden. At -141°C two peaks begin to appear at the sides of, and at the expense of, the main peak, and at -170°C the two signals are separated by about 1.4τ . The mean chemical shift of the methylene protons is 7.8τ , almost unchanged from that observed at higher temperatures. From a consideration of the dihedral angles between the methylene and vinyl hydrogens ($124 \pm 3^{\circ}$ and $4 \pm 3^{\circ}$ from Dreiding models) and the calculated coupling constants ($J_{124^{\circ}} = 3.4$ and $J_{4^{\circ}} = 8.0$) Jensen and Smith¹²¹ assign the high-field hydrogen ($J_{\text{H-vinyl}} = 4.0 \pm 0.3$) to (LVIIIb) and the low-field one ($J_{\text{H-vinyl}} = 7.2 \pm 0.3$) to

(LVII (b)). In the case of 7-deuteriocycloheptatriene it is calculated that the structure (LVIII (b)) with the hydrogen in the quasi-axial position is favoured, and this is supported by other spectroscopic evidence.¹²³ This difference in stability is attributed to greater eclipsing effects, of the quasi-equatorial-7-hydrogen with the 1- and 6- hydrogens for protium than deuterium. From a consideration of the diamagnetic anisotropy of the double bond¹²⁴, Anet¹²² also concludes that the resonance of the quasi-axial proton should occur at higher field than the quasi-equatorial one, at least in cycloheptatriene.

Stereochemistry of Tricarbonylcycloheptatrienecobalt Derivatives

In the 1-substituted cyclopentadiene-cyclopentadienyl-cobalt complexes (obtained by nucleophilic attack on cobalticinium salts or by reaction of various halides with cobaltocene) it was originally postulated²² that the substituent occupied the endo-position with respect to the metal atom. This postulation²² was made on the ground that the low intense C-H stretching frequency in the infrared spectrum (designated C-H_α) appearing in the unsubstituted complexes (LIX) was absent in the substituted complexes.



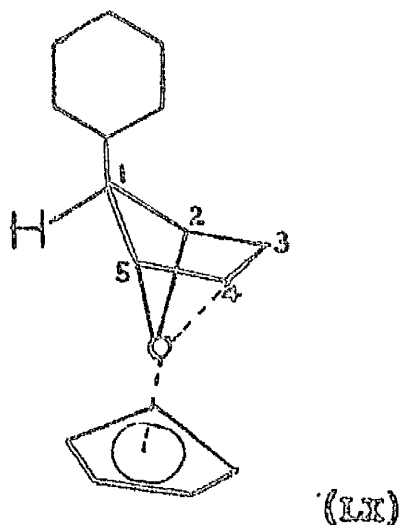
(LIX)

Wilkinson and his coworkers interpreted²² the N.M.R. spectra of these complexes to agree with endo-substitution. Thus, in cyclopentadienyl-1-methyl-cyclopentadienecobalt, the methyl group proton resonance occurs at (τ 9.77), a high value compared to normal aliphatic methyl proton resonance. This upfield shift is explained by assuming shielding of the methyl protons due to the close proximity of the metal atom, and this would not be the case if the methyl group were in the exo-position.

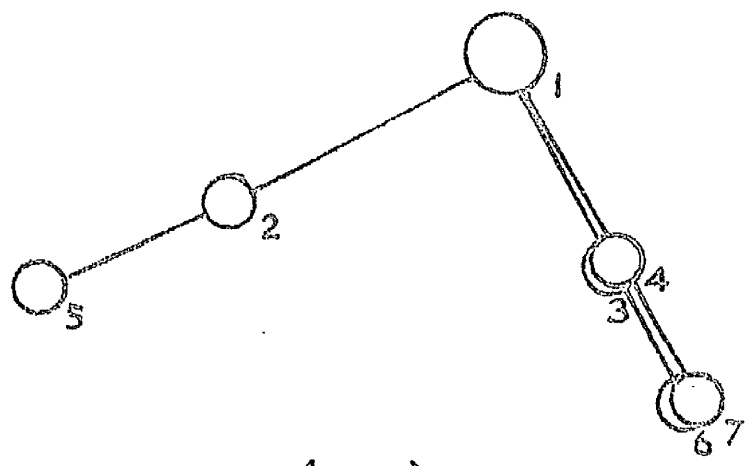
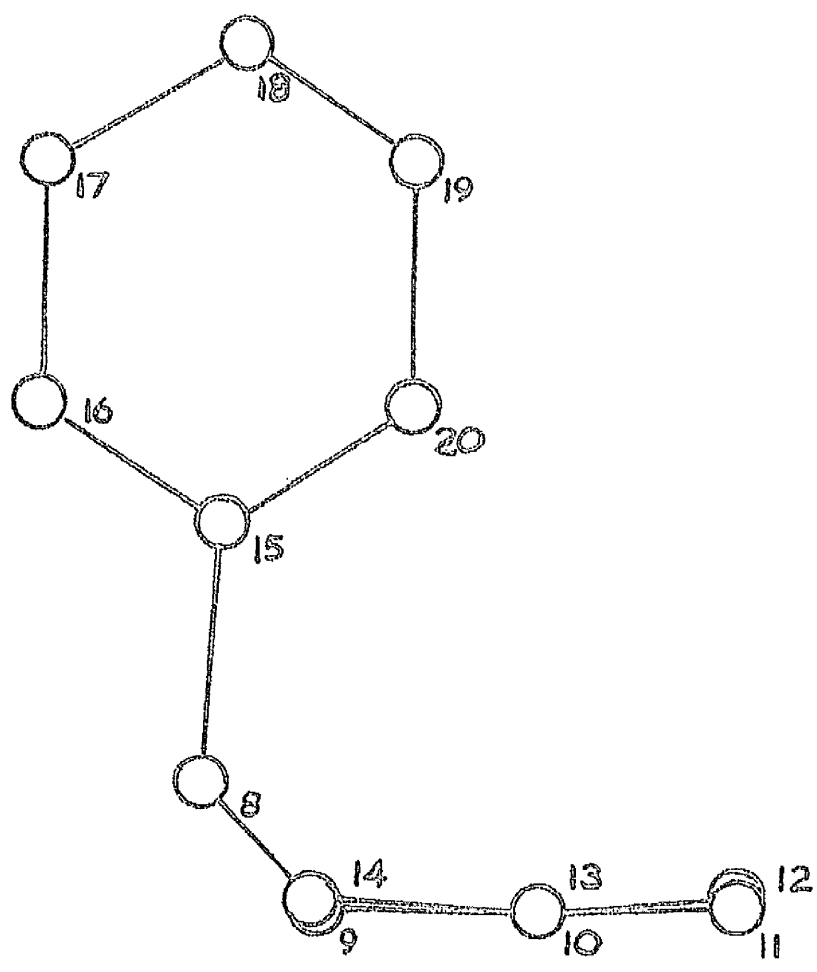
Similar arguments were made in favour of endo-substitution in those isomers of the π -cyclohexadienyl^{70,186} and tricarbonylcycloheptatriene⁷⁸ metal complexes, which were obtained by similar modes of preparation and exhibited similarities in spectra.

However, x-ray studies⁴⁹ of π -cyclopentadienyl-1-phenylcyclopentadienecobalt (LK) have shown that the phenyl

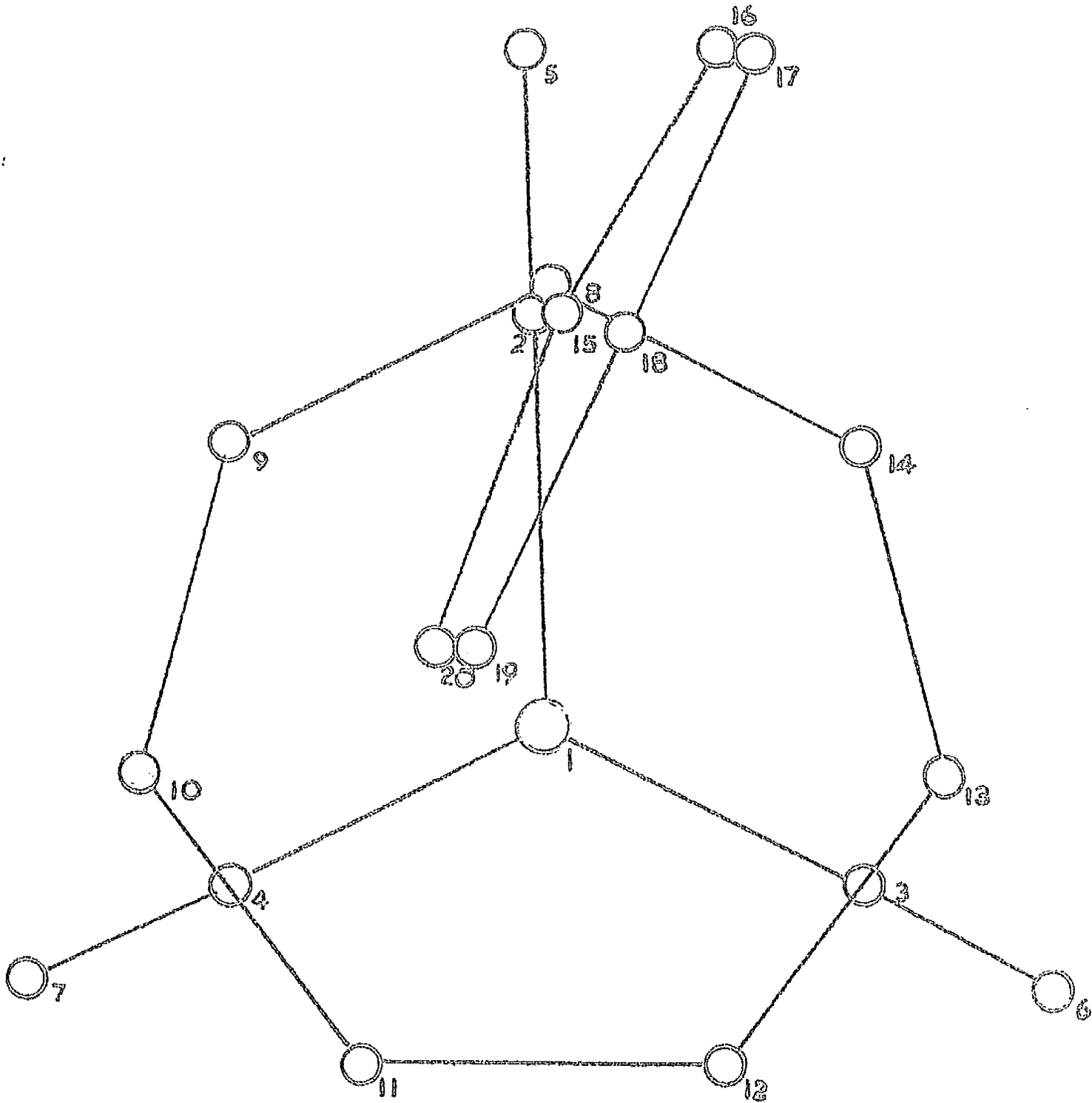
group occupies the exo-position with respect to the metal atom.



This result made it reasonable to assume that, in all of the substituted cyclopentadiene, cyclohexadienyl and cycloheptatriene metal complexes, previously designated endo-, the substituent is, in fact, in the exo- configuration. The N.M.R. spectra of η^5 -1-methyl cyclohexadienyltricarbonylmanganese and other η^5 -cyclohexadienyl derivatives have now been interpreted⁷¹ to agree with exo-substitution and a recent x-ray study¹²⁶ of tricarbonyl- η^5 -7-phenylcycloheptatrienechromium (LXI) (obtained by a similar method of preparation⁷⁹) shows that the phenyl group occupies the exo-position.



(LXIa)



(LXEd)

TABLE I

Bond Distances together with their Standard Deviations

<u>Bond</u>	<u>d(Å)</u>	<u>σ(d)</u>
Cr - C ₂	1.814	0.011
Cr - C ₃	1.824	0.014
Cr - C ₄	1.787	0.013
Cr - C ₈	2.873	0.010
Cr - C ₉	2.316	0.011
Cr - C ₁₀	2.206	0.011
Cr - C ₁₁	2.197	0.012
Cr - C ₁₂	2.213	0.011
Cr - C ₁₃	2.206	0.011
Cr - C ₁₄	2.298	0.011
C ₂ - O ₅	1.178	0.014
C ₃ - O ₆	1.153	0.017
C ₄ - O ₇	1.190	0.017
C ₈ - C ₉	1.530	0.015
C ₉ - C ₁₀	1.365	0.015
C ₁₀ - C ₁₁	1.433	0.016
C ₁₁ - C ₁₂	1.413	0.016
C ₁₂ - C ₁₃	1.408	0.016
C ₁₃ - C ₁₄	1.332	0.015
C ₈ - C ₁₄	1.531	0.015
C ₈ - C ₁₅	1.508	0.015
C ₁₅ - C ₁₆	1.397	0.017
C ₁₆ - C ₁₇	1.406	0.021
C ₁₇ - C ₁₈	1.384	0.021
C ₁₈ - C ₁₉	1.334	0.019
C ₁₉ - C ₂₀	1.431	0.017
C ₁₅ - C ₂₀	1.378	0.015

TABLE II

Bond Angles together with their Standard Deviations

<u>Angle</u>	<u>θ</u>	<u>σ(θ)</u>
$C_3 - C_7 - C_8$	91.43	0.55
$C_2 - C_7 - C_4$	89.70	0.54
$C_3 - C_7 - C_4$	85.29	0.60
$C_7 - C_2 - O_5$	176.84	0.95
$C_7 - C_3 - O_6$	176.61	0.99
$C_7 - C_4 - O_7$	176.86	1.16
$C_9 - C_9 - C_{10}$	105.85	0.83
$C_9 - C_9 - C_{10}$	128.88	0.95
$C_9 - C_{10} - C_{11}$	126.96	1.01
$C_{10} - C_{11} - C_{12}$	127.22	1.06
$C_{11} - C_{12} - C_{13}$	126.51	1.05
$C_{12} - C_{13} - C_{14}$	129.74	1.04
$C_{13} - C_{14} - C_8$	127.10	0.97
$C_{14} - C_{15} - C_{20}$	116.29	1.02
$C_{15} - C_{16} - C_{17}$	121.70	1.23
$C_{16} - C_{17} - C_{18}$	118.24	1.37
$C_{17} - C_{18} - C_{19}$	121.33	1.34
$C_{18} - C_{19} - C_{20}$	120.86	1.19
$C_{19} - C_{20} - C_{16}$	119.50	1.02

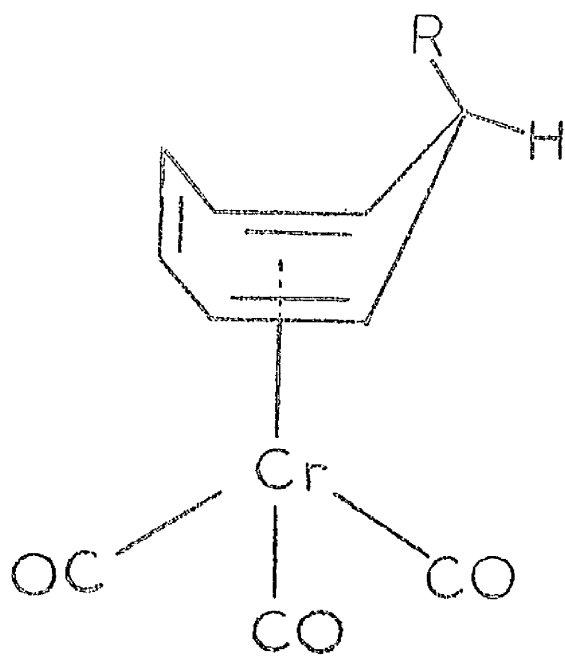
Mechanism of Formation of 7-Substituted Tricarbonylcycloheptatrienechromium Derivatives.

It may be assumed that reaction of 7-substituted cycloheptatrienes with hexacarbonylchromium occurs by a 'broadside' attack, accompanied by an intramolecular shift and extrusion of carbon monoxide as suggested¹⁸⁷ for the reaction of substituted benzenes and hexacarbonylchromium. Smith⁷⁸ has suggested that steric factors would ensure the formation of the exo-substituted product (LXIII). However, reaction of 7-substituted cycloheptatrienes with hexacarbonylchromium or with tricarbonyltripyridinechromium in the presence of boron trifluoride has been shown to produce predominantly the endo-stereoisomer (LXIV). It is believed that this must be attributed to the preferred 'equatorial' conformation of the parent cycloheptatriene bearing a bulky substituent (LXII).

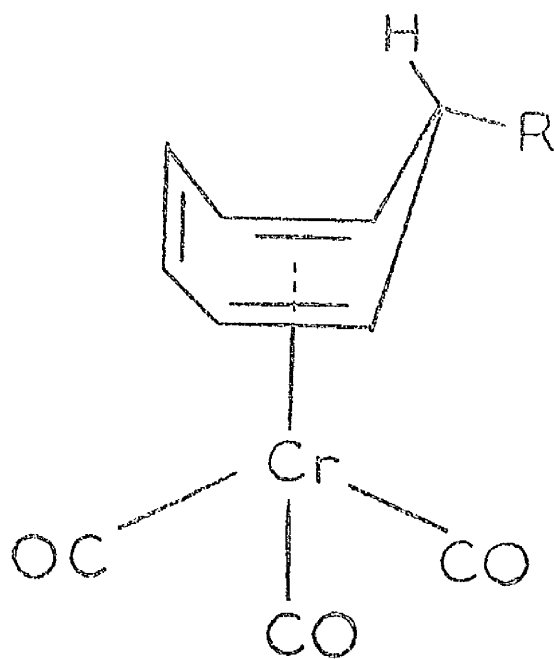
In all cases where the atom attached to C₇ is a saturated carbon atom the endo-stereoisomer (LXIV) was the exclusive product. In only two cases (LXII, R = Ph or R = CN) was it accompanied by the exo-stereoisomer (LXIII). It is not known whether cycloheptatrienes with these less sterically demanding substituents exist to a relatively large extent in the 'axial' conformation, favoured possibly by



(LXXII)



(LXXIII)



(LXXIV)

dipole-dipole interaction between the substituent and the cycloheptatriene ring or whether ring inversion during the reaction is, in some way, facilitated in these cases.

On the basis of a mechanism suggested¹²⁰ for the postulated²³ endo-substitution in derivatives of cyclopentadienylcyclopentadienecobalt, Smith⁷⁶ proposed that addition of anions to the tricarbonyltropyliumchromium cation would lead to endo-substituted derivatives by a mechanism involving initial attack of the anion on the metal, followed by an intramolecular shift to give the desired compound. Reaction of phenyl Grignard reagent with tricarbonyltropyliumchromium fluoroborate produces exclusively the exo-stereoisomer and all other related additions have now been shown to follow the same stereochemical course. The postulated intermediate bonding of the anion to the metal^{120,76} therefore plays no part in such reactions. It is believed that the attack of nucleophiles from the side remote from the metal may be the result of largely steric factors.

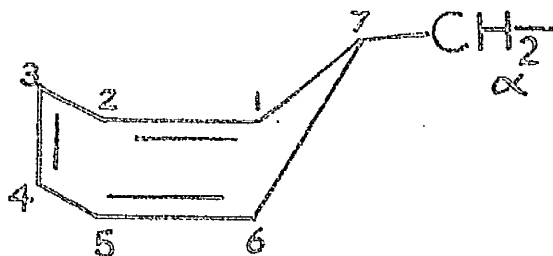
Tricarbonyl-7-exomethoxycycloheptatrienecromium readily undergoes displacement of the methoxy group by other anions to give products having the same stereochemistry as the starting material.

This suggests that the reaction follows an S_N1 type of mechanism but in the absence of confirmatory kinetic evidence an S_N2' displacement mechanism (with allylic rearrangement) cannot be excluded.

Interpretation of N.M.R. Spectra of 7-Substituted Tricarbonyl cycloheptatrienechromium Complexes.

The N.M.R. spectra of a number of 7-substituted cycloheptatrienes and their stereoisomeric tricarbonylchromium complexes are reproduced on pages 66 - 71. These spectra have been interpreted to agree with the configurations proposed on the basis of the X-ray analysis¹²⁶ of tricarbonyl-7-exophenylcycloheptatrienechromium.

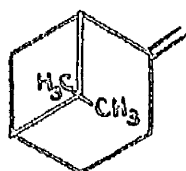
Since the primary object of this study has been to determine the configuration of the 7-substituent, attention has been focussed on the chemical shifts of the methylene proton H_7 and protons (if any) of the 7-substituent, α to the ring, and on the coupling constant of H_7 and the vinylic protons $H_1, 6$. (for numbering see LXV).



(LXV)

Two substituents which allow examination of the resonance of protons α to the ring are the 7-propargyl and 7-ethoxycarbonylmethyl (N.M.R. 7-12). From these spectra it is seen that, for the parent cycloheptatriene and the corresponding endo-complex, the α -methylene proton signals occur at the same τ value, whereas in the exo-complex the signal is displaced upfield by about 1.5 τ . Moreover, the H_γ signals occur at the same τ value for the parent cycloheptatriene and the endo-complex, but in the exo-complex the signal is displaced downfield. The spectra therefore indicate that in the parent cycloheptatrienes and the endo-complexes, H_γ is shielded, whereas in the exo-complexes the α methylene protons are shielded. The parent cycloheptatrienes are believed to exist preferentially in the 'equatorial' conformation and the spectral data are therefore in agreement with the complexes designated endo- having the 'equatorial' conformation, and those designated exo- having the 'axial' conformation. The shielding of 'axial' protons and deshielding of 'equatorial' protons is attributed to the diamagnetic anisotropy of the double bonds of the cycloheptatriene ring. This is in agreement with previous evidence¹²⁴ that protons which are situated above the plane of an olefinic double bond are abnormally shielded. A comparison¹²⁵ of the N.M.R. spectra of α -pinene (LXVI) and β -pinene (LXVII)

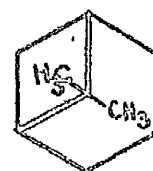
with that of norpinane (LXVIII) reveals that the frequency of one of the gem.-dimethyl groups in both the unsaturated compounds is diamagnetically shifted by 0.20-0.30 p.p.m. In these examples it is suggested¹²⁴ that the magnitudes of the diamagnetic shifts are relatively small as a consequence of the free rotation of the methyl groups.



(LXVI)



(LXVII)



(LXVIII)

Other features of the spectra (N.M.R. 1-12) which are in agreement with the assigned configurations are the coupling constants for the $H_{1,6}$ and H_7 protons. From a consideration of Droiding models the dihedral angles between the cycloheptatriene ring methylene and vinyl hydrogens (J_H axial-vinyl = 125° ; J_H equatorial-vinyl = 4°) were obtained. The coupling constants for these dihedral angles ($J_{126^\circ} = 4$ c.p.s; $J_{4^\circ} = 0$ c.p.s). obtained from the Karplus curve¹²⁹, are in agreement with the

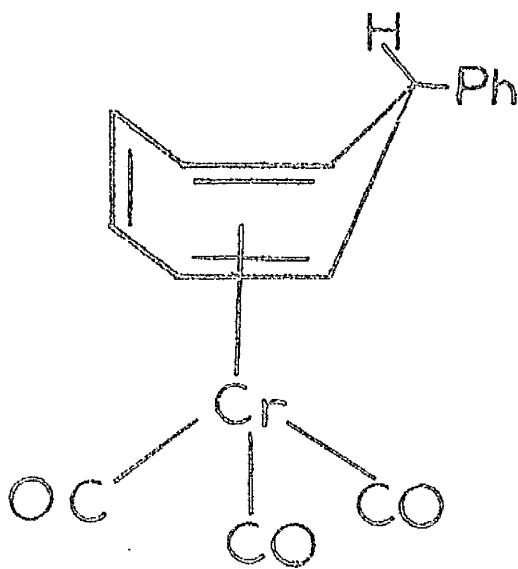
values obtained in the spectra. In the endo complexes, with H_7 in the 'axial' conformation $J_{H-vinyl} = 4.0$ c.p.s. whereas in the exo-complexes, with H_7 in the 'equatorial' conformation, $J_{H-vinyl} = 8.0$ c.p.s.

In the spectra of all of the exo-complexes, the chemical shifts of the olefinic protons of the cycloheptatriene ring, are in good agreement with the values reported by Wilkinson^{7a} for tricarbonylcycloheptatrienechromium ($H_{3,4} = 4.0$; $H_{2,3} = 5.2$; $H_{1,6} = 6.6$). In the corresponding endo-complexes, the signals of $H_{3,4}$ and $H_{2,3}$ occur essentially at the values quoted above, but the signals for $H_{1,6}$ are displaced to higher fields - a feature for which no satisfactory explanation is suggested.

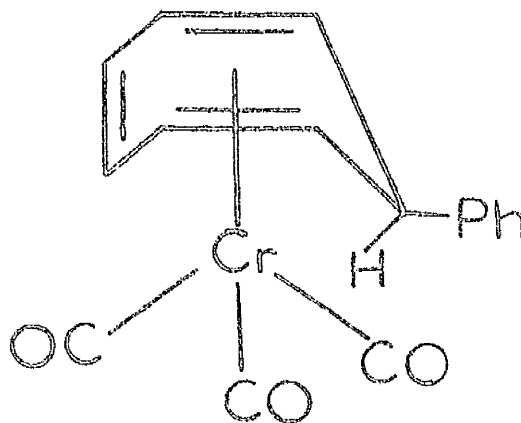
In the spectra of the 7-propargyl series (N.M.R. 7-9) an interesting feature is the splitting of the α methylene proton resonance. In the exo-complex the signal pattern of the methylene protons is a double doublet produced by coupling with the terminal acetylenic proton and the ring methylene proton. In the parent cycloheptatriene and the endo-complex however, one of the doublets is again split into a double doublet by coupling with an $H_{1,6}$ proton. This suggests restricted rotation about the ring-methylene carbon single bond, but again no satisfactory explanation for this is available.

Only one stereoisomeric tricarbonyl-7-methoxy-cycloheptatrienechromium has been isolated. This has been designated exo- on the basis of its mode of preparation and its N.M.R. spectrum (N.M.R. 16) which, by comparison with the spectrum of the parent cycloheptatriene, exhibits shielding of the methoxyl protons and deshielding of the H₇ proton.

The N.M.R. spectrum (N.M.R.15) of the black crystalline material, m.p. 73-74°C isolated from the reaction of 7-phenyl-cycloheptatriene and tricarbonylcycloheptatrienechromium is almost identical to that (N.M.R.2) of tricarbonyl-7-endo-phenylcycloheptatrienechromium. The spectrum is therefore compatible with either the structure (LXIX) with the substituent endo- or structure (LXX) with the substituent exo-.



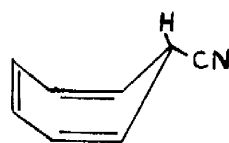
(LXIX)



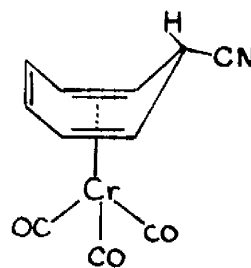
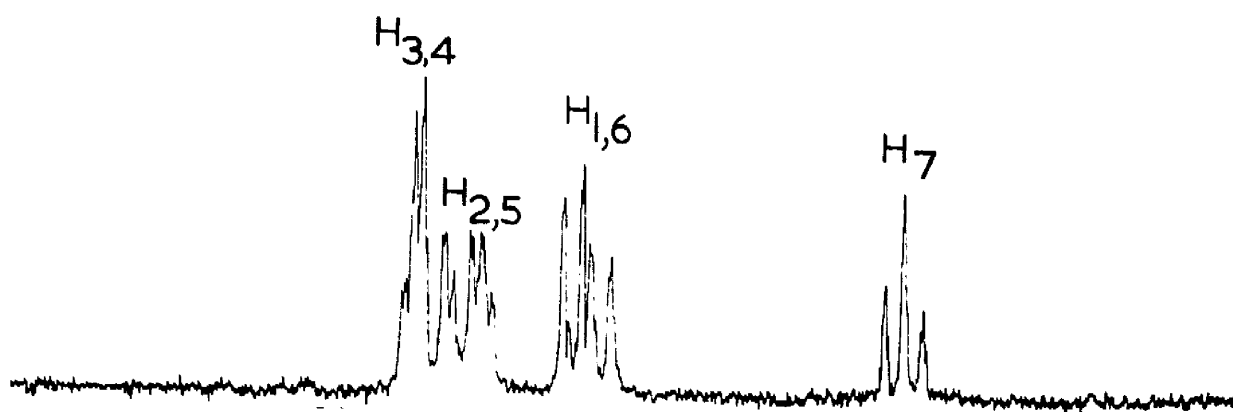
(LXX)

It is unlikely that this compound is, in fact, tricarbonyl 7-endo-phenylcycloheptatrienechromium (LXIX) since it has a very different colour in solution, and on alumina, and was separated from the latter compound on an alumina column. The structure (LXX) is therefore suggested for this isomeric tricarbonyl-7-phenylcycloheptatrienechromium, pending the result of an X-ray analysis which is now in progress.

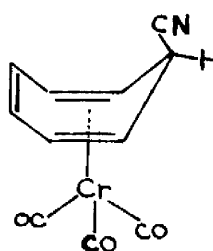
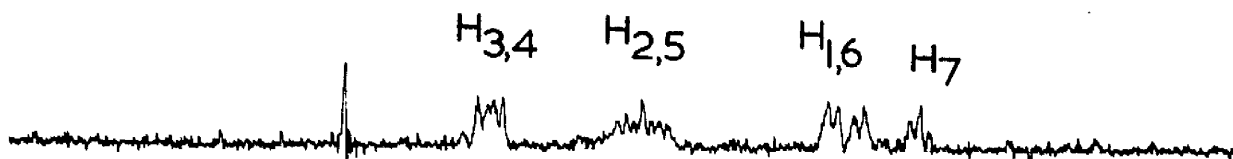
From the reaction of 7-dimethylaminocycloheptatriene with hexacarbonylchromium or tricarbonylcycloheptatrienechromium the product was expected to be tricarbonyl-7-endo-dimethylaminocycloheptatrienechromium. The N.M.R. spectrum (N.M.R.14) of the product is not, however, consistent with those of normal tricarbonylcycloheptatrienechromium derivatives. It would appear that some rearrangement has occurred, but, at present, the data available are insufficient to allow assignment of structure to this compound.



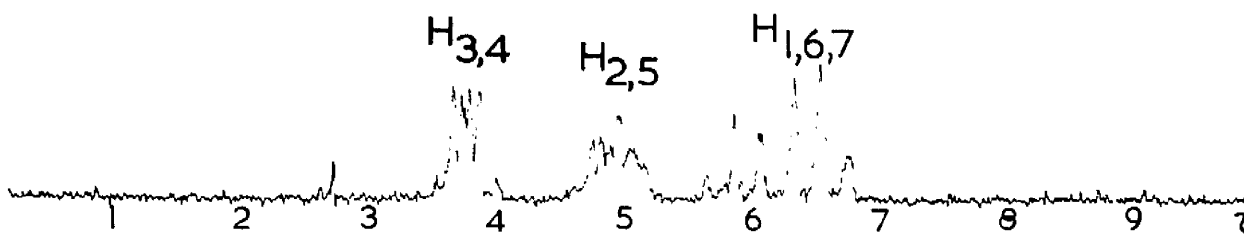
N.M.R. 4.

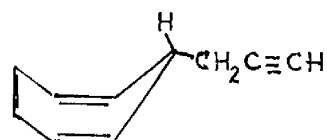


N.M.R. 5.

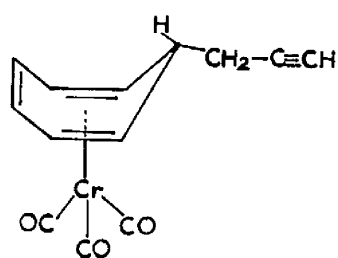
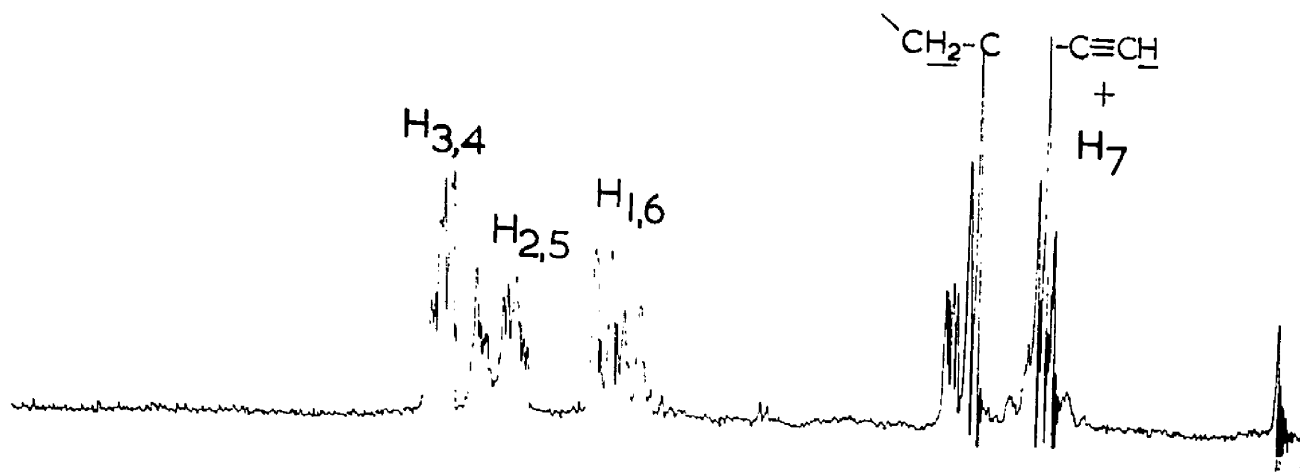


N.M.R. 6.

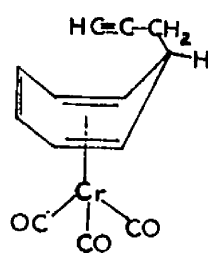
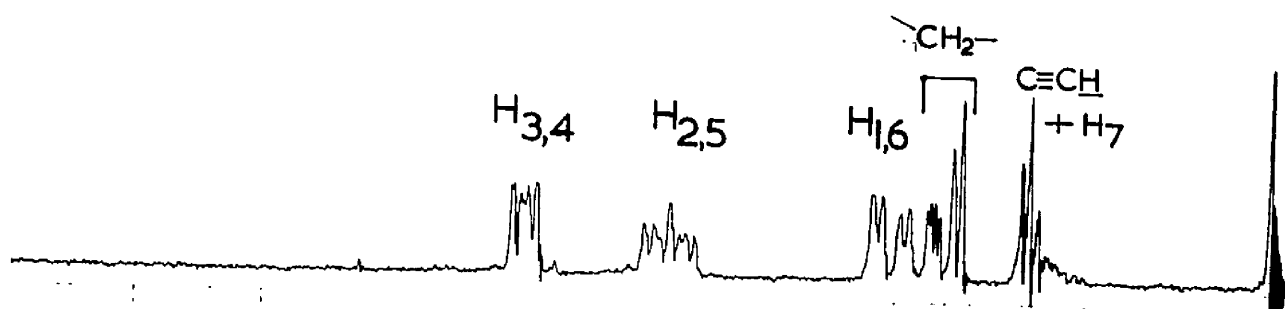




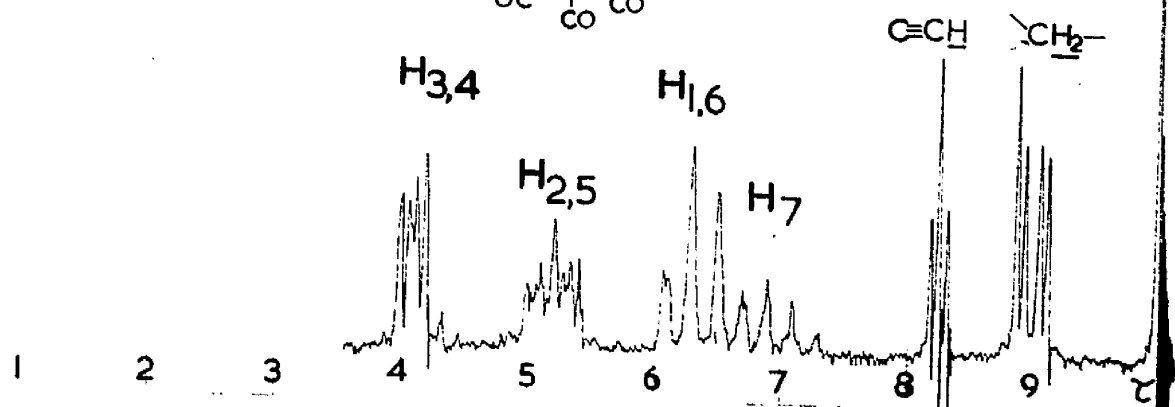
N.M.R. 7.

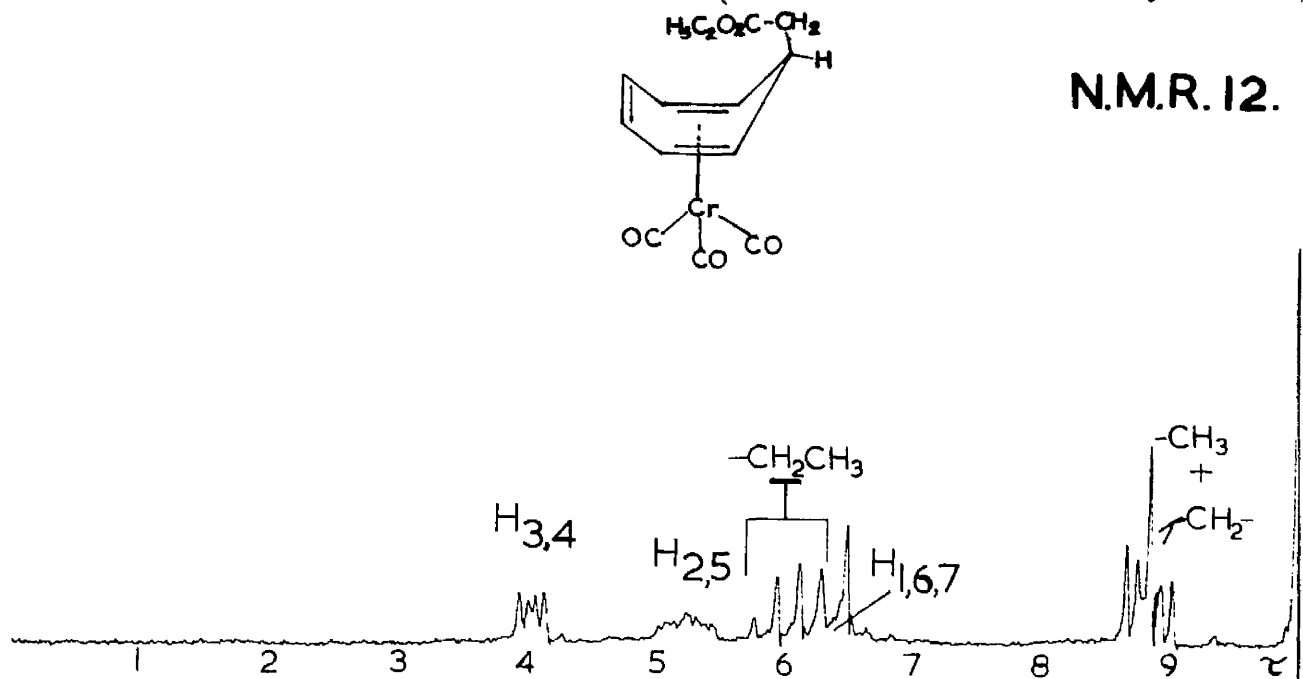
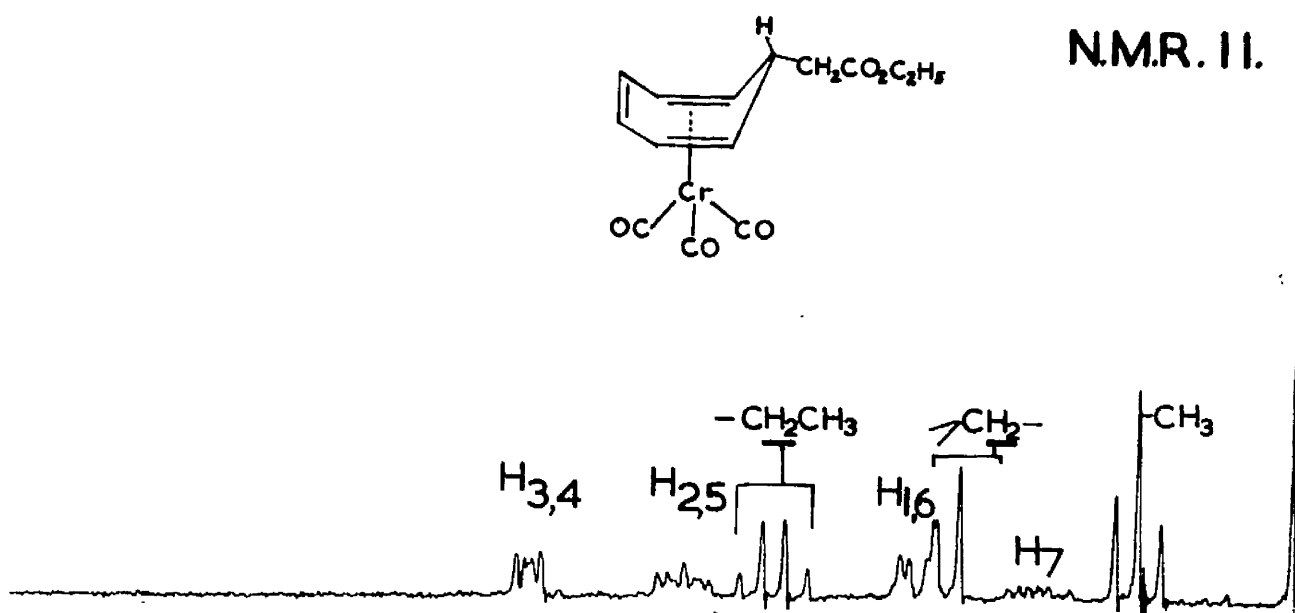
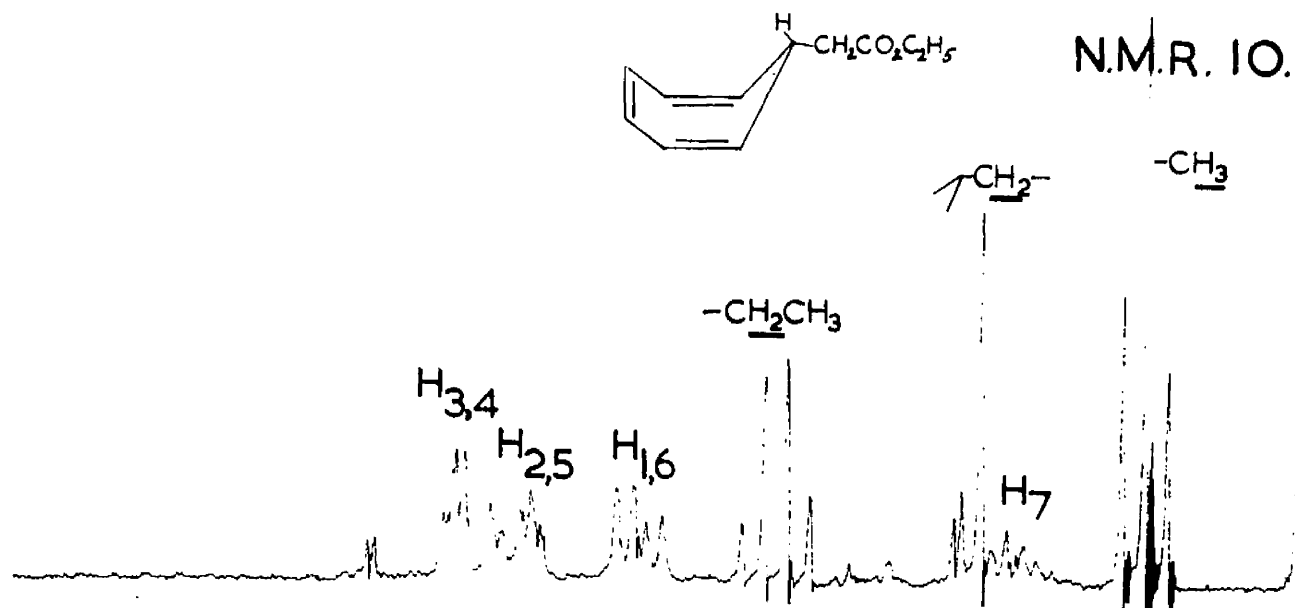


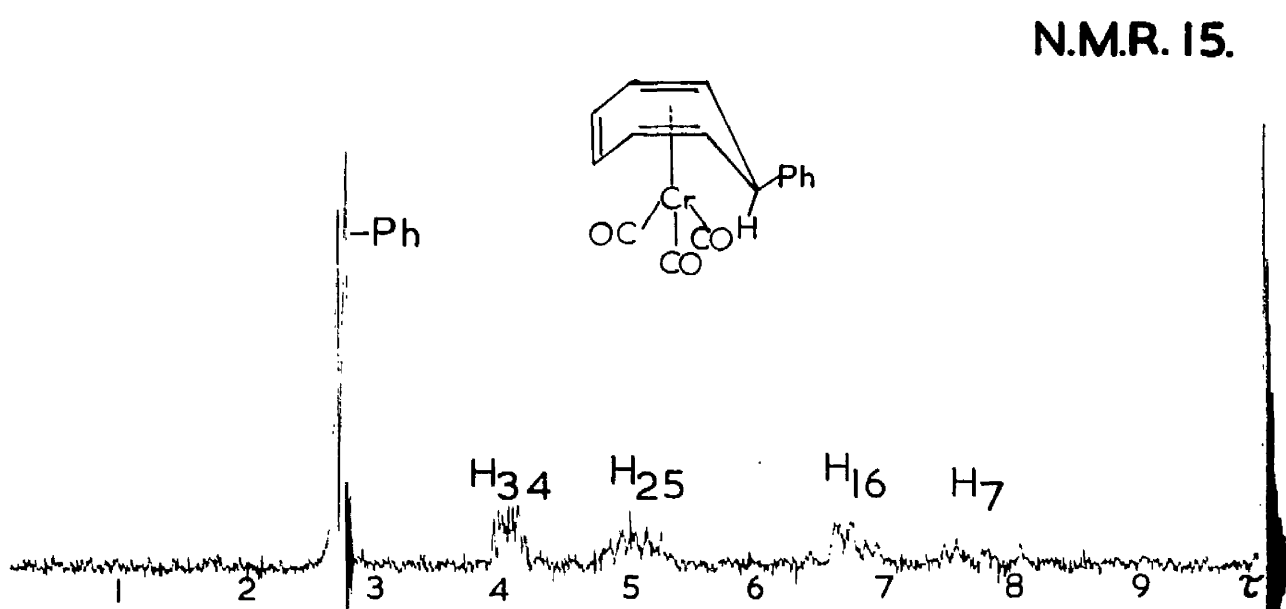
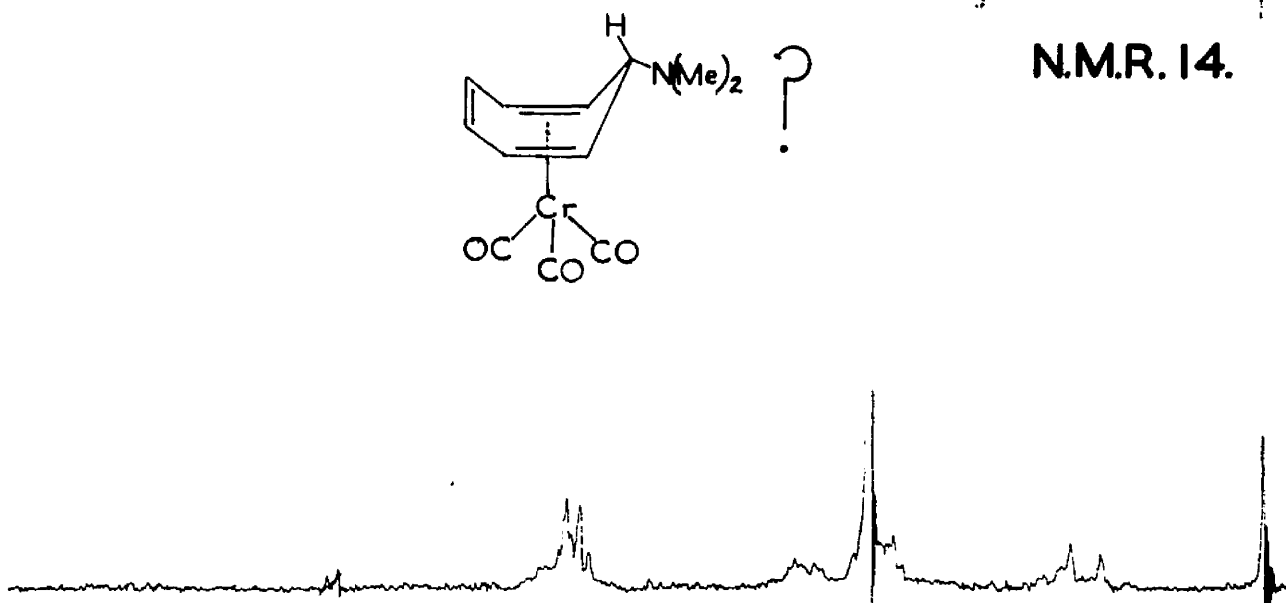
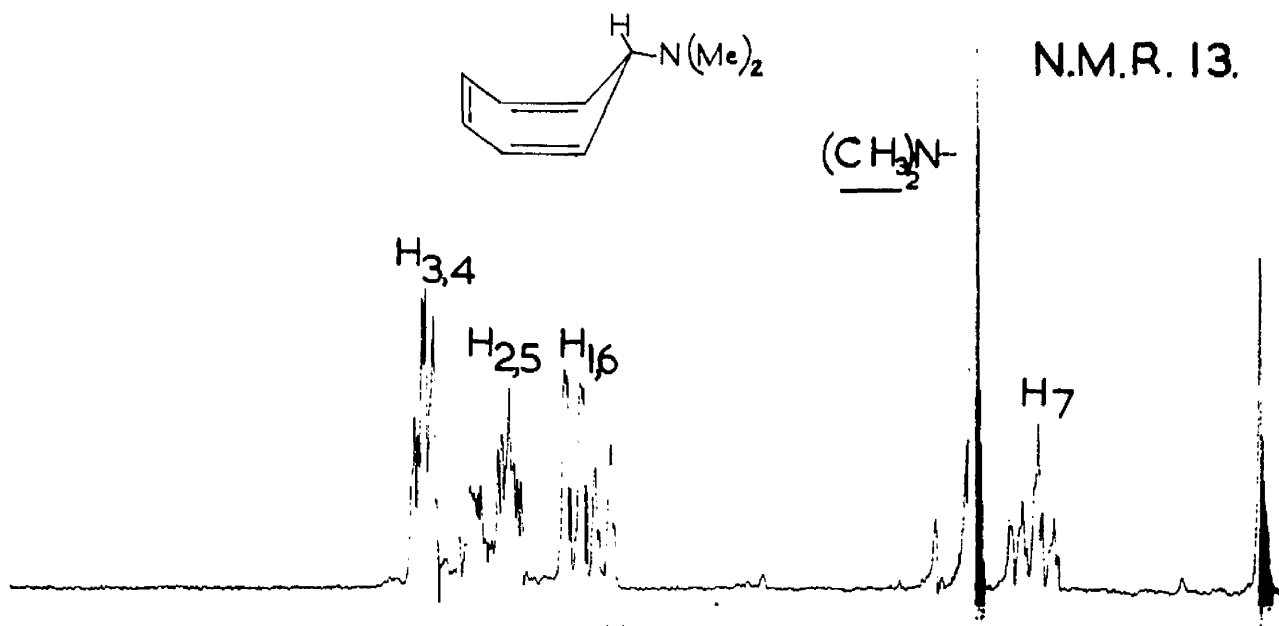
N.M.R. 8.

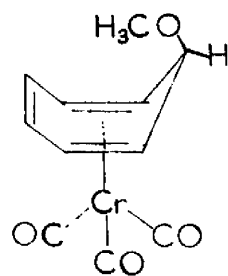


N.M.R. 9.

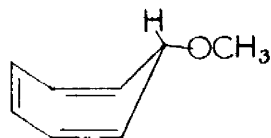
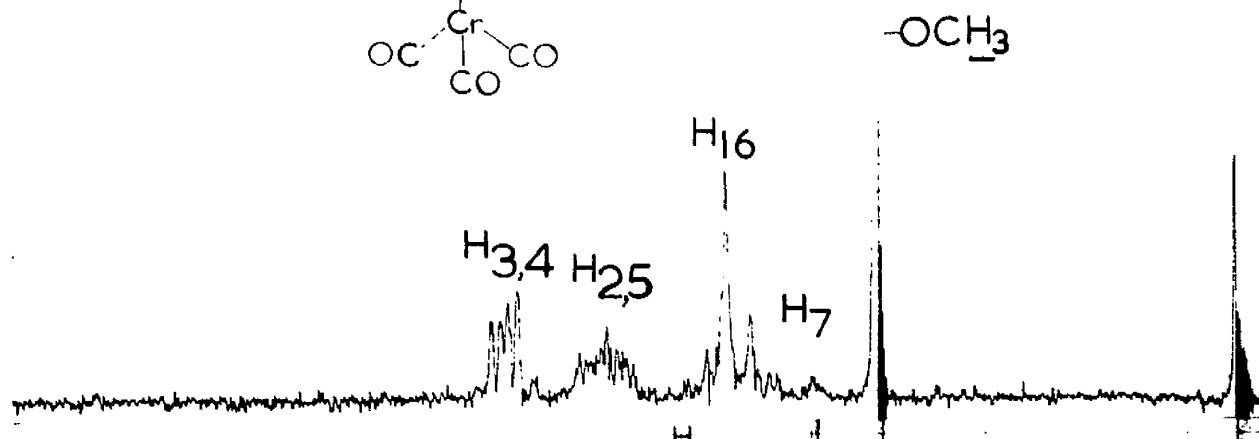




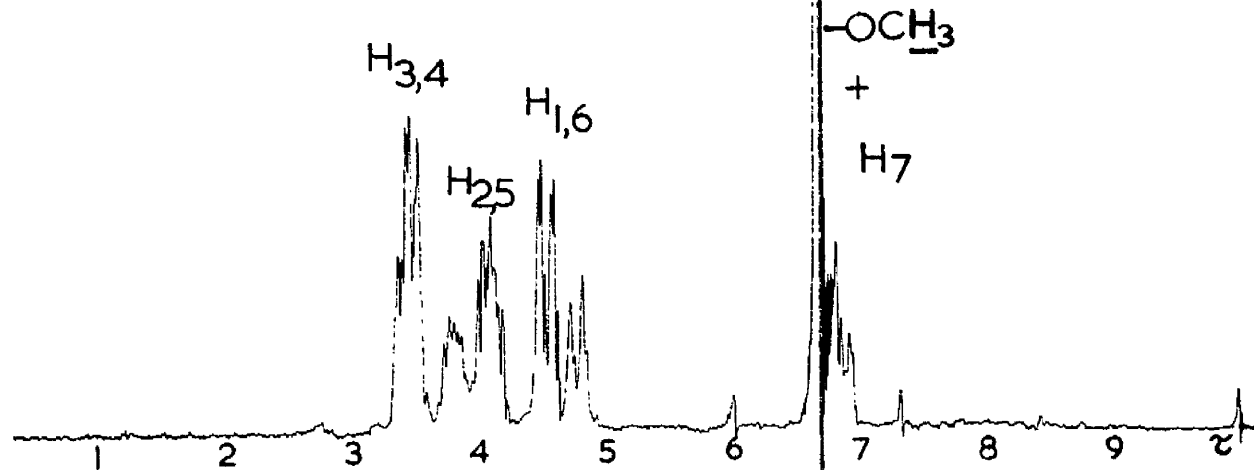




N.M.R. 16.



N.M.R. 17.



EXPERIMENTAL
=====

Experimental Procedures

All reactions were carried out under an atmosphere of nitrogen which had been purified by deoxygenation with Fieser's solution,¹³⁰ and desiccation with concentrated sulphuric acid.

Solvents employed were only specially dried when necessary; ligroin refers to the petroleum ether fraction of boiling range 60-80°C.

Strohmayer apparatus¹⁰⁸ - In all experiments involving diglyme as solvent the side arm was heated as follows:- Upper chamber 60°C; Lower chamber 80°C. In experiments involving petroleum ether, b.p. 80-100°C, or b.p. 100-120°C the side arm was not heated.

Chromatographies were carried out on Spence's 'Activated Alumina Ungraded', which was neutralised by storing in ethyl acetate for 72 hours, filtering, washing with methanol, then water, and drying at 160°C for 6 hours, 'X' hours deactivated alumina refers to alumina which had been exposed to the air for 'X' hours. All chromatography columns were protected from light.

All melting points were measured in sealed evacuated capillary tubes, and are uncorrected; molecular weights were determined cryoscopically in benzene solution.

Infrared spectra were recorded as 0.5-1.0% potassium chloride discs, or in carbon tetrachloride solution for solids, and as 0.5 mm. films between rock salt plates for liquids.

N.M.R. spectra were recorded in carbon disulphide or deuteriochloroform solutions on a Perkin Elmer 40 m/c Spectrometer, using tetramethylsilane as internal standard.

In reactions involving organometallic compounds yields are based on unrecovered starting material unless otherwise stated.

75 178

Tricarbonylcycloheptatrienochromium

Freshly sublimed hexacarbonylchromium (4.4 g., 0.02 mole) and redistilled cycloheptatriene (2.8 g., 0.03 mole) were heated for 18 hr. (bath temperature 165-170°C) in a refluxing mixture of pure diglyme (15 ml.) and dry, aromatic-free petroleum ether b.p. 100-120°C (45 ml.) in an apparatus¹⁰⁸ designed to automatically return subliming hexacarbonylchromium to the reaction zone. The mixture was cooled in an ice-bath and filtered into air-free water (150 ml.) to remove unchanged hexacarbonylchromium (0.22 g.). The filtrates were extracted with ether (2 x 50 ml.) and the ether extract washed with water. After filtration through Celite, the ethereal solution was dried (Na_2SO_4) for 30 min. out of contact with light. Evaporation under reduced pressure to ca. 15 ml. was followed by addition of petroleum ether b.p. 40-60°C (20 ml.) and chilling to -78°C. Deep red needles (4.19 g., 96.7% based on unrecovered hexacarbonylchromium), m.p. 129-130°C (lit.⁷⁶ m.p. 129-130°C) appeared and were filtered off.

Note. It is essential to use rigorously purified diglyme in this preparation, since traces of peroxides can lead to complete decomposition. The following method of purification was found most convenient:-

Diglyme was heated to reflux for 24 hr. over calcium hydride, distilled under an atmosphere of nitrogen and stored at 0°C over sodium wire.

100

Tricarbonyltripyridinechromium.

Hexacarbonylchromium (4.0 g., 0.016 mole), pyridine (30 ml., excess) and aromatic-free petroleum ether, b.p. 80-100°C (30 ml.) were heated to reflux for 40 hr., in the Ströhmeier apparatus¹⁶⁵ (bath temperature 155-160°). The mixture was cooled to 0°C and the red needles (6.4 g., 94%) which formed were separated by filtration, washed thoroughly with ligroin, dried and stored under nitrogen at 0°C.

Reaction of Tricarbonyltripyridinechromium with Cycloheptatriene.

Tricarbonyltripyridinechromium (1.12 g., 0.003 mole) and cycloheptatriene (0.368 g., 0.004 mole) were added to dry diethyl ether (100 ml.). Freshly distilled boron trifluoride diethyl etherate (1.42 g., 0.01 mole) was then added and the reaction mixture stirred for 1 hr. at 35-40°C., cooled to room temperature and filtered. The red filtrate was washed with water (3 x 100 ml.), dried (MgSO₄), evaporated to dryness under reduced pressure, and chromatographed on neutral alumina (60 g.). Elution with ligroin gave a small yellow band yielding a trace amount of a yellow gum, and a main red band which afforded red needles (from ligroin) of tricarbonylcycloheptatrienechromium (0.55 g., 60%), m.p. 129-130°C, identified on the basis of mixed m.p. and infrared spectral comparison with an authentic sample.

Reaction of Tricarbonyltripyridinechromium with 7-(ethoxycarbonyl methyl)cycloheptatriene. ¹⁰⁷

Tricarbonyltripyridinechromium (1.12 g., 0.003 mole) and 7-(ethoxycarbonylmethyl)cycloheptatriene ¹⁰⁷ (0.712 g., 0.004 mol) were added to dry diethyl ether (100 ml.). Freshly distilled boron trifluoride diethyl etherate (1.42 g., 0.01 mole) was added and the mixture stirred for 1 hr. at 38-40°C (bath temperature) and filtered. The ether filtrates were washed with water (3 x 100 ml.), dried (MgSO₄) and evaporated to dryness under reduced pressure. The red solid residue was chromatographed on neutral alumina (2 hr. deactivated) giving two distinct bands. The first, a yellow band, was eluted with ligroin to give yellow needles (0.134 g., 27%). Recrystallization from pentane afforded yellow needles of pentacarbonylpyridinechromium, m.p. 94-95°C. Soluble in common organic solvents.

Found: C, 44.1; H, 2.0; N, 5.2; O, 29.7

C₁₀H₇NCrO₅ requires C, 44.3; H, 1.9; N, 5.2; O, 29.7%

I.R. \checkmark max. (CCl₄) 1940, 2030 (HC-O) cm.⁻¹

The second, a red band, was eluted with benzene/ligroin (1:1) to give red crystals (from ligroin) of tricarbonyl-7-endo-(ethoxycarbonylmethyl)cycloheptatrienechromium (0.690 g., 69%), m.p. 78-79°C (lit. ⁷⁸ m.p. 49-50°C) identified on the

basis of mixed m.p. and infrared spectral comparison with an authentic sample.

Reaction of Tricarbonyltripyridinechromium with 7-[di(ethoxy-carbonyl)-methyl]cycloheptatriene.¹⁰⁷

This reaction was carried out under conditions identical to those of the above experiment. Pentacarbonylpyridinechromium was obtained in 53% yield, and tricarbonyl-7-endo-[di(ethoxy-carbonyl)methyl]cycloheptatrienechromium⁷⁸, m.p. 77-78°C in 63% yield, identified on the basis of mixed m.p. and infrared spectral comparison with authentic samples.

In both of these experiments the yields of monopyridine complex are calculated on the basis of $5Cr(CO)_5Py_2 \rightarrow 3Cr(CO)_5Py$.

Tricarbonyl-7-exopropargylcycloheptatrienechromium

To zinc turnings (1.30 g., 0.02 g. atom) under tetrahydrofuran (5 ml.) was added a crystal of iodine, followed by dropwise addition over 15 min., of propargyl bromide (2.7 g., 0.02 mole) together with tricarbonyl-7-exomethoxycycloheptatrienechromium¹¹⁰ (2.58 g., 0.01 mole) in tetrahydrofuran (20 ml.). A slightly exothermic reaction began after a few minutes and towards the end of the reaction a hot water bath was used to maintain gentle refluxing. The cooled solution was poured into water (200 ml.) and the mixture was extracted with ligroin (5 x 20 ml.). The extract was washed with cold

water, dried (Na_2SO_4) and concentrated in vacuo. Hexacarbonyl (bicycloheptatrienyl)bis-chromium (0.05 g.), m.p. 222°C dec. (lit.⁷⁶ m.p. $224-225^\circ\text{C}$) separated as red needles, and the concentrated filtrate was chromatographed on neutral alumina using ligroin as eluent. Tricarbonyl(bicycloheptatrienyl) chromium (0.004 g.), m.p. $146-147^\circ\text{C}$, (lit.⁷⁶ m.p. $148-149^\circ\text{C}$) was followed by tricarbonyl-7-oxopropargylcycloheptatriene-chromium, red platelets (from ligroin), m.p. $77-78^\circ\text{C}$ (1.2 g., 43%).

Found: C, 58.9; H, 3.9%; M.W. 273 (cryoscopic in benzene)

$\text{C}_{15}\text{H}_{10}\text{CrO}_3$ requires C, 58.65; H, 3.8%; M.W. 266

I.R. \checkmark (CCl₄) 3320 ($\equiv\text{C-H}$), 1992, 1932, 1908 (NC-O)cm.⁻¹
max.

The N.M.R. spectrum is reproduced on page 68, N.M.R. 9.

In a second experiment this product was obtained in 91% yield. The difference is attributed to the condition of the zinc used.

U.V. irradiation of this compound (1 g.) in hexane solution (650 ml.) caused rapid and complete decomposition.

Tricarbonyl-7-oxoallylcycloheptatrienechromium.

Tricarbonyl-7-oxopropargylcycloheptatrienechromium (0.53 g., 0.002 mole) was added to a suspension of pre-reduced Lindlar¹⁰⁸ catalyst (0.30 g.) in tetrahydrofuran (30 ml.) and the mixture stirred magnetically in an atmosphere of hydrogen.

Uptake of hydrogen began almost immediately and ceased after 15 min. when ca. 40 ml. had been absorbed. The mixture was filtered, the filtrate evaporated under reduced pressure, and the refiltered, the filtrate evaporated under reduced pressure, and the with petroleum ether, b.p. 40-60°C gave a single red band which afforded tricarbonyl-7-exoallylcycloheptatrienechromium (0.51 g., 95%) as red platelets (from pentane), m.p. 66-67°C.

Found: C, 58.3; H, 4.35;

$C_{13}H_{12}CrO_3$ requires C, 58.2; H, 4.5%.

I.R. ν_{max} (CCl_4) 1992, 1925, 1900 ($HC-O$) cm^{-1}

N.M.R. data are given in the appendix.

U.V. irradiation of this compound (1 g.) in hexane (650 ml.) for 1 hr. caused partial decomposition and the starting material was recovered in 68% yield.

7-Propargylcycloheptatriene.

To zinc turnings (13.0 g., 0.2 g. atom) under tetrahydrofuran (50 ml.) was added a crystal of iodine followed by dropwise addition over 30 min. of a mixture of propargyl bromide (24.0 g., 0.2 mole) and 7-methoxycycloheptatriene¹⁰⁰ (12.2 g., 0.1 mole) in tetrahydrofuran (100 ml.). A strongly exothermic reaction began almost immediately and towards the end of the reaction a hot water bath was used to maintain gentle refluxing. The cooled solution was poured into water (2 litre) and the

mixture extracted with ether (5 x 150 ml.). The ether extract was washed with water, dried (MgSO_4), and evaporated under reduced pressure to give a pale yellow oil (12.1 g.).

Distillation in vacuo afforded 7-propargylcycloheptatriene (8.36 g., 64%), a colourless mobile liquid, b.p. 35-36°C (0.6 mm.)

Found: C, 92.2; H, 7.8;

$\text{C}_{10}\text{H}_{10}$ requires: C, 92.3; H, 7.7%

I.R. ν_{max} . 3340 cm.^{-2} ($\equiv\text{C-H}$). The N.M.R. spectrum is reproduced on page 68, N.M.R. 7.

An unidentified colourless viscous liquid (3.14 g.) distilled at 134-135°C (0.6 mm.)

Tricarbonyl-7-endopropargylcycloheptatrienechromium.

(a) By Reaction of Tricarbonyltripyridinechromium with 7-Propargylcycloheptatriene.

Tricarbonyltripyridinechromium (2.24 g., 0.006 mole) and 7-propargylcycloheptatriene (1.04 g., 0.008 mole) were added to dry diethyl ether (200 ml.), followed by boron trifluoride diethyl etherate (2.84 g., 0.02 mole), and the mixture stirred for 1 hr. at 38-40°C (bath temperature). After filtration the deep-red ether solution was washed with water (3 x 200 ml.), dried (MgSO_4), evaporated to dryness under reduced pressure, and the red semi-solid residue chromatographed on neutral alumina. Elution with ligroin afforded

tricarbonyl-7-endo-propargylcycloheptatrienechromium (0.85 g., 52%) red platelets (from ligroin), m.p. 78-79°C

Found: C, 58.75; H, 3.7; O, 18.1;

$C_{13}H_{10}CrO_3$ requires C, 58.65; H, 3.6; O, 18.0%.

I.R. ν_{max} . (CCl₄) 3320 ($\equiv C-H$) 1995, 1935, 1905 (MC-O) ca. ⁻¹.

The N.M.R. spectrum is reproduced on page 68, N.M.R. 8

Benzene eluted a small red band which afforded an intractable red gum (0.12 g.).

(b) By Reaction of 7-Propargylcycloheptatriene with Hexacarbonylchromium. -

Hexacarbonylchromium (2.2 g., 0.01 mole) and 7-propargylcycloheptatriene (1.95 g., 0.015 mole) were heated in a refluxing mixture of diglyme (20 ml.) and aromatic-free petroleum ether b.p. 80-100°C (40 ml.) in the Strohmeier apparatus²⁰⁶ (bath temperature 155-160°C) for 18 hr. A small amount of a brown solid was precipitated during the reaction. The reaction mixture was cooled to 0°C, and filtered into air-free water to remove unchanged hexacarbonylchromium (0.26 g.). The filtrates were extracted with ether (3 x 50 ml.), dried (MgSO₄), evaporated under reduced pressure, and the residual red gum chromatographed on neutral alumina. Ligroin eluted a red band which afforded tricarbonyl-7-endo-propargylcycloheptatrienechromium (0.90 g., 38% based on unrecovered hexacarbonylchromium) red platelets, (from ligroin), m.p. 78-79°C identified on the basis of mixed

m.p. and infrared spectral comparison with an authentic sample. Benzene eluted a second red band from which an intractable red gum (0.16 g.) was obtained.

Tricarbonyl-7-endoallylcycloheptatrienechromium.

Hydrogenation of tricarbonyl-7-endopropargylcycloheptatriene-chromium over Lindlar¹⁰⁸ catalyst in tetrahydrofuran, afforded an almost quantitative yield of tricarbonyl-7-endoallylcycloheptatrienechromium, red needles, (from pentane), m.p. 62-63°C.

Found: C, 50.5; H, 4.6;

$C_{13}H_{12}CrO_3$ requires: C, 50.2; H, 4.5%

I.R. ν_{max} . (CCl₄) 1995, 1925, 1900 (MC-O) cm.⁻¹

[For experimental details see tricarbonyl-7-exoallylcycloheptatrienechromium].

U.V. irradiation in hexane, or prolonged heating in refluxing toluene, of both the endopropargyl- and endoallyl- complexes resulted in partial decomposition with recovery of quantities of starting materials only.

Reaction of Tricarbonylcycloheptatrienylchromium Fluoroborate⁷⁸ with Potassium Cyanide.

'Analar' potassium cyanide (0.26 g., 0.004 mole) in water (10 ml.) was added to a solution of tricarbonylcycloheptatrienylchromium fluoroborate⁷⁸ (0.94 g., 0.003 mole) in water (150 ml.) and the mixture stirred for 30 min. at room temperature. The aqueous mixture was extracted with ether (2 x 100 ml.) and the

other extract washed with water, dried (Na_2SO_4), evaporated to dryness and chromatographed on neutral alumina (2 hr. deactivate). Elution with ligroin-benzene (1:1) gave two red bands. The first band afforded orange crystals (from ligroin) of tricarbonyl (bicycloheptatrienyl)chromium (0.023 g., 5%), m.p. 147-148°C, identified by mixed m.p. and infrared spectral comparison with an authentic sample. The second band afforded deep red needles (from ether ligroin) of tricarbonyl-7-cyanoheptatriene-chromium (0.695 g., 92%) m.p. 118-119°C identified by infrared spectral comparison with an authentic sample (lit.¹¹⁰ m.p. 118-119°C).

Reaction of Tricarbonyltripyridinechromium with 7-Cyanoheptatriene. -

To tricarbonyltripyridinechromium (2.24 g., 0.006 mole) and 7-cyanoheptatriene¹¹¹ (0.95 g., 0.006 mole) in dry diethyl ether (200 ml.) was added boron trifluoride diethyl etherate (2.85 g., 0.02 mole) and the mixture stirred for 1 hr. at 38-40°C (bath temperature). After filtration, the deep-red ether solution was washed with water (3 x 100 ml.), dried (MgSO_4), and evaporated to dryness under reduced pressure, leaving a red oily residue which was chromatographed on neutral alumina. Ligroin eluted a yellow band which afforded yellow needles (from pentane) of pentacarbonyl-7-cyanoheptatrienechromium (0.22 g., 20%), m.p. 96-97°C. soluble in all

common organic solvents.

Found: C, 50.6; H, 2.5; N, 4.6; O, 26.0

$C_{13}H_7N_2CrO_5$ requires C, 50.5; H, 2.3; N, 4.5; O, 25.9%

I.R. ν max. (CCl_4) 2082, 1962, (shoulders at 1995 and 1930)
($NC=O$) 2242 ($C\equiv N$) cm^{-1}

N.M.R. data are given in the appendix.

Ligroin-benzene (2:1) eluted a broad red band which afforded a red solid (1.06 g., 70%) m.p. 105-110°C. Further chromatograph of this material on a 7 ft. column, using ligroin/benzene (4:1) as eluent gave a single broad red band which was collected in five separate fractions.

(i) 0.12 g., m.p. 133-134°C.

(ii) 0.18 g., m.p. 105-110°C.

(iii-v) 0.68 g., m.p. 118-119°C.

Fraction (i) afforded red platelets (from ether-ligroin), m.p. 134-135°C of tricarbonyl-7-endocyanocycloheptatrienochromium, which is unstable to air at room temperature.

Found: C, 52.0; H, 3.05; N, 5.6

$C_{11}H_7N_2CrO_5$ requires C, 52.2; H, 2.9; N, 5.5%

I.R. ν max. (CCl_4) 2000, 1942 1906 ($NC=O$) 2250 ($-C\equiv N$) cm^{-1}

The N.M.R. spectrum is reproduced on page 67 N.M.R. 5.

Fractions (iii-v) afforded red needles (from ether-ligroin), m.p. 118-119°C of tricarbonyl-7-exocyanocycloheptatrienochromium identified on the basis of mixed m.p. and infrared

spectral comparison with an authentic sample. Its N.M.R. spectrum is reproduced on p.57 N.M.R. 6. Further chromatography of fraction (ii) afforded 0.05 g., of the endo-isomer and 0.11 g. of the exo-isomer. This reaction therefore afforded the isomeric complexes in the ratio endo:exo (2:9).

Reaction of Tricarbonylcycloheptatrienylchromium Fluoroborate^{7a} with Aqueous Dimethylamine.

Aqueous dimethylamine 25% w v (5 ml., excess) was added to a stirred solution of tricarbonylcycloheptatrienylchromium fluoroborate^{7a} (0.63 g., 0.002 mole) in water (100 ml.) and a flocculent orange precipitate immediately appeared. The mixture was stirred for a further 15 min. at room temperature and extracted with ether (3 x 50 ml.). The ether extract was dried (MgSO₄) and evaporated to dryness under reduced pressure to give an orange solid (0.51 g., 94%). Recrystallisation from pentane afforded orange needles of tricarbonyl-7-exo-dimethylamino-cycloheptatrienechromium, m.p.85-86°C, soluble in common organic solvents, and in dilute hydrochloric acid. This compound was found to be insufficiently stable to permit reproducible analyses or to give an N.M.R. spectrum. I.R. \checkmark _{max.} (KCl) 1972, 1890, 1855, shoulder at 1920 (MC-O) cm.⁻¹

Reaction of 7-Dimethylaminocycloheptatriene¹¹¹ with Hexacarbonylchromium.

7-Dimethylaminocycloheptatriene¹¹¹ (2.70 g., 0.02 mole) and hexacarbonylchromium (3.3 g., 0.015 mole) were added to a mixture of diglyme (20 ml.) and aromatic-free petroleum ether, b.p. 80-100°C (50 ml.). The mixture was heated to reflux for 18 hr. in the Stronmeier apparatus¹⁰⁵ (bath temperature 155-160°C). The resultant deep-red solution was cooled to 0°C and filtered into air-free water (no unchanged hexacarbonylchromium was obtained). The filtrates were extracted with ether (4 x 50 ml) and the ether extract washed with water, dried (MgSO₄), and evaporated to dryness under reduced pressure. The red solid residue was dissolved in benzene-ligroin and chromatographed on neutral alumina. Elution with ligroin-benzene (2:1) afforded tricarbonyl-7-endo-dimethylaminocycloheptatrienechromium (3.7 g., 91%) as red platelets, m.p. 165-166° (from ether-ligroin).

Found: C, 53.3; H, 5.1; N, 5.1;

$C_{12}H_{13}NCrO_3$ requires C, 53.2; H, 4.95; N, 5.2%

I.R. ν_{max} (KCl) 1940, 1830, shoulder at 1855 (MC-0)

The N.M.R. spectrum is reproduced on page 70, N.M.R. 14.

A second small red band which stuck to the column was not investigated further.

Reaction of 7-Dimethylaminocycloheptatriene,¹¹¹ with tricarbonyl-
cycloheptatrienechromium.

7-Dimethylaminocycloheptatriene,¹¹¹ (1.35 g., 0.01 mole) and tricarbonylcycloheptatrienechromium (0.912 g., 0.004 mole) were dissolved in aromatic-free petroleum ether, b.p. 100-120° C. (40 ml.), and heated to reflux for 18 hr. in the Strohmeier apparatus¹⁰⁵ (bath temp. 140-145°C). A trace amount of a black decomposition product was deposited. The solution was cooled, filtered through Kieselguhr, and evaporated to dryness under reduced pressure. The red solid residue was dissolved in benzene-ligroin and chromatographed on neutral alumina. Elution with ligroin gave a small yellow band which afforded a trace amount of a pale yellow oil, closely followed by a red band which afforded tricarbonylcycloheptatrienechromium (0.2 g., 21%), m.p. 129-130°C. Elution with ligroin-benzene (2:1) afforded red platelets (from ether-ligroin), m.p. 165-166°C. of tricarbonyl-7-endodimethylaminocycloheptatrienechromium (0.77 g., 71%) which was identified by mixed m.p. and infrared spectral comparison with an authentic sample.

Reductive Degradation of Tricarbonyl-7-endodimethylaminocyclo-
heptatrienechromium with sodium borohydride.

To a stirred suspension of tricarbonyl-7-endodimethylamino-
cycloheptatrienechromium (2.71 g., 0.01 mole) in methanol (40 ml.)

basified with sodium hydroxide, sodium borohydride (excess) was added, in portions, over 1 hr. After a further 1 hr. the reaction mixture was thrown into water and extracted with ether (3 x 50 ml.). The faintly-red ether extract was washed with water, dried (MgSO_4), and evaporated under reduced pressure to give a pale yellow oil. The oily residue was acidified with dilute hydrochloric acid in the presence of chloroform and the fractions separated. The chloroform fraction was washed, dried (MgSO_4) and evaporated to dryness, leaving no residue. The aqueous acidic fraction was made basic with sodium hydroxide and extracted with ether. The ether extract was washed, dried (MgSO_4), and evaporated under reduced pressure to give a pale yellow oil (0.15 g.). The infrared and N.M.R. spectra of this oil showed methyl absorption, but showed no evidence of the cycloheptatriene moiety.

Addition of this oil to a saturated ethanolic solution of picric acid afforded a yellow picrate, m.p. 151-152°C (from ethanol). The picrate of 7-dimethylaminocycloheptatriene has m.p. 159-160°. These picrates have a mixed m.p. 124-127°C.

Tricarbonyl-7-exo[di(ethoxycarbonyl)methyl]cycloheptatriene-chromium.

(a) To zinc turnings (0.39 g., 0.006 g. atom) under tetrahydrofuran (5 ml.) was added a crystal of iodine and 5 ml. of a

solution of diethylbromo-malonate (1.44 g., 0.006 mole) together with tricarbonyl-7-exomethoxycycloheptatrienechromium¹¹⁰ (0.77 g., 0.003 mole) in tetrahydrofuran (20 ml.). A slightly exothermic reaction began almost immediately and the remainder of the solution was added dropwise over a 10 min. period. The mixture was stirred for a further 1 hr. at room temperature, poured into cold water (150 ml.) and extracted with ligroin (4 x 20 ml.). The extract was washed with cold water (2 x 100 ml.), dried (Na_2SO_4), concentrated in vacuo and chromatographed on neutral alumina (60 g., deactivated 2 hr.). Elution with ligroin afforded tricarbonyl(bicycloheptatrienyl)chromium (0.012 g.), m.p. 146-147°C. Elution with ligroin-benzene (1:1) afforded tricarbonyl-7-exe[di(ethoxycarbonyl)methyl]cycloheptatrienechromium (0.920 g., 81%) as red needles (from ligroin), m.p. 121-122°C (lit.⁷⁰ m.p. 122-123°C) identified by mixed m.p. and infrared spectral comparison with an authentic sample.

(b) To a solution of sodium ethoxide (from sodium 0.012 g., 0.0005 g. atom) in absolute ethanol (2 ml.) was added a solution of diethyl malonate (0.480 g., 0.003 mole) in tetrahydrofuran (10 ml.) and the solution was stirred for 10 min. A solution of tricarbonyl-7-exomethoxycycloheptatrienechromium¹¹⁰ (0.516 g., 0.002 mole) in tetrahydrofuran (10 ml.) was added and stirring was continued for 3 hr. at room temperature. The solvents were removed in vacuo and the red residue was extracted with ligroin

(5 x 20 ml.). Evaporation of this extract to dryness yielded a red solid which was chromatographed on neutral alumina (60 g.) to give one red band. Elution with ligroin-benzene (1:1) afforded tricarbonyl-7-exo[di(ethoxycarbonyl)methyl]cycloheptatriene chromium (0.691 g., 92%), m.p. 121-122°C.

Alkaline Hydrolysis of Tricarbonyl 7-(Ethoxycarbonylmethyl)- and 7-[Di(ethoxycarbonyl)methyl]-cycloheptatrienechromium Complexes

Tricarbonyl-7-endo-(ethoxycarbonylmethyl)cycloheptatriene-chromium^{7B} (0.31 g., 0.001 mole) dissolved in methanol (40 ml.) was added to aqueous sodium hydroxide (0.08 g., 0.002 mole in 10 ml.) and the mixture stirred for 2 hr. at room temperature. After evaporation to dryness in vacuo the oily residue was extracted with benzene to remove unchanged ester, and the sodium salt redissolved in water. Acidification in the presence of chloroform, separation, drying (CaCl₂), and evaporation of the chloroform layer left tricarbonyl-7-endo(carboxymethyl)cycloheptatrienechromium (0.24 g., 84%) as a deep red solid, m.p. 165-167°C. Recrystallisation from ether-ligroin afforded plates, m.p. 170-171°C.

Found: C, 50.3; H, 3.7

C₁₀H₁₂CrO₆ requires: C, 50.35; H, 3.5%

I.R. ν max. (KCl) 1990, 1925, 1885, (MC-O) and 1700
(-C(OH)=O) cm.⁻¹.

Similar alkaline hydrolysis of tricarbonyl-7-exo-(ethoxycarbonyl-methyl)cycloheptatrienechromium⁷⁸ yielded tricarbonyl-7-exo-(carboxymethyl)cycloheptatrienechromium in 87% yield.

Crystallisation from ether-ligroin afforded red plates, m.p. 159-160°C (lit., m.p. 151-152°C).

Alkaline hydrolysis under the above conditions of tricarbonyl 7-[di(ethoxycarbonyl)methyl]cycloheptatrienechromium⁷⁸ (both endo- and exo- isomers) afforded products which could not be extracted from the aqueous acidic layer.

Tricarbonyl-7-exo-p-tolylthiocycloheptatrienechromium.

Toluene-p-thiol (0.25 g., 0.002 mole) was added to a solution of sodium hydride (0.05 g., 0.002 mole) in tetrahydrofuran. The resultant suspension was added to a stirred solution of tricarbonyl-7-exomethoxycycloheptatrienechromium¹¹⁰ (0.52 g., 0.002 mole) in tetrahydrofuran (30 ml.) and stirring continued for 1 hr. at room temperature. The mixture was then poured into water (200 ml.) and extracted with ether (5 x 20 ml.). The ether extract was washed with water, dried (Na_2SO_4) and evaporated to give a red oil. Crystallisation from ligroin yielded red needles of tricarbonyl-7-exo-p-tolylthio-cycloheptatrienechromium (0.38 g., 54%), m.p. 78°C. (dec.).

Found: C, 58.2; H, 4.3; Mol. Wt. 363 (cryoscopic in C_6H_6)

$\text{C}_{17}\text{H}_{14}\text{CrO}_3\text{S}$ requires C, 58.2; H, 4.0% Mol. Wt. 350.

I.R ν_{max} . (CCl_4) 2000, 1930, 1905 (NC-O) cm^{-1}

The N.M.R. spectrum showed peaks at τ 2.97 and τ 7.69 of relative intensity (4:3) respectively.

Reactions of Tricarbonyl-7-exomethoxycycloheptatrienechromium¹¹⁰
with the Sodium Salt of N-Methylaniline or Potassium Cyanide.

Reaction of tricarbonyl-7-exomethoxycycloheptatrienechromium¹¹⁰ with the sodium salt of N-methylaniline or potassium cyanide under the above conditions resulted in the formation of hexacarbonyl(bicycloheptatrienyl)bis-chromium and tricarbonyl(bicycloheptatrienyl)chromium. None of the desired amino- or cyano- derivatives respectively, was isolated.

Reaction of Tricarbonyl-7-exodimethylaminocycloheptatrienechromium
with the Sodium Salt of Toluene-p-thiol.

Toluene-p-thiol (0.5 g.; 0.004 mole) was added to a solution of sodium hydride (0.10 g.; 0.004 mole) in tetrahydrofuran (10 ml.). The resultant suspension was added to a stirred solution of tricarbonyl-7-exodimethylaminocycloheptatrienechromium (1.1 g.; 0.004 mole) in tetrahydrofuran (50 ml.) and stirring continued for 30 min. at room temperature. Partial decomposition occurred. The mixture was filtered into water, extracted with ether, and the ether extract washed, dried ($MgSO_4$), and evaporated under reduced pressure to give a red oil, which was chromatographed on neutral alumina (6 hr. deactivated) Elution with ligroin-benzene (2:1) gave a single red band which

afforded tricarbonyl-7-exo-p-tolylthiocycloheptatrienechromium (0.51 g., 36%), m.p. 78°C (dec.), identified on the basis of mixed m.p. and infrared spectral comparison with an authentic sample. A brown band which stuck to the column was not investigated further.

Reaction of Tricarbonylcycloheptatrienylchromium Fluoroborate⁷⁸
with Sodium Sulphide.

To cold water (100 ml.) was added excess of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (1.44 g.; 0.006 mole) and stirred until dissolved. Tricarbonylcycloheptatrienylchromium fluoroborate⁷⁸ (1.68 g., 0.006 mole) in water (100 ml.) was added with stirring, and a flocculent red precipitate was immediately formed. Stirring was continued for 30 min. at room temperature and the suspension was filtered and washed with cold water (2 x 100 ml.). The red residue was extracted with chloroform, the extract dried (MgSO_4), and the solvent removed under reduced pressure. Red crystals of bis-exo-(tricarbonylcycloheptatrienylchromium) sulphide (1.42 g., 98%) separated on removal of chloroform. Recrystallisation from chloroform-ligroin yielded red needles, m.p. 98-99°C.

Found: C, 49.2; H, 2.9; S, 6.6.

$\text{C}_{20}\text{H}_{14}\text{Cr}_2\text{O}_3\text{S}$ requires: C, 49.4; H, 2.9; S, 6.6%

I.R. ν max. (KCl) 2000, 1928, 1900 (MC-O) cm.⁻¹

N.M.R. data are given in the appendix.

Reaction of Bis-exo-(tricarbonylcycloheptatrienylchromium)
sulphide with Triphenylmethyl Fluoroborate¹¹³

Triphenylmethyl fluoroborate¹¹² (0.64 g., 0.002 mole) in methylene chloride (20 ml.) was added dropwise to a stirred solution of bis-exo-(tricarbonylcycloheptatrienylchromium) sulphide (0.97 g., 0.002 mole) in methylene chloride (20 ml.) and the mixture stirred for 30 min. at room temperature. The flocculent orange precipitate which formed was filtered, washed with methylene chloride (2 x 10 ml.) and dried to give tricarbonylcycloheptatrienylchromium fluoroborate⁷⁶ (0.61 g.; 97%). Recrystallisation from acetone afforded deep red needles; m.p. > 300°C. Evaporation of the methylene chloride filtrates under reduced pressure gave a red semi-solid which was chromatographed on neutral alumina (2 hr. deactivated). Elution with benzene-ligroin (2:1) gave a single red band which afforded a mixture of a red and a white solid (0.91 g.) which could not be separated by further chromatography. By fractional crystallisation small amounts of bis-exo-(tricarbonylcycloheptatrienylchromium)sulphide and triphenylmethanol were obtained. These were identified by m.p., and infrared spectra comparison with authentic samples.

Reaction of Tricarbonyltripyridinechromium with 7-Phenylcycloheptatriene.

To tricarbonyltripyridinechromium (2.24 g., 0.006 mole) and 7-phenylcycloheptatriene¹⁰⁹ (1.34 g., 0.008 mole) in dry ether (200 ml.) boron trifluoride diethyl etherate (2.84 g., 0.2 mole) was added and the mixture stirred for 1 hr. at 38-40°C (bath temperature). After filtration, the red ether solution was washed with water (4 x 100 ml.), dried (MgSO₄), evaporated to dryness under reduced pressure, and the red solid residue chromatographed on neutral alumina. Ligroin eluted a single red band which afforded a red crystalline solid (1.21 g., 68%), m.p. 103-107°C. Further chromatography of this material on a 7 ft. column using petroleum ether, b.p. 40-60°C as eluent gave a single broad red band which was collected in five separate fractions.

(1) 0.14 g., m.p. 113-114°C

(2) 0.18 g., m.p. 113-114°C

(3) 0.22 g., m.p. 104-107°C

(4) 0.28 g., m.p. 131-132°C

(5) 0.31 g., m.p. 133-134°C

Fractions (1 and 2) afforded tricarbonyl-7-endophenylcycloheptatrienechromium as red needles (from ligroin), m.p. 114-115°C

Found: C, 62.9; H, 4.1:

C₁₆H₁₃CrO₃ requires C, 63.15; H, 4.0%.

I.R. \checkmark max. (CCl₄) 1995, 1928, 1906. (HC-O) cm.⁻¹

The N.M.R. spectrum is reproduced on page 66 N.M.R.2
 Fractions (4 and 5) afforded tricarbonyl-7-exophenylcyclohepta-
 trienochromium⁷⁸ as red needles (from ligroin), m.p. 134-135°C.,
 identified on the basis of mixed m.p. and infrared spectral
 comparison with an authentic sample. Its N.M.R. spectrum is
 reproduced on page 66 N.M.R.3. Further chromatography of
 fraction (3) afforded 0.08 g., of the endo-isomer and 0.11 g.,
 of the exo-isomer. This reaction therefore afforded the
 isomeric complexes in the ratio endo:exo (1 : 1).

Reaction of 7-Phenylcycloheptatriene¹⁰⁹ with Tricarbonylcyclo-
heptatrienochromium.

Tricarbonylcycloheptatrienochromium (1.14 g., 0.005 mole)
 and 7-phenylcycloheptatriene¹⁰⁹ (1.18 g., 0.007 mole) were
 added to aromatic-free petroleum ether, b.p. 80-100°C (60 ml.)
 and the mixture heated to reflux for 18 hr. in the Ströhmeier
 apparatus¹⁰⁸ (bath temperature 140-145°C). Slight decomposition
 occurred during the reaction. After cooling, the deep-red
 solution was filtered, evaporated to dryness under reduced
 pressure and chromatographed on neutral alumina. Elution with
 ligroin afforded two red bands closely followed by a brown band.
 The first red band afforded unchanged tricarbonylcycloheptatriene-
 chromium (0.54 g., 47%), m.p. 129-130°C. The second red band

afforded tricarbonyl-7-endophenylcycloheptatrienechromium (0.015 g.; 1%) red needles (from ligroin) m.p. 114-115°C identified by mixed m.p. and infrared spectral comparison with an authentic sample. The brown band afforded an isomeric tricarbonyl-7-phenylcycloheptatrienechromium (0.130 g.; 8.5%) dark red crystals (from ligroin), m.p. 73-74°C.

Found: C, 63.4; H, 4.0; O, 15.6%; M.W. 344;

$C_{10}H_{12}CrO_3$ requires C, 63.15; H, 4.0; O, 15.8% M.W. 304.

I.R. ν_{max} . (KCl) 1982, 1888, 1855 (HC-O) cm^{-1}

The N.M.R. spectrum is reproduced on page 70 N.M.R.15.

Reaction of 7-Phenylcycloheptatriene¹⁰⁹ with Hexacarbonylchromium

Hexacarbonylchromium (2.2 g., 0.01 mole) and 7-phenylcycloheptatriene¹⁰⁹ (2.5 g., 0.015 mole) were heated in a refluxing mixture of diglyme (20 ml.) and aromatic-free petroleum ether, b.p. 80-100°C (40 ml.) in the Ströhmeier apparatus¹⁰⁸ (bath temperature 155-160°C) for 18 hr. A small amount of dark brown solid was precipitated. The reaction mixture was cooled to 0°C and filtered into air-free water (no hexacarbonylchromium was recovered). The filtrate was extracted with ether (3 x 50 ml.) washed, dried ($MgSO_4$) and evaporated under reduced pressure, and the residual deep-red gum chromatographed on neutral alumina. Ligroin eluted a broad brown band preceded by a red front which

afforded tricarbonyl-7-endophenylcycloheptatrienechromium (0.12 g.; 4%) red needles, m.p. 114-115°C identified on the basis of mixed m.p. and infrared spectral comparison with an authentic sample. The main brown band afforded a red solid mixture from which dark-red crystals (0.005 g.; 1%) of tricarbonyl-7-phenylcycloheptatrienechromium (see previous experiment), m.p. 73-74° were isolated mechanically. Ligroin:benzene (2:1) eluted a small yellow band which decomposed on the column.

Attempted Interconversion of Stereoisomeric Species.

The following experiments were carried out on tricarbonyl-7-exo-(ethoxycarbonylmethyl)cycloheptatrienechromium, and tricarbonyl-7-phenylcycloheptatrienechromium (exo or endo).

(a) Treatment with boron trifluoride diethyletherate in refluxing ether in the presence of tricarbonyltripyridinechromium.

(b) Treatment with boron trifluoride diethyletherate in refluxing ether in the presence of 7-(ethoxycarbonylmethyl)-cycloheptatriene¹⁰⁷ or 7-phenylcycloheptatriene,¹⁰⁸ respectively.

(c) Heating in a refluxing mixture of diglyme and aromatic free petroleum ether, b.p. 100-120°C, with or without 7-(ethoxycarbonyl)methylcycloheptatriene¹⁰⁷ or 7-phenylcycloheptatriene¹⁰⁸ respectively.

In no case was conversion to the corresponding stereoisomer observed.

Attempted Reductions of Tricarbonyl-7-(ethoxycarbonylmethyl)-cycloheptatrienechromium (exo- and endo- isomers).

The following unsuccessful attempts were made:-

- (a) Bouveault-Blanc¹¹³ method using sodium-ethanol or sodium-isopropylalcohol - complete decomposition.
- (b) Modification¹¹⁴ of (a) using boiling toluene as solvent, with slow addition of sodium and alcohol - complete decomposition.
- (c) Lithium aluminium hydride in ether or benzene at 0°C or room temperature - immediate decomposition.
- (d) Lithium borohydride in ether. At reflux - complete decomposition. At room temperature or 0°C - decomposition with partial recovery of unchanged ester.
- (e) Lithium tri-tert-butoxyaluminumhydride in diglyme at -70°C for 2 hr. - Slight decomposition, and starting material recovered in 86% yield.

Reaction of 2-(7-cycloheptatrienyl)ethanol¹⁰⁷ with Hexacarbonylchromium.

Reaction in a refluxing mixture of diglyme and petroleum ether, b.p. 100-120°C, in the Strohmeier apparatus¹⁰⁸ (bath temperature 160-165°C) resulted in precipitation of an unidentified high-melting red solid, found to be insoluble in all common organic solvents, I.R. \checkmark _{MAX.} (KCl) 2000, 1930, 1092 (MC-O) cm.⁻¹

From reaction in refluxing petroleum ether, b.p. 100-120° (bath temperature 130°C) a poor yield of a red gummy product was obtained. I.R. 3440, (O-H) 2000, 1925, 1895, (MC-O) cm.^{-1} . Attempted crystallisation or sublimation of this material failed to give a solid product.

Attempts to obtain a crystalline product by acetylation of the starting alcohol or the red gummy material also met with failure.

Miscellaneous Reactions of Tricarbonyl-7-oxomethoxycycloheptatrienechromium. ¹¹⁰

- (a) Reaction with phenol in refluxing tetrahydrofuran afforded a red gummy product. All attempts to obtain a crystalline solid from this product failed.
- (b) From reaction with ferrocene in tetrahydrofuran at room temperature, both starting materials were recovered unchanged. Reaction in refluxing tetrahydrofuran afforded only hexacarbonyl-(bicycloheptatrienyl)bis-chromium and unchanged ferrocene.
- (c) Reaction with chloro- or bromo-acetal in the presence of zinc turnings in tetrahydrofuran afforded only hexacarbonyl (bicycloheptatrienyl)bis-chromium and tricarbonyl(bicycloheptatrienyl)chromium.

(d) Treatment with Li/Hg (2%) in dry ether, followed by addition of solid carbon dioxide, resulted in partial decomposition. Only hexacarbonyl(bicycloheptatrienyl)bis-chromium was isolated.

Miscellaneous Reactions with Tricarbonyltripyridinechromium

The following compounds were treated with boron trifluoride diethyl etherate, in the presence of tricarbonyltripyridinechromium, in ether at 38-40°C (bath temperature).

7-Methoxycycloheptatriene,¹⁰⁹ bicycloheptatrienylether,¹⁰⁹
 2-(7-cycloheptatrienyl)ethanol,¹⁰⁷ 7-dimethylaminocyclohepta-
 triene,¹¹¹ benzyl cyanide, benzyl chloride, hexafluorobenzene,
 allo-ocimene, pyrrole and N-methyl pyrrole.

In every case, pentacarbonylpyridinechromium was obtained. In the case of 7-methoxycycloheptatriene, hexacarbonyl (bicycloheptatrienyl)bis-chromium was isolated in 5% yield. In no case was the desired tricarbonylchromium complex isolated.

A P P E N D I X
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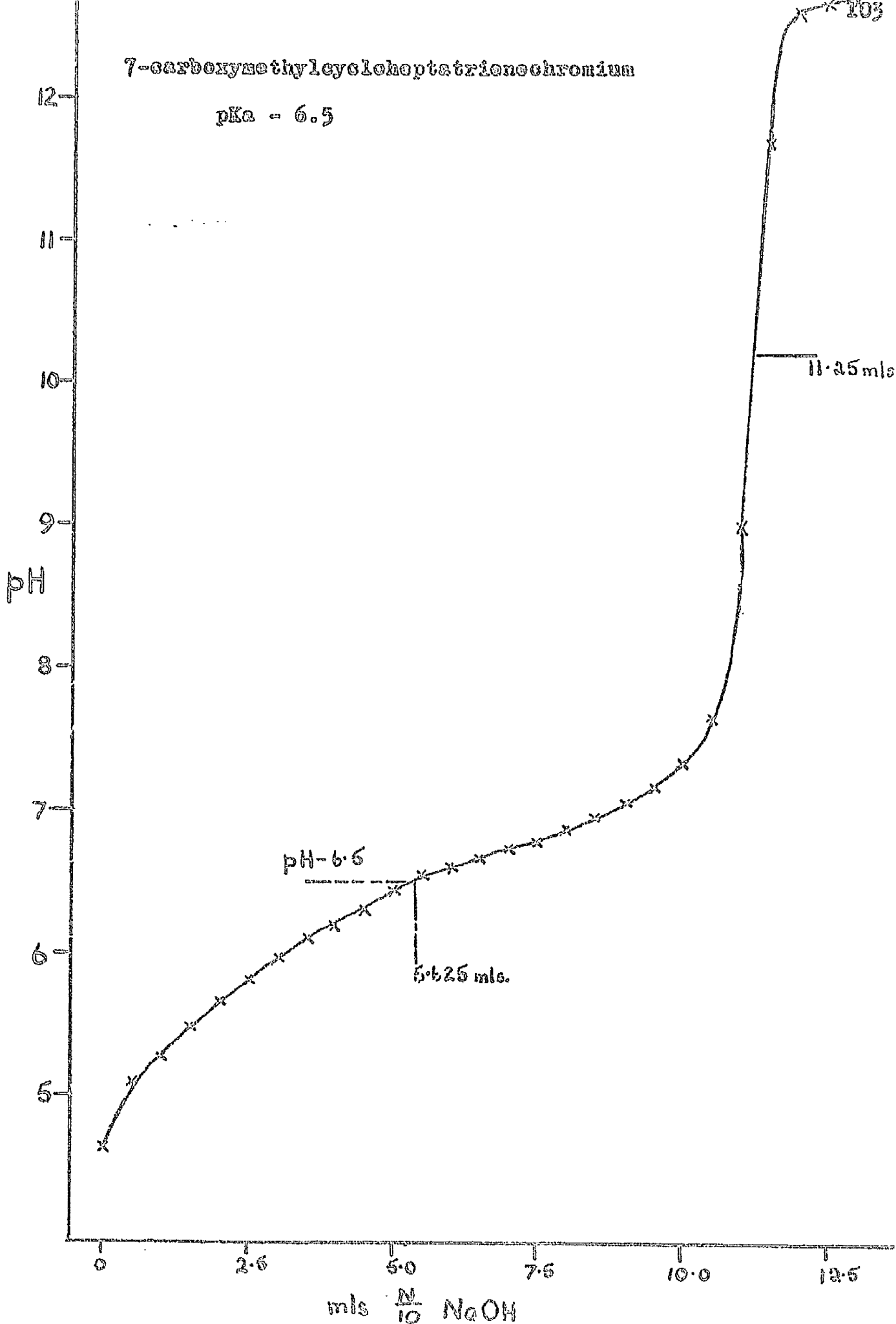
TABLE III

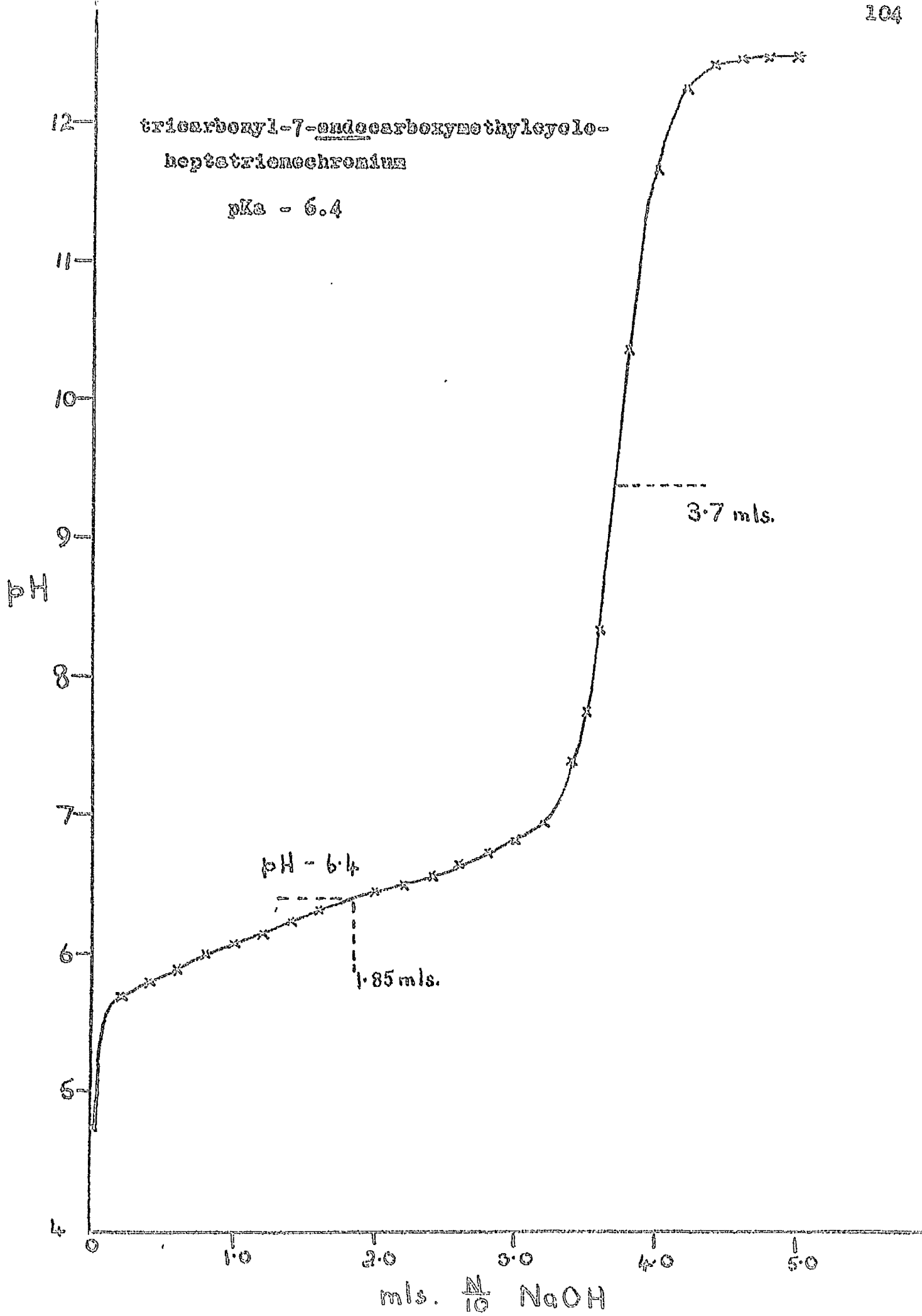
Nuclear Magnetic Resonance Spectra

Compound	values	(signal centre)
Tricarbonyl-7-exo-allylcyclo- heptatrienechromium	$H_{3,4} - 4.05$	(multiplet)
	$H_{2,6} - 5.2$	(multiplet)
	$-\underline{CH} = \underline{CH}_2 - 5.0$	(complex)
	$H_{1,8} - 6.4$	(multiplet)
	$H_7 - 7.1$	(multiplet)
	$\alpha-CH_2 - 9.0$	(double triplet)
Bis-exo-(tricarbonylcyclo- heptatrienechromium) sulphide	$H_{3,4} - 4.0$	(multiplet)
	$H_{2,6} - 5.2$	(multiplet)
	$H_{1,8,7} - 6.1$	(complex)
Pentacarbonylpyridine- chromium	$H_{3,4} - 3.15$	(multiplet)
	$H_{2,6} - 3.5$	(multiplet)
	$H_{1,8} - 4.6$	(double triplet)
	$H_7 - 6.5$	(triplet)

7-carboxymethylcycloheptatrienechromium

pKa = 6.5

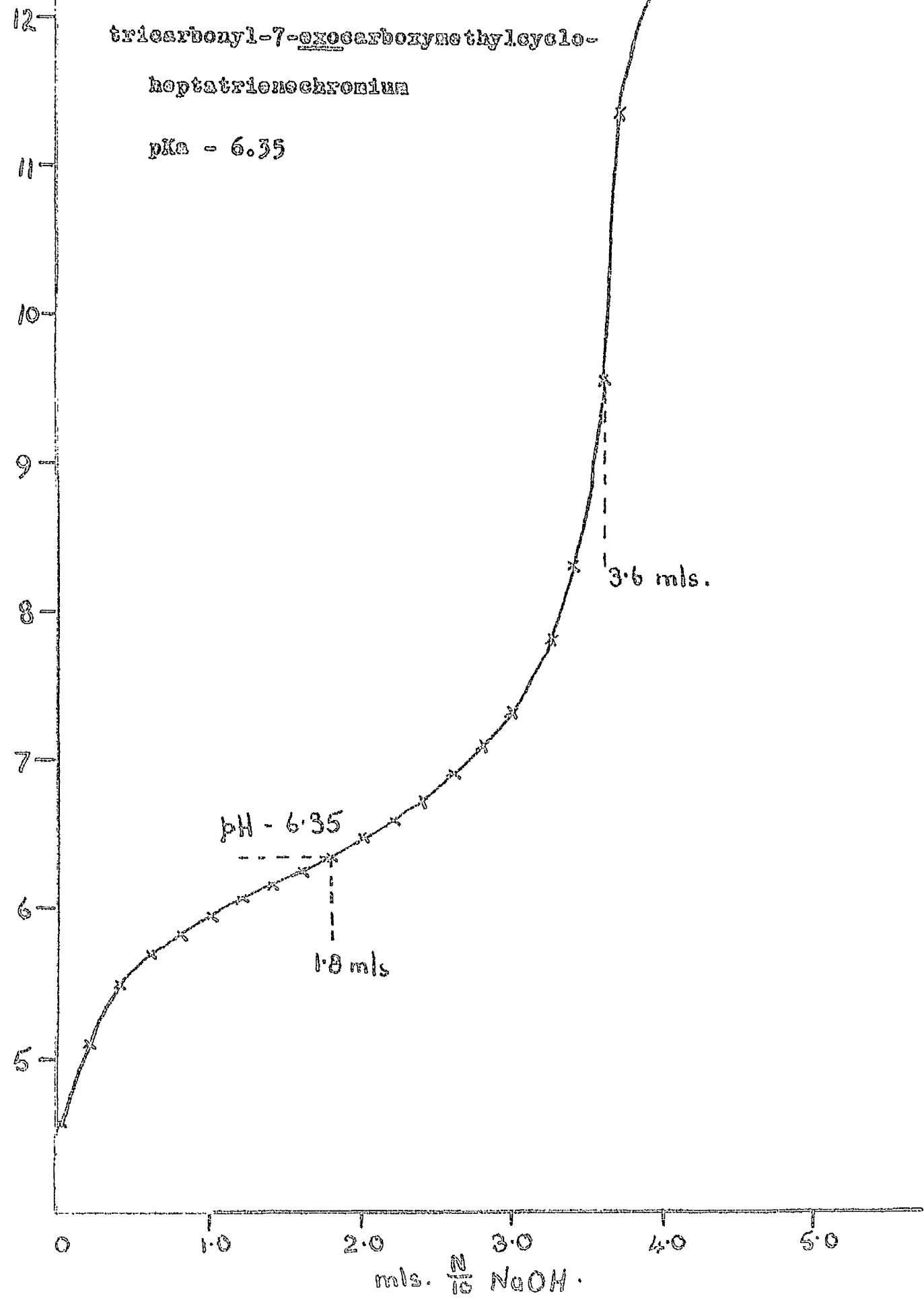




triacetyl-7-exocarbonymethylenecyclo-
heptatrienechromium

pKa = 6.35

pH



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