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Monosubstituted cyclopentadienyl half-sandwich transition metal complexes

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ABBREVIATIONS

t-Bu	*tert*-butyl
Cat	catalyst
CD	circular dichroism
cot	cyclooctatetraene
dippe	bis(di-isopropylphosphino)ethane
dmpe	bis(dimethylphosphino)ethane
dmpm	bis(dimethylphosphino)methane
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
DVB	divinylbenzene
ee	enantiomeric excess
electro	electrochemistry
EM	electron microscopy
ES	electronic spectroscopy
ESR	electron spin resonance
Et	ethyl
hplc	high-pressure liquid chromatography
IR	infrared
isom	isomerisation studies
kin	kinetic studies
LDA	lithium diisopropylamide
Me	methyl
MO	molecular orbital
MS	mass spectroscopy
NM	neomenthyl
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NQR	nuclear quadrupole resonance
OS	osmometry
nPe	neo-pentyl
PES	photoelectron spectroscopy
Ph	phenyl
polym	polymerisation studies
i-Pr	iso-propyl
PS	polystyryl
RS	Raman spectroscopy
TMS	trimethylsilyl
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
UPS	ultraviolet photoelectron spectroscopy
UV	ultraviolet spectroscopy

VIS	visible spectroscopy
VT	variable temperature
XPS	X-ray photoelectron spectroscopy
X-ray	X-ray crystallography
XRF	X-ray fluorescence spectroscopy

A. SCOPE OF THE REVIEW

Substituted and unsubstituted cyclopentadienyl ligands are found in tens of thousands of organometallic complexes [1]. They stabilise metals in both high and low oxidation states and can bind to a metal through one to five of the ring carbon atoms [2]. Multi-cyclopentadienyl complexes (e.g. $(C_5H_5)_4Ti$ [3]) are also known. Indeed, the synthesis and the structure elucidation of ferrocene, $(\eta^5\text{-}C_5H_5)_2Fe$, is generally regarded as *the* significant event in the emergence of the field of organometallic chemistry (see, for example, ref. 4).

Much time and effort has been spent in ascertaining and correlating steric and electronic properties of Group 15 donor ligands with the reactivity patterns of metal complexes containing these ligands (see, for example, ref. 5). This, in part, relates to the range of molecular catalysts which employ these ligands and the fine tuning of catalytic behaviour that can accompany fine tuning of the electronic/steric effects of the Group 15 donor ligands [6]. By contrast, a paucity of data is available on the control of reactivity in cyclopentadienylmetal complexes via the modification of the electronic/steric effects of the cyclopentadienyl ligand. Indeed, the steric effect due to substituents on the cyclopentadienyl ligand is normally not considered in most studies involving such complexes.

We have undertaken a review and analysis of transition metal complexes containing monosubstituted cyclopentadienyl ligands in order to assess the effect of the ring substituent on both the reactivity and physical properties of the cyclopentadienylmetal complex. Our interest in this area was stimulated by our study of the steric properties of the ring substituent, brought about by our own synthetic and NMR studies on $(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I$ (R = Me, *t*-Bu etc.; L = Group 15 donor ligand) complexes [7].

The synthesis, physical properties, and steric and electronic effects of cyclopentadienyl complexes discussed in this review have been restricted to a limited range of complexes which highlight the principal changes caused by placing substituents on the cyclopentadienyl ligand. In particular, we have limited this review to complexes with the following characteristics.

(a) Monosubstituted cyclopentadienyl ligands. Where appropriate multiple ring substitution (2–5 substituents) will be described, but a survey of this range of complexes will not be given here.

(b) η^5-Cyclopentadienylmetal complexes, i.e. complexes in which the metal is bonded to all five ring carbons. This will include symmetrical (**1**), allyl-ene (**2**) and diene (**3**) ring–metal bonding modes [8].

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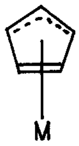

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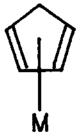

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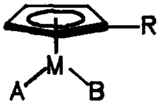
(c) Half-sandwich complexes, i.e. metal complexes in which the metal is η^5-bonded to only *one* cyclopentadienyl ring.

(d) Complexes in which the metal is a d-block element.

This review will thus mainly be concerned with complexes of the type **4**–**6** in



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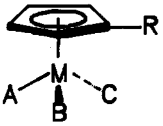

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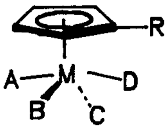

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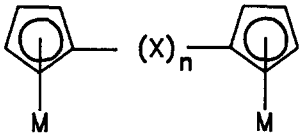
in which A–D = two-electron anionic or neutral ligand, M = transition metal, and R = ring substituent.

Complexes in which the metal is coordinated to another metal through the ring substituent, e.g. **7** and **8**, will be mentioned where appropriate.



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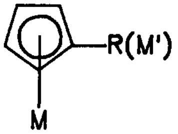

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The major objectives in analysing and reviewing complexes of the type **4**–**6** will be:

(a) to present the synthetic routes available for the synthesis of both the substituted cyclopentadienyl ligand and the substituted cyclopentadienylmetal complexes;

(b) to establish the range of $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{ML}_x$ complexes that have been synthesised to date;

(c) to analyse the crystallographic data available on substituted cyclopentadienyl complexes; in particular ring conformational effects;

(d) to assess the reactivity and physical properties (e.g. NMR data) of the resulting complexes.

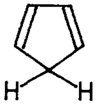
A number of reviews have previously been written on cyclopentadienylmetal complexes (see refs. 9, which lists early reviews, and 10). The early reviews [11–13] give a complete listing of all cyclopentadienyl and substituted cyclopentadienyl complexes known at the time. In 1969, Bublitz and Reinhart [14] published a review on *substituted* cyclopentadienyl complexes (predominantly sandwich complexes). This was possible since only a limited number of complexes pertinent to this review had at that time been synthesised. Other reviews relating to some aspects of this work (e.g. Group 6 metals [15]) will be referred to in the text. More recently, Rausch and co-workers have reviewed the synthetic procedures used to obtain a wide range of substituted cyclopentadienylmetal complexes [16,17].

It is to be noted that a related review on (arene)ML$_x$ complexes, in which the effects of arene substituents on ring conformations relative to the ligand set L$_x$ were assessed, has been published [18].

This review covers the work published in the literature until early 1990.

B. HISTORICAL INTRODUCTION

Cyclopentadiene was first discovered as a product in the carbonization of coal in the 1890s, and by the turn of the century its structure had been elucidated [19–22]. Cyclopentadiene (**9**), or more correctly dicyclopentadiene (**10**), is still produced commercially by this method, although the predominant source of cyclopentadiene today is via the thermal cracking of hydrocarbons in the presence of steam [23]. This method also produces methylcyclopentadiene. The thermal cracking of hydrocarbons in ethene production is also a source of cyclopentadiene. It is worth noting that there is no convenient process presently in use for the sole production of cyclopentadiene [23].



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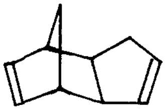

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Since cyclopentadiene formally contains two functionalities, the double bonds and the active methylene group, an enormous range of cyclopentadiene derivatives can be, and has been, synthesised [22]. For instance, as early as 1896, the chlorination of the double bond in cyclopentadiene aided in the elucidation of the compound's structure [20]. The unique properties of cyclopentadiene, however, are due to the high aromatic stabilisation of its anion. Thiele in 1900, as reported in a paper entitled *Über Ketonreaktionen bei den Cyclopentadiën* [24], was the first chemist to synthesise substituted derivatives of cyclopentadiene by reaction of the active methylene group of the cyclopentadiene. Reactions performed by Thiele are shown in Fig. 1.

The formation of fulvenes via the condensation of a ketone with a cyclopentadienyl ring is a facile method for producing substituted cyclopentadienes and is still used today (see Sect. C.(i)(a)).

One year later, Thiele [25] isolated the first *metal*–cyclopentadienyl derivative, $K[C_5H_5]$, from the reaction of potassium with C_5H_6. During the next 50 years, a wide range of substituted cyclopentadienylmetal derivatives was synthesised but it was only in 1951 that the first reaction of a cyclopentadiene ring with a transition metal was reported [26]. This reaction, which produced ferrocene, had far-reaching implications for the study of complexes containing a carbon–metal bond, and the event is regarded as the birth of organometallic chemistry.

The original synthesis of ferrocene by Kealy and Pauson [26] and Miller et al. [27] has been adequately described in the literature and will not be discussed further here [28,29]. After these initial reports, a number of studies were carried out to generalise the findings, such as reaction of other metals with cyclopentadienes, reaction of the cyclopentadienyl ring attached to the metal, and the use of substituted cyclopentadienes to prepare substituted cyclopentadienylmetal complexes. From these early (and subsequent) studies it became apparent that, although a number of cyclopentadienylmetal complexes could be modified by reaction of the *bonded* ring (e.g. in ferrocene), this approach did not extend to all ring metal complexes or even to ring modification for all substituents.

It appears that the first attempt to synthesise a substituted cyclopentadiene ring for reaction with a transition metal was performed by Pauson in 1954 [30]. In this report, a range of multiply phenyl-substituted ring derivatives of ferrocene was prepared by reaction of $FeCl_2$ with a cyclopentadienyl Grignard reagent made from the substituted cyclopentadiene ligand. The monophenyl-substituted ferrocene was later also prepared directly from ferrocene [31].

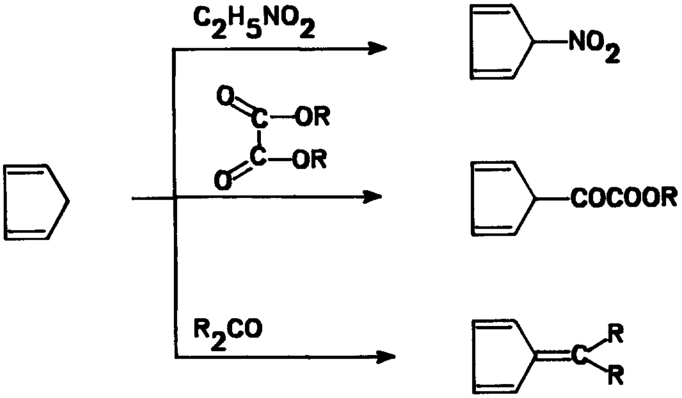


Fig. 1. Reactions of cyclopentadiene performed by Thiele [24].

Pauson [30] also reported the synthesis of an alkyl-substituted ferrocene, $(\eta^5\text{-C}_5H_4CHPh_2)_2Fe$, on reaction of a fulvene with $FeCl_2$ under the appropriate reaction conditions. The use of fulvenes to synthesise substituted ferrocenes was subsequently reported by other authors; and the reactions gave a range of substituted cyclopentadienyl complexes, where the substituent is determined by the reagent used to abstract the active fulvene hydrogen atom [32–36]. Alternative syntheses of substituted ferrocene complexes required the use of diazocyclopentadienes [37], cyclopentenones [30,38] and ligand displacement reactions [39].

An extension of the above methods to the preparation of substituted cyclopentadienyl complexes involving other metals soon followed the early ferrocene work (see, for example, ref. 40). However, the first systematic study of the synthesis of a series of substituted cyclopentadienyl ligands of half-sandwich complexes, the material of this review, was reported in 1960 by Abel et al. [41]. In this publication, a series of substituted $[(\eta^5\text{-C}_5H_4R)Mo(CO)_3]_2$ complexes, which were synthesised from the reaction of $Mo(CO)_6$ and a series of fulvenes, was reported. The study demonstrated that the local symmetry associated with the carbonyl ligands was not influenced by the symmetry of the ring substituent.

In the almost forty years since the discovery of ferrocene, a wide range of cyclopentadienyl ligands has now become available for use in synthesis. A variety of cyclopentadienyl-containing complexes has been used in a broad range of catalytic reactions, but their full potential has as yet not been realised.

Little mention will be made in this review of complexes containing the methyl-substituted cyclopentadienyl group. Many complexes containing this ligand have been synthesised simply because of the ready availability of C_5H_5Me (e.g. as in $(\eta^5\text{-C}_5H_4Me)Mn(CO)_3$), or the increased solubility conferred on a methyl-cyclopentadienyl complex relative to a complex containing the unsubstituted cyclopentadienyl ring. However, in general the role of the methyl group in the chemistry of the complex has had no bearing on the investigations reported.

Finally, multiply substituted cyclopentadienyl rings, although having played a major role in the development of some areas of organometallic chemistry, will not be discussed here. The particular impact of the electronic and steric properties of the $\eta^5\text{-C}_5Me_5$ ligand on the chemistry of $(\eta^5\text{-C}_5Me_5)ML_x$ complexes was reviewed some years ago [42], but space does not permit a discussion of this important class of ligands in this review.

C. SYNTHETIC STRATEGIES FOR THE SYNTHESIS OF MONOSUBSTITUTED CYCLOPENTADIENYL COMPLEXES

Several procedures are available for the synthesis of the complexes under discussion, and the various approaches can be classified as described below.

(a) Preparation of a substituted cyclopentadiene ring followed by attachment of the ring to a metal. The cyclopentadiene ring can be derived from fulvenes, cyclopentenones, cyclopentadienes, etc.

(b) Introduction of a cyclopentadienyl substituent after preparation of a cyclopentadienylmetal complex. This includes metallation reactions of the cyclopentadienyl ring.

(c) Cyclopentadienyl transfer from one metal to another metal.

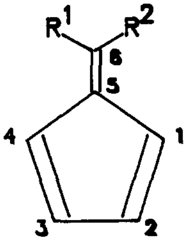
(d) Creation of a cyclopentadienyl ligand from an organic fragment. This could include fragments attached to a metal template.

A brief discussion of some aspects of the above procedures will be given, which will highlight the methods for making the uncomplexed cyclopentadienyl ligand. This will be followed by a listing of the major types of C_5H_5R (or $C_5H_4R^-$) ligands that have been synthesised and used to date.

(i) General synthetic strategies for the synthesis of monosubstituted cyclopentadienyl ligands

(a) Strategies utilising fulvenes [43]

(1) Preparation of fulvenes. Only C-6-mono-, and disubstituted, as well as the unsubstituted fulvenes, (**11**, R^1, $R^2 = H$) are of interest in the present context.



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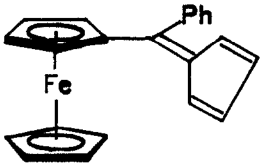
Thiele's original method [24], which involved the condensation reaction of ketones and aldehydes with cyclopentadiene in an alcohol (ethanol or methanol) in the presence of molar amounts of the corresponding sodium or potassium alkoxide, still appears to be the best method for the preparation of fulvenes carrying aryl substituents (**11**, $R^1 =$ aryl, $R^2 =$ aryl, alkyl, H) [44]. The method, although useful for the preparation of the parent fulvene and dialkyl-substituted fulvenes, has been modified for the preparation of the more sensitive mono-alkyl fulvenes (**11**, $R^1 =$ alkyl, $R^2 = H$) by using THF as a co-solvent [45] and ion-exchangers as the base catalyst [46]. Thiele's method for the preparation of aryl-fulvenes has also been successfully extended to the synthesis of metallocenylfulvenes, for instance, 6-ferrocenyl-6-phenylfulvene (**12**) and 6-cymantrenyl-6-phenylfulvene (**13**) [47,48], which were



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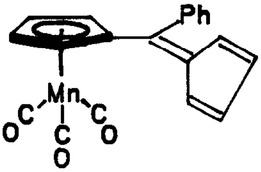

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prepared from the corresponding ketones. Compounds **12** and **13** serve as ligands in the synthesis of organometallic complexes.

6,6-Dialkylfulvenes are now readily synthesised by the method of Freiesleben [49], in which primary or secondary amines are used as catalysts and an alcohol as solvent. The method has also been successfully used to prepare mono-alkyl-substituted fulvenes (**11**, $R^1=$alkyl, $R^2=H$) [50], but appears not to have been used for the preparation of unsubstituted fulvene. The parent hydrocarbon (**11**, $R^1=R^2=H$) is best prepared either by treatment of acetoxymethylcyclopentadiene with NEt_3 [51] or preferably by "reductive deamination" of 6-dimethylaminofulvene (**11**, $R^1=NMe_2$, $R^2=H$) [52]. This process involves the nucleophilic displacement of the dimethylamino substituent by hydride, using $LiAlH_4$.

The corresponding reaction of 6-dimethylaminofulvene with organolithium reagents is a general method for the preparation of 6-monosubstituted fulvenes, e.g. 6-methylfulvene [52,53], and the method should provide access to other variously substituted fulvenes.

Unsubstituted fulvene is also accessible by a variety of isomerisation reactions, of which the transition metal-catalysed isomerisation of benzvalene could be of preparative interest [54]. 6-Dimethylaminofulvene (**11**, $R^1=NMe_2$, $R^2=H$) is readily prepared by the condensation reaction of sodium cyclopentadienide with *N*,*N*-dimethylformamide-dimethyl sulphate (synthesised from DMF and dimethyl sulphate) in THF [55] or by similar methods [56]. It is also useful in the preparation of other fulvenes (see above).

Various disubstituted fulvenes (**11**, R^1, $R^2=NR_2$ or OR) are accessible by similar routes using the corresponding carbonium-oxonium or carbonium-oxonium-immonium salts as starting materials [57]. 6-Methoxyfulvene (**11**, $R^1=OMe$, $R^2=H$) may be obtained by *O*-alkylation of the sodium salt of "6-hydroxyfulvene" (formylcyclopentadiene) [58].

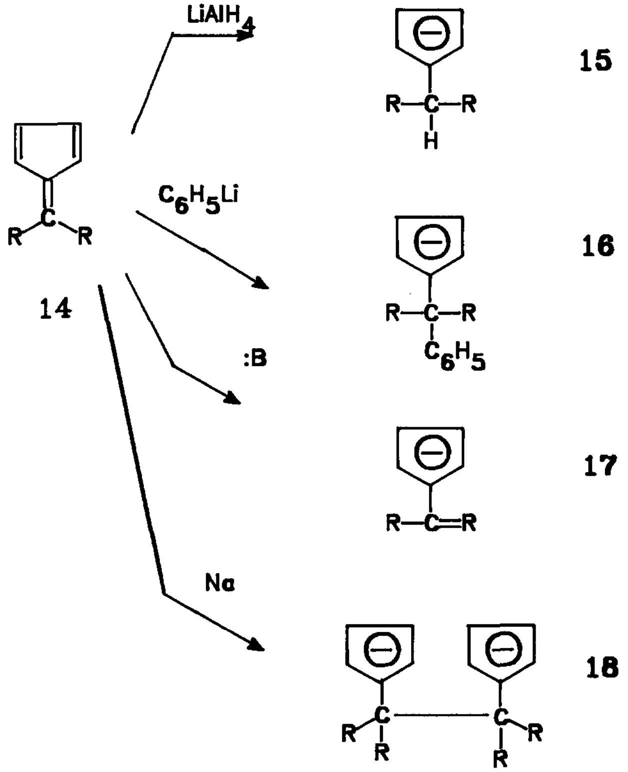
(2) Utilization of fulvenes in the preparation of (η^5-C_5H_4R)ML_x complexes. Among the known C-6-mono- and di-substituted fulvenes, the following have found frequent application in organometallic chemistry: 6-dimethylamino- and 6,6-bis(dimethylamino)fulvene; 6-alkyl-, 6-aryl-, 6,6-dialkyl-, 6,6-diaryl- and 6-alkyl-6-aryl-fulvenes (aryl = phenyl or substituted phenyl).

Fulvenes have found application in the preparation of monosubstituted cyclopentadienyl complexes in a number of ways.

(a) They can act as precursors to stable organometallic fulvene complexes, which may then be converted in a second reaction to the substituted cyclopentadienyl complexes.

(b) Fulvenes can yield the required cyclopentadienyl complexes directly on reaction with an organometallic species, by inter- or intramolecular hydrogen abstraction. In these reactions [59(a)], the cyclopentadienyl anion generated from a fulvene is directly attached to the metal. Examples of this reaction are to be found in Sect. D.

(c) Fulvenes (**14**) may first be converted to monosubstituted cyclopentadienes or their anions (**15**–**18**), and these dienes or anions are then reacted with a metal or a metal salt.



Fulvenes (**11**) are expected to be attacked by nucleophiles at the exocyclic carbon atom (C-6) from considerations of product stability (production of an “aromatic” cyclopentadienyl anion), frontier molecular orbital coefficients (highest LUMO coefficient on C-6) and from the polarisation of the molecule (C-6 carries a small positive net charge) [60]. From the same type of considerations, fulvenes should be attacked by electrophiles on the five-membered ring at position 1 or 4 [61]. These predictions are found to be correct. The reaction of fulvenes with nucleophiles ($LiAlH_4$; lithium-organics; Grignard compounds) is thus an important method for the preparation of substituted cyclopentadienes, and their anions, and for the interconversion of fulvenes (e.g. preparation of unsubstituted fulvene from 6-dimethylaminofulvene). Compare this with the reactivity of some organometallic fulvene complexes, where protonation occurs at the exocyclic carbon, whereas with others the exocyclic carbon atom is attacked by nucleophiles. Both these latter cases are of particular interest for the preparation of substituted cyclopentadienyl complexes.

Actual reactions of the cyclopentadienyl anions, generated from fulvenes, will be given in Sect. D. Some of the more important methods used for generating cyclopentadienyl anions from fulvenes are discussed in more detail below.

Cyclopentadienyl anions formed by reduction of fulvenes. Lithium aluminium hydride reduces fulvenes to the corresponding substituted cyclopentadienyl anions by hydride transfer from the reagent to the exocyclic carbon atom (**14**→**15**). This method was first used by Ziegler et al. [62], and is of very general applicability [63]. The substituted lithium cyclopentadienide formed may be used directly in situ for the preparation of transition metal complexes as the AlH_3 produced in the reaction does not seem to interfere with the reactions [34(b),64–66]. Quenching of the reactions yields the corresponding substituted cyclopentadienes as a mixture of mostly the 2- and 3-isomers.

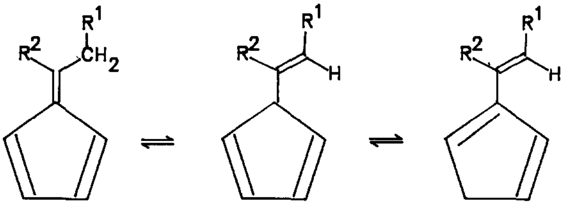
Other reduction methods use Grignard reagents which contain a β-hydrogen atom, usually ethylmagnesium bromide or isopropylmagnesium bromide, but this is normally only a side reaction to the nucleophilic addition of the magnesium alkyl to the exocyclic carbon atom. Electropositive metals or their amalgams have also been used as reducing agents (e.g. Na with 6,6-diphenylfulvene) [67,68].

Purely aliphatic fulvenes, e.g. 6,6-dimethylfulvene, dimerise on treatment with electropositive metals (usually Na) (**18**). Head-to-head dimerisation occurs as expected from the fact that the fulvene LUMO coefficient is largest on C-6 [67]. The dimeric bridging sodium cyclopentadienide may be used directly in the preparation of transition metal complexes [33,35,66].

Vinylcyclopentadienyl anions by deprotonation of fulvenes. The tautomerism of fulvenes with α-hydrogens (**19**–**21**) can be exploited for the preparation of vinylcyclopentadienyl anions.

Deprotonation of various 6-methylfulvenes with LDA yields the corresponding anions (**17**) which may be used directly for the preparation of a wide variety of vinylcyclopentadienyl complexes [53,69]. This is a very general method and is independent of the nature of R.

Cyclopentadienyl anions formed by addition of "carbanions" to fulvenes [59(b)]. Addition of organolithium compounds and Grignard reagents to the exocyclic carbon



19 **20** **21**

of fulvenes (which behave analogously to ketones) is a relatively general and very important method for the preparation of substituted cyclopentadienes and their anions (e.g. **14**→**16**). Reduction of the fulvene to the corresponding cyclopentadiene frequently takes place. This is especially observed with fulvenes carrying bulky groups in the 6-position, and the reaction is also influenced by the type of organometallic reagent used. Tertiary as well as allyl- and benzylmagnesium halides preferentially give addition compounds, and react faster than the primary and secondary reagents. An excess of organometallic reagent is generally used and the end of the weakly exothermic reaction can be recognised by the disappearance of the yellow fulvene colour. Preferred solvents are ethers. If higher temperatures are necessary, two moles of ether per mole of magnesium are needed (formation of the di-etherate), or high boiling ethers (e.g. anisole) are used [70]. Lithium reagents add to fulvenes in the same way as Grignard reagents [33,34(b),64,66,70,71]. An excess of free alkyl halide has to be avoided, since these react with the cyclopentadienyl anion according to the Wurtz-type synthesis (see Sect. C.(i)(b)). The substituted lithium cyclopentadienides or cyclopentadienylmagnesium halides have been used directly in numerous syntheses of organometallic complexes [72]. Quenching of the primary addition product yields the corresponding substituted cyclopentadienes as a mixture of 2- and 3-isomers.

(b) Cyclopentadienide salts ("Wurtz synthesis") [59(b)]

The reaction of lithium, sodium, potassium, or thallium cyclopentadienides or cyclopentadienylmagnesium halides with alkyl halides or other alkylating reagents in ethers, hydrocarbon solvents, or liquid ammonia, presents a versatile method for the preparation of alkyl-substituted cyclopentadienes.

The magnesium bromides of cyclopentadiene are easily prepared from cyclopentadiene and ethylmagnesium bromide [73]. If higher reaction temperatures are necessary, the diethyl ether typically used for the preparation of Grignard reagents is replaced by higher boiling ethers, or high boiling hydrocarbon solvents. Alternatively, only two moles of ether are used per mole of magnesium to form the dietherate complex.

Cyclopentadienyllithium is obtained from cyclopentadiene and phenyllithium [74(a)] or butyllithium [74(b)]. Li[C_5H_5] has been used to synthesise a wide range of $C_5H_4R^-$ ligands in which R is a primary, secondary or tertiary alkyl group.

Sodium cyclopentadienide can be prepared in a number of ways [75] and may be obtained in high purity as its crystalline DME complex. Reaction of cyclopentadiene with sodium amide in liquid ammonia provides an alternative route to Na[C_5H_5].

Potassium cyclopentadienide is prepared from cyclopentadiene and potassium metal in benzene, toluene, or xylene [25]. Potassium dispersions in the latter two solvents can easily be prepared by the use of ultrasound. K[C_5H_5] has been reacted successfully with primary alkyl bromides and iodides, benzyl chloride, and triphenylchloromethane but *tert.*-butyl bromide does not react with the K[C_5H_5] [76(a)].

The use of cyclopentadienylmagnesium bromides is not suitable for non-activated alkyl halides although primary alkyl sulphates are reactive. The reactions with the cyclopentadienide salts usually yield mixtures of the 1- and the 2-isomers (except with the silyl derivatives, which preferentially exist as the 2-isomer). Pure 1-isomers can, however, be obtained under certain conditions [76(b)]. Only products of mono-alkylation are formed in Wurtz reactions, since the C–H acidity of the substituted cyclopentadienes is lower than that of the unsubstituted compound [76(c)].

Thallium cyclopentadienide salts are usually prepared from Tl_2SO_4 [77] or preferably TlOEt [78–81]. The latter material can either be purchased (e.g. Aldrich) or made from Tl metal [78]. The Tl[C_5H_5] is a relatively air-stable material which reacts readily with metal halides to give (η^5-C_5H_5)ML_x complexes or with reagents to introduce a ring substituent to give C_5H_5R. Substituted cyclopentadienide salts can also be synthesised and provide access to a range of Tl[C_5H_4R] reagents for reaction with metal salts to produce [η^5-C_5H_4R]ML_x complexes. The method has proved quite versatile, and Singh et al. [81] have recently listed a range of substituents that can be introduced by this technique.

(c) Creation of cyclopentadienes from organic fragments

An alternative procedure to the synthesis of substituted cyclopentadienes via the classical routes listed in Sects. C.(i)(a) and C.(i)(b), and above, is to synthesise the substituted cyclopentadiene from organic fragments. There are many methods available for the synthesis of multiply substituted derivatives (for some recent examples, see ref. 82), but this route has been little used for the synthesis of the monosubstituted complexes. Some examples which have been used are shown below.

(a) Reaction of α-bromoacetophenone with sodium ethylacetoacetate to give **22a** [83].

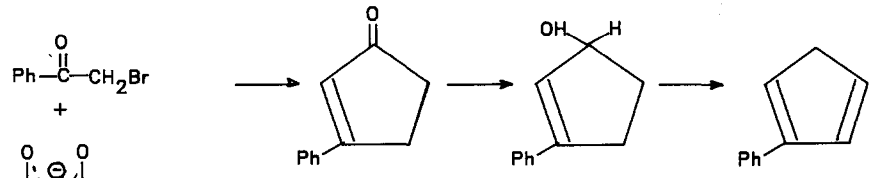
(b) Reaction of cyclopentenones [30,83] to give **22a**.

(c) Retro Diels–Alder reactions [84,85] to give **22b**.

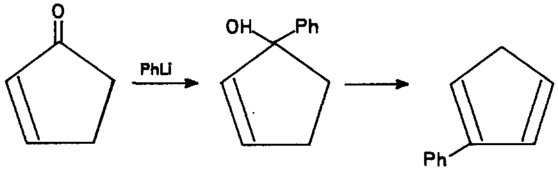
(d) Cyclisation reactions [86] to give **23**.

(d) Release of the substituted cyclopentadiene from a metal: synthesis of substituted cyclopentadienes

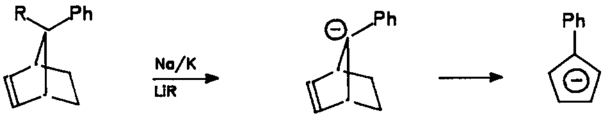
Nickelocene (**24**) has been found to react with various polyhalomethanes (**25**) in the presence of triphenylphosphine to form substituted cyclopentadienes (**29**) and (η^5-cyclopentadienyl)bis(triphenylphosphine)nickel(II) salts (**28**) [87–89].



22a

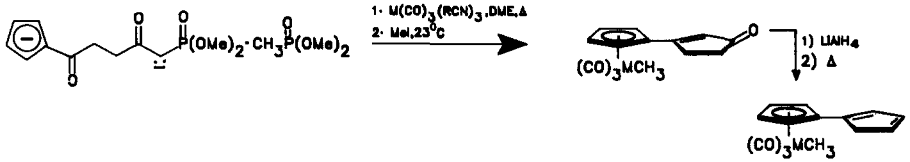


22a



R=Cl,OH

22b

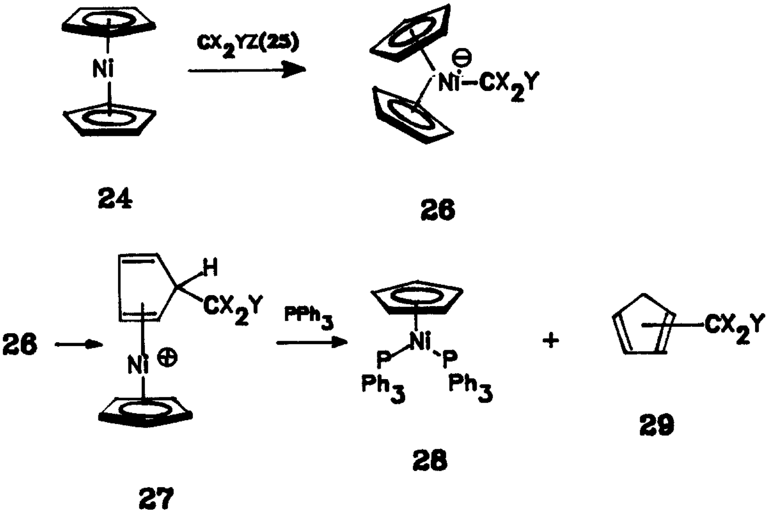


23

The proposed first step in the reaction is the alkylation of the central nickel atom to form intermediate **26**, which should then rearrange to the substituted cyclopentadiene complex **27**. Alternatively, **27** may be formed directly from **24** and **25**. Reaction of **27** with triphenylphosphine then results in ligand displacement to yield **28** and **29**.

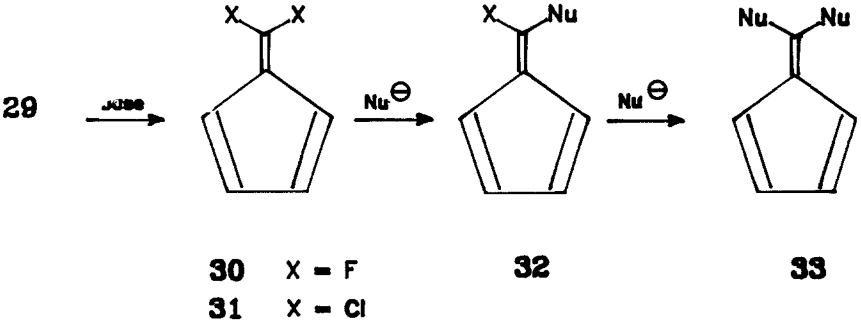
Polyhalomethyl-substituted cyclopentadienes (**29**) form dihalofulvenes **30** and **31** in the presence of base. The latter easily undergo nucleophilic substitution (with amines, alcohols as nucleophiles) to form stabilised fulvenes **32** and **33** [87,88].

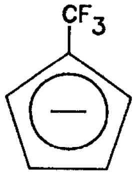
Trifluoromethylcyclopentadiene (**29**, X = Y = F) has been converted to the thallium derivative (**34**) by treatment with thallous ethoxide in ether and has found application in the syntheses of a range of metal complexes [89].



25a $X=Y=F, Z=I$
b $X=F, Y=Z=Br$
c $X=Y=Z=Cl$
d $X=Y=Z=Br$

29a $X=Y=F$ $(Z=F)$
b $X=F, Y=Br,$ $(Z=Br)$
c $X=Y=Cl$ $(Z=Cl)$
d $X=Y=Br$ $(Z=Br)$

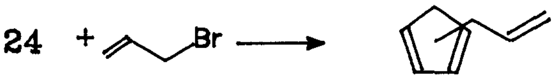




34

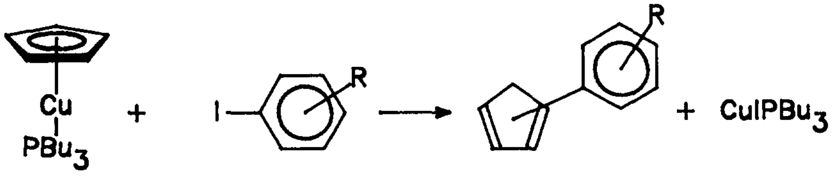
In a similar fashion, nickelocene (**24**) reacts with triphenylmethyl chloride or 3-bromopropene to form (triphenylmethyl)cyclopentadiene (**35**) [90] and allylcyclopentadiene (**36**) [87], respectively.

35



36

The reaction mixture obtained from the reaction of **24** with trichloromethylbenzene appears to contain phenyldichloromethylcyclopentadiene. On treatment with base, 6-chloro-6-phenylfulvene is obtained [87]. Cyclopentadienylcopper(I) tributylphosphine (**37**) reacts with iodobenzenes to give arylcyclopentadienes (**38**) [84]. The reaction mechanism may be similar to that discussed above for the reactions of **24**.



37 **38**

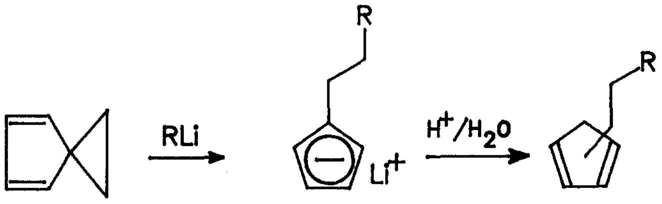
(e) Substituted cyclopentadienes by nucleophilic ring-opening of spiro[2.4]hepta-4,6-diene with organolithium compounds

Reaction of the spiro compound (**39**) with strong nucleophiles RLi yields substituted cyclopentadienyl anions (**40**), which may be used directly in the synthesis of organometallic complexes, or alternatively converted to the corresponding cyclopentadienes (**41**) by hydrolytic workup.

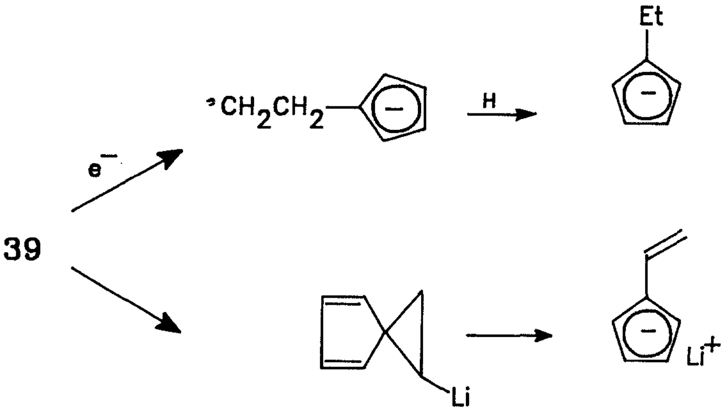
For simple organolithiums (Ph, *n*-Bu, *t*-Bu) [91] the reaction is not of preparative interest, because of two effectively competing reactions:

(a) Reduction of **39** to the ethylcyclopentadienyl anion **42**, by single electron transfer. Compound **42** is also formed from **39** by the action of sodium in liquid ammonia [92] via the same mechanism.

(b) Hydrogen–lithium exchange on **39**, leading to the vinylcyclopentadienyl anion **43**.



39 **40** **41**



42

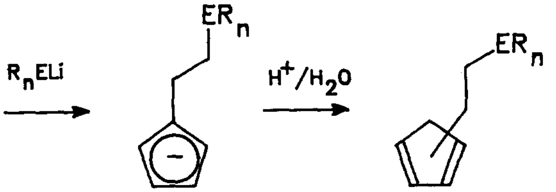
43

The lithium compounds of resonance-stabilised anions give better yields of **40** (e.g. lithio-alkylnitriles [93], 2-/3-lithiomethylpyridine [91], 2-lithiomethylquinoline [91], *trans,trans*-1,3-diphenyl-2-azaallyllithium [91]).

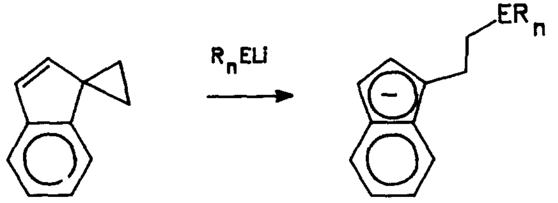
Compound **39** reacts smoothly with a number of organo-element-lithium compounds to form the substituted ethylcyclopentadienyl anions **40**. The reaction has been reported for lithium diphenylphosphide [94] and arsenide [95(a)] as well as other lithiated phosphines [95(b)] and arsines [94,95(c)], triphenylgermyllithium [91] and triphenylplumbyllithium [91]. The "element"-substituted ethylcyclopentadienyl anions [95(b)] have been used for the synthesis of a number of substituted ferrocenes, and the corresponding cyclopentadienes (**44**) are also isolable (where E = P, As ($n = 2$), Ge, Pb ($n = 3$)). The same method has been used for the preparation of the corresponding substituted indenyl derivatives (**46**), from spiro-compound **45** [96].

Nucleophilic cyclopropane-ring-opening of **39** and methyl-substituted derivatives **47** can also be effected with $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, to yield metal-alkyl-substituted cyclopentadienyl anion (**48**) and cyclopentadiene (**49**) [97]. Compounds

39

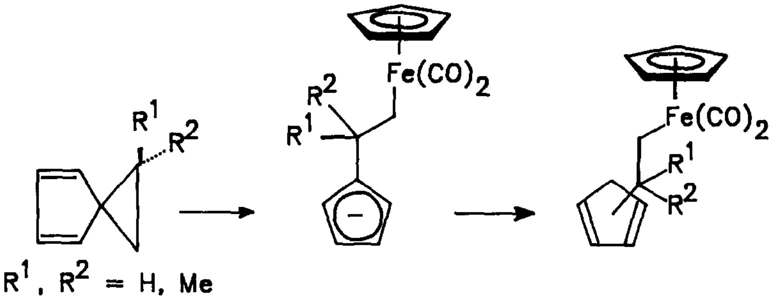


44



45 **46**

48 and **49** can act as functional building blocks in the synthesis of various organometallic complexes [97].



47 **48** **49**

(f) Creation of substituted cyclopentadienyl ligands from organic fragments bonded to a metal

This, in principle, is an attractive route to the synthesis of cyclopentadienyl and substituted cyclopentadienyl ligands. It has indeed been used in a number of instances, but only to produce multiply substituted cyclopentadienyl complexes in the following ways:

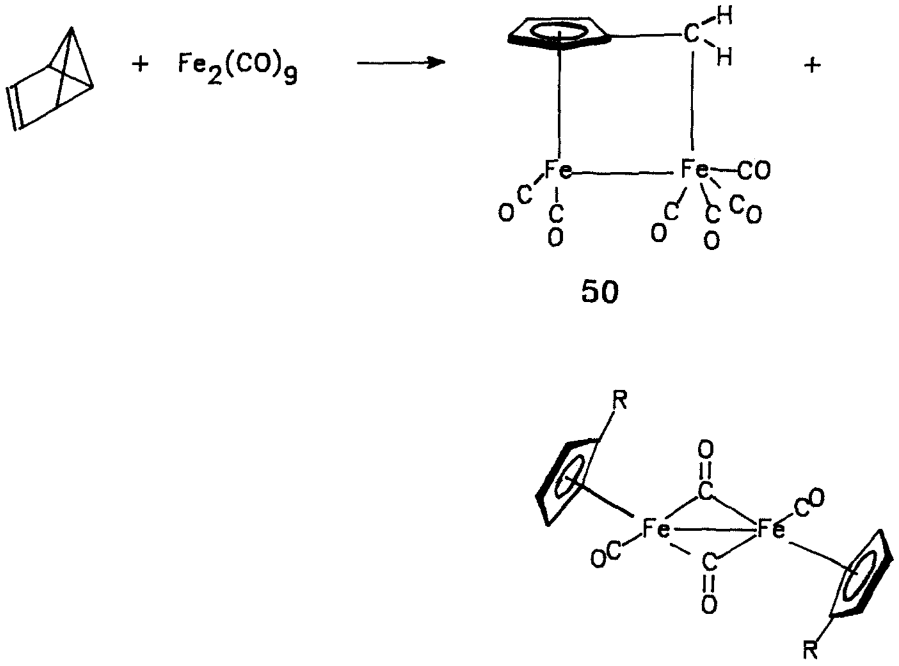
(a) by coupling of metal-bound allyl groups with acetylenes [98];

(b) by addition of diazoacetates to metallacyclopentadienes which have been formed from acetylenes [99];

(c) by addition of acetylenes to W(VI) alkylidenes [100]; and

(d) by cyclic condensation of alkynes [101,102].

An alternative procedure, which involves the synthesis of a cyclopentadienyl ligand from a single organic fragment, is exemplified by the conversion of a polycyclic molecule which contains a vinylcyclopropyl group into a cyclopentadienyl ligand. Benzvalene is an interesting substrate for these reactions. The room temperature reaction of benzvalene in ether with $Fe_2(CO)_9$ gives **50**, **51** and **52** in a ratio of 1 : 1 : 1 [103]. All intermediates involved in this reaction could be characterised when benzvalene was reacted photochemically with $Fe(CO)_5$.

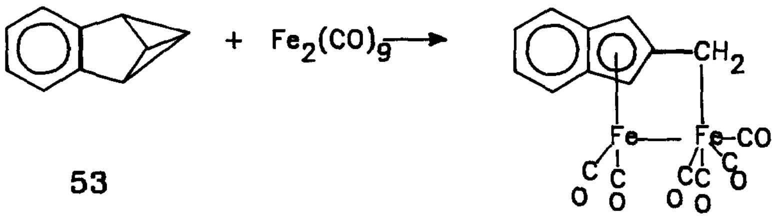


50

R = H (**51**)
R = Me(**52**)

Conversely, the reaction of benzobenzvalene (**53**) with $Fe_2(CO)_9$ yields only the benzofulvene complex **54**, and no π-indenyl complexes analogous to **51** or **52** [104].

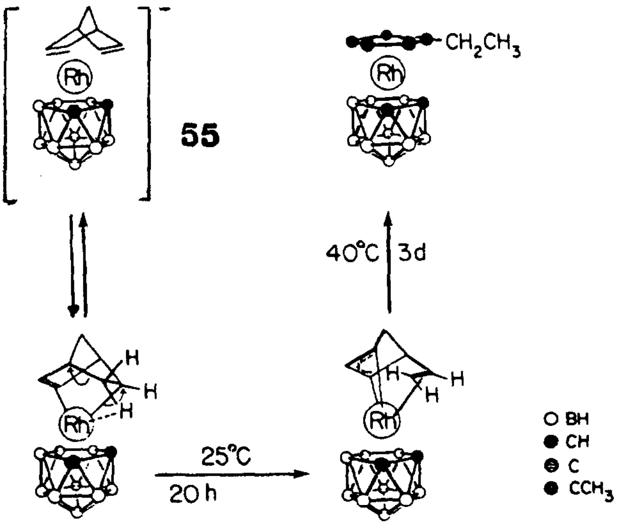
There is also a unique example of the generation of a substituted cyclopentadienyl ligand from a bound norbornadiene ligand. Aromatisation of the norbornadiene ligand of the rhodacarborane anion, [closo-3,3-(η^4-bicyclo(2.2.1)hepta-2,5-diene)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$]$^-$ (**55**), to the η^5-ethylcyclopentadienyl ligand occurred upon protonation of **55**. Both an unstable species (**56**), which contains an agostic H atom,



53

54

and an η^2-vinyl-η^3-cyclopentenyl complex (**57**), have been identified as intermediates and characterised by X-ray diffraction studies [105].



55

56

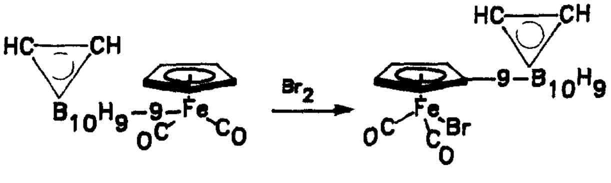
57

(ii) Preparation of monosubstituted cyclopentadienyl ligands according to ligand type

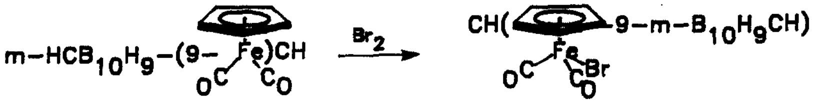
(a) Boron-substituted cyclopentadienylmetal complexes

Although the syntheses of $C_5H_5BEt_2$ [106] and $C_5H_5BCl_2$ [107] have been reported, reactions of boron-substituted cyclopentadienes with metal complexes have only recently been explored [108]. This was achieved by reacting $C_5H_5BMe_2\cdot py$ (synthesised by addition of $Na[C_5H_5]$ to $BMe_2Br\cdot py$) with Co and Rh carbonyl complexes.

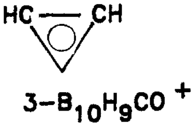
Carboranyl cyclopentadienyl complexes in which the carboranyl group is attached via the B atom to the ring have been synthesised by the metal-to-ring shift reaction [109]. The action of 1 mole of bromine on the cyclopentadienyl-carboranyl-iron-dicarbonyl complexes **58** or **59** in CCl_4 solution at 20°C promotes smooth rearrangement of the complexes, and involves cleavage of the iron–boron σ-bond. A migration of the 9-*o*- or 9-*m*-carboranyl group onto the cyclopentadienyl ring takes place to give π-(*o*-carboran-9-yl)cyclopentadienyl- and π-(*m*-carboran-9-yl)cyclopentadienyldicarbonyliron bromides (**60**) and (**61**), respectively [109(a)]. Similar reactions were found to occur for the 3-*o*-carboranyl group (**62**) [109(b)].



58 **60**



59 **61**



62

Reaction of $(\eta^5\text{-}C_5H_5)M(CO)_3$ (M = Mn, Re) with Li yields the $(\eta^5\text{-}C_5H_4Li)M(CO)_3$ complex. This salt reacts readily with the appropriate boron complex to yield $[\eta^5\text{-}C_5H_4B(OH)_2]M(CO)_3$, which is a useful reagent for preparing $(\eta^5\text{-}C_5H_4BX_2)M(CO)_3$ (X = Cl, Br) complexes [110(a)]. Direct reaction of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ with BX_2Y (X = Y = Br; X = I and Y = I, Ph, Me) in refluxing CS_2 is also possible and gives $(\eta^5\text{-}C_5H_4BX_2)Mn(CO)_3$ in high yield. Further, the iodo complex readily reacts with a variety of Lewis acids to yield $(\eta^5\text{-}C_5H_4Z)Mn(CO)_3$ (Z = Cl, Br, Me) [110(b)]. The reaction is believed to occur by an electrophilic attack at the metal, followed by electrophile transfer to the cyclopentadienyl ring

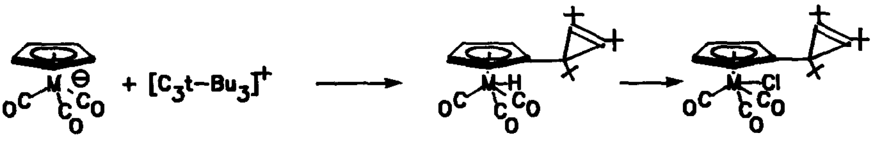
[110(b)]. A further example of this type of reaction involves the shift of BPh_3 on Fe in $[(\eta^5\text{-}C_5H_5)Fe(CO_2)BPh_3]^-$ to the ring to yield ultimately $[(\eta^5\text{-}C_5H_4BPh_3)Fe_2(CO)_4(\eta^5\text{-}C_5H_5)]^-$ [110(c)].

(b) Alkyl-substituted cyclopentadienylmetal complexes

A variety of alkyl substituents have been attached to cyclopentadienyl ligands either prior to or after attachment of the cyclopentadienyl ligand to the metal. Typical strategies that can be employed involve reaction of the metal with an appropriate fulvene, the "Wurtz synthesis", the metal-to-ring shift reaction, etc.

Typical products of the above reactions, $(\eta^5\text{-}C_5H_4R)ML_x$, have been listed in the tables. Some examples involving variations of the more classical methods are described below.

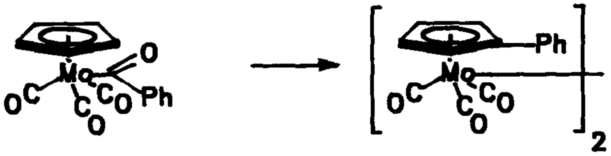
(a) Friedel–Crafts alkylation reactions of "metal-aromatics" have not achieved the importance of the corresponding acylation reactions. Green and Hughes [111] have reported an example of an electrophilic ring substitution reaction of a cyclopentadienyl ring attached to anionic Group 6 metal carbonyls. The reactions of the $(\eta^5\text{-}C_5H_5)M(CO)_3^-$ anions (M = Mo, W) with the 1,2,3-tri-*t*-butylcyclopropenium cation gave, in almost quantitative yield, the hydrido-complexes **63**, which could be converted to the air-stable complexes **64** by treatment with CCl_4. The formation of



63 **64**

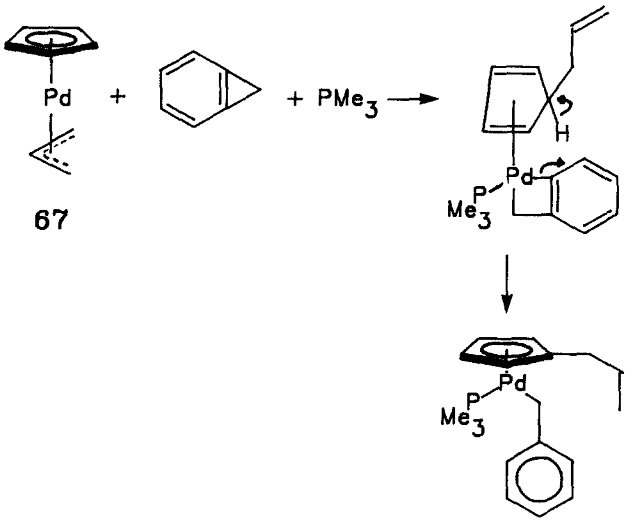
63 most probably proceeds via exo-attack of the electrophile on the cyclopentadienyl ring, the resultant endo-hydrogen undergoing a shift to the metal. It is surprising that the usually preferred one-electron reduction of cyclopropenium cations to the corresponding radicals does not take place in this case. Approach of the electrophile to the metal centre (apparently necessary for the electron transfer to occur) appears sterically precluded in these reactions.

(b) Thermal decarbonylation of benzoyl derivatives $(\eta^5\text{-}C_5H_5)Mo(CO)_3COPh$ (**65**) yields the phenylcyclopentadienyl complex **66** readily and in quantitative yield [112].



65 **66**

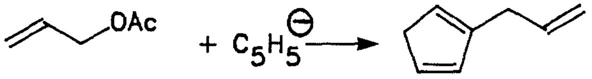
(c) Reaction of cyclopropabenzene with the palladium(II) complex **67** and trimethylphosphine affords the allylcyclopentadienyl complex **68** (80%). It is assumed that **68** is formed by alkylation of the cyclopentadienyl moiety by the allyl ligand. Thus, addition of a cyclopropabenzene molecule results in the opening of one of the two C–C single bonds of the three-membered ring, followed by hydrogen migration to the cyclopropabenzene. The involvement of a metallacycle as an intermediate has been postulated [113].



67

68

(d) The Pd-catalysed alkylation of cyclopentadiene rings has been achieved when allylic esters are treated with $C_5H_5^-$. This route provides high yields of $C_5H_4CH_2CH{=}CHR$ (e.g. **69**) [114].



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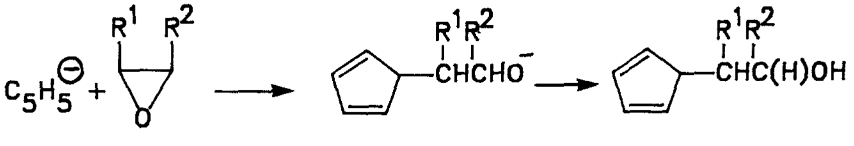
(e) *Two*-carbon moieties can be regiospecifically introduced onto a cyclopentadienyl ring [115]. Thus, reaction of $C_5H_5^-$ with epoxides leads to **70**.



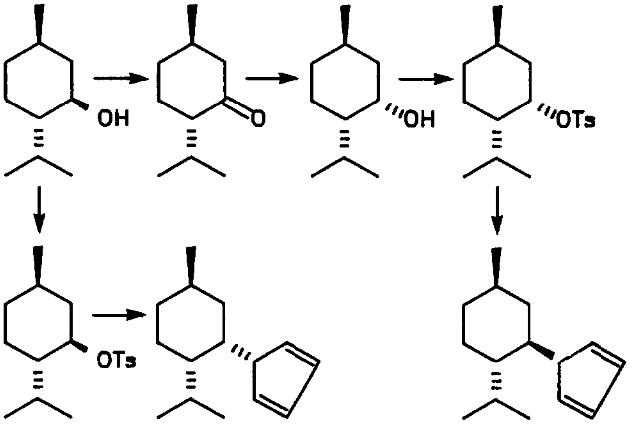
$R^1{=}H$; $R^2{=}H, Me, n\text{-}C_6H_{13}$

70

(f) The cyclopentadienyl ligand can provide a site for introducing chirality into a metal complex. This can be achieved by using a chiral ring substituent or introducing two (or more) different substituents onto a ring [116].

The chiral substituted cyclopentadiene can be synthesised by two methods: (i) addition of a chiral substituent to a cyclopentadienyl anion [117,118], and (ii) conversion of an appropriate fulvene to a substituted cyclopentadienyl anion [119,120].

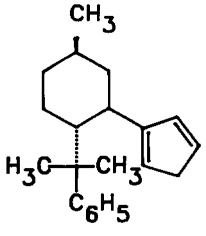
The first example of the synthesis of a cyclopentadiene containing a chiral substituent was reported in 1974 [120]. The chiral substituent was derived from readily available (–)menthol in the sequence shown below.



71 **72**

The menthyl (**71**) and neomenthyl (**72**) cyclopentadiene derivatives have since been attached to a variety of metals, and their effect in catalytic reactions has been investigated [117].

Other chiral substituents have been attached to cyclopentadiene and have generated **73** [117] and **74** [119,120].



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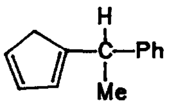
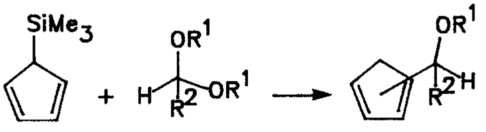


74

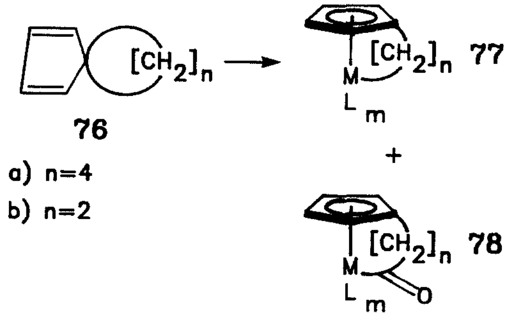
The condensation of $C_5H_5SiMe_3$ with acetals, ketals and orthoesters also yields a range of cyclopentadienes with chiral substituents (**75**) [121].

(g) Alkylene-bridged σ-alkyl-π-cyclopentadienylmetal complexes can be pre-



75

pared by metal-induced ring-opening of spiro[*n*.4]alkadienes. Spiro[*n*.4]alkadienes (**76**) react with complexes of zero-valent transition-metal complexes (e.g. iron and molybdenum) at room temperature with C–C bond cleavage to give the alkylene-bridged σ-alkyl-π-cyclopentadienylmetal complexes (**77**) or, with simultaneous CO insertion, to give the corresponding acyl derivatives (**78**) [122,123(a)]. More drastic reaction conditions lead to polynuclear complexes with a substituted cyclopentadienyl ligand [123(b)]. The driving force for these reactions is the formation of the cyclically conjugated cyclopentadienyl system [123(c)].



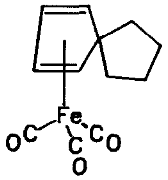
76

a) n=4
b) n=2

77

78

The reaction of spiro[4.4]nona-1,3-diene (**76a**) with $Fe_2(CO)_9$ in refluxing benzene yields **79** as the major product in ca. 40% yield. Using careful workup procedures, it is, however, possible to obtain the alkylene-bridged σ-alkyl-π-cyclopentadienyl complex **80** [122]. Compound **76a** also reacts with molybdenum(0)-compounds of the type $Mo(CO)_3L_3$ in hexane at room temperature to give **81**.



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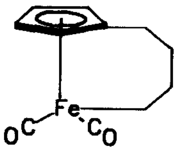

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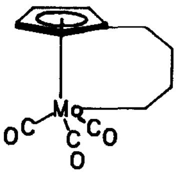
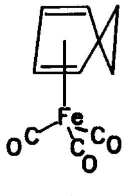


81

The reaction of spiro[2.4]hepta-4,6-diene (**76b**) with iron carbonyls has been investigated by several groups. Hallam and Pauson [123(b)] performed the reaction with iron pentacarbonyl at 140°C and could not isolate mononuclear complexes. DePuy et al. [124] obtained a compound in 38% yield from $Fe_2(CO)_9$ which they incorrectly assigned as **82**, and which is now known to be **83** [122]. Reinvestigation of the reaction by Eilbracht [122] showed that, under the conditions described [124], only a small amount of the product is obtained. By variation of the workup procedure, the yield could be increased to 22% [122]. Spiro[2.4]hepta-4,6-diene (**76b**) reacts with $Mo(CO)_3L_3$ at room temperature to give the molybdenum complex **84** in 17% yield.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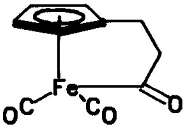
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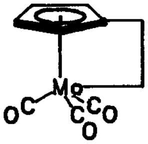
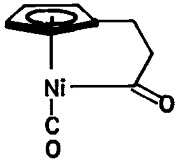

84

Heating of spiro[2.4]hepta-4,6-diene (**76b**) with $Ni(CO)_4$ in refluxing hexane yields the bridging acylcyclopentadienyl complex **85** in 18% yield and the dinuclear di(cyclopentadienyl)dinickel compound **86** in 19–49% yield [122].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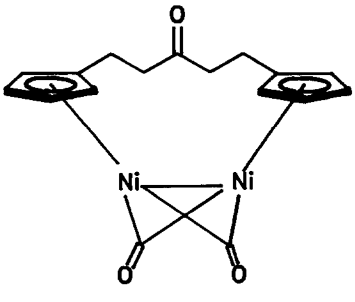
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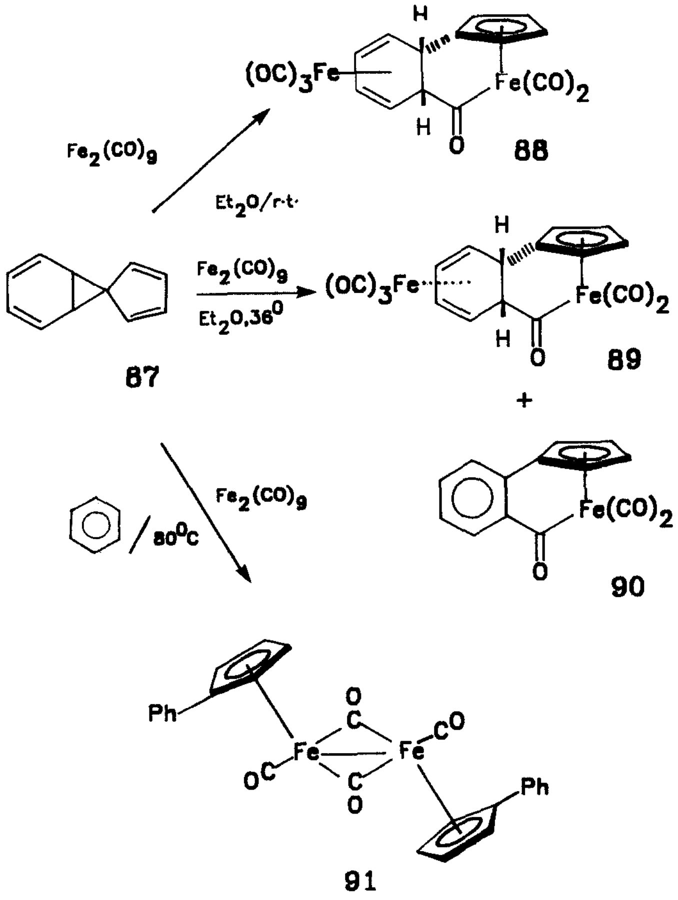
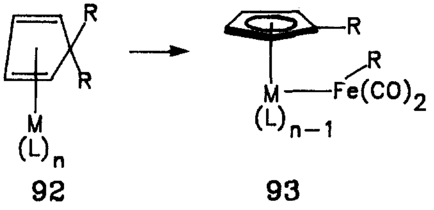
The formation of an acyl complex (**88**) analogous to **83** has been reported from the reaction of spiro[2.4]cyclopentadiene-1,7′-norcara-2′,4′-diene (**87**) with $Fe_2(CO)_9$ at room temperature in ether [123(a)]. If the reaction is conducted at a slightly higher temperature (36°C) the acyl-complex **89** (stereoisomer of **88**) is obtained in 78% yield, as well as **90** in 5% yield. The reaction in benzene at 80°C yielded the phenylcyclopentadienyliron dimer **91**, a reaction that could be of preparative interest. No yields have been reported for this reaction [123(a)].

The corresponding reactions of substituted derivatives of **76b** and **87** have also been reported [122,123(a)].

The primary step in these reactions is probably the formation of a cyclopentadiene complex of general type **92** (e.g. **79**, **82**), which, after loss of a further ligand L, is transformed to the bridging σ-alkyl-π-cyclopentadienyl complexes **77**, i.e. via an "oxidative addition" of the metal to the C—C bond. In the presence of extra $Fe_2(CO)_9$, the product obtained is **93**. The reactions of **76a** show that the metal-induced C—C



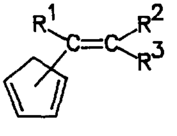


cleavage reactions are not restricted to strained hydrocarbons. The high tendency to form the π-cyclopentadienyl ligand supports the C–C cleavage reactions.

(c) Vinyl substituents

Ligands which contain vinyl substituents (**94**) are useful precursors in the synthesis of polymers. Attachment of metal fragments to the polymer produces "dangling" metal moieties (**95**) [17] and these polymer-supported complexes can be used in catalytic reactions.

An obvious route to **94** is via the addition of a suitable base to a substituted fulvene. In initial studies in this area, 6,6-dimethylfulvene was reacted with CPh_3^- to give **96**, which was not isolated [125(a)]. Later studies reported the use of bases such as NH_2^- [34(b)], *t*-BuO^- [125(b)] and PPh_2CH_2Li [72(c)]. Only in the latter case was the vinylcyclopentadienyl salt (**96**) isolated, although the ligand could be trapped by reaction with suitable metal salts [125(b)]. Reaction of a metal carbonyl directly with a fulvene also provides a route to the vinylcyclopentadienyl ligand. In the earliest study in this area, reaction of 6,6-dimethylfulvene with $Co_2(CO)_8$ gave an inseparable mixture of **97** and **98** [126]. This route has been used by other workers since these early studies (see Sect. D). An alternative route which has given the required complex **99** as one component in a mixture of products is by the reaction of spirocyclopentadienes with metal carbonyls [122].



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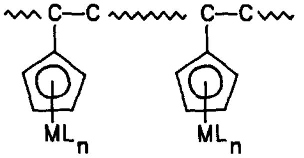

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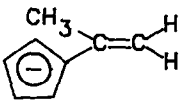

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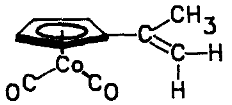

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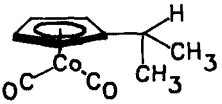

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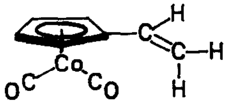


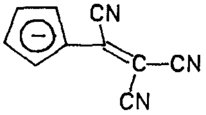
99

Direct reaction of $Tl[C_5H_5]$ with $(CN)_2C{=}C(CN)_2$ produces the stabilised vinyl ligand **100**, which has been reacted with numerous metal carbonyl complexes to produce $(\eta^5\text{-}C_5H_4C(CN){=}C(CN)_2)ML_x$ complexes (see Sect. D) [127]. The major breakthrough in this area of chemistry occurred with the publication in 1982 of the synthesis of **96** and **101** from the reaction of 6,6-dimethyl- and 6-methylfulvene in the presence of the base lithium diisopropylamide [69]. This reaction produced lithium salts of **96** and **101** in high yield (80–90%) as air-sensitive white solids. Since this publication, the vinyl salts have been reacted with many metal complexes by Rausch, Pittman and others to produce $(\eta^5\text{-}C_5H_4\text{vinyl})ML_x$ complexes, which are discussed more fully in Sect. D.

(d) Syntheses of acyl- and related cyclopentadienylmetal complexes

The three most important methods which have found widespread use in the syntheses of acyl- and related substituted cyclopentadienylmetal complexes are:

(a) Friedel–Crafts acylation of "metal aromatic" systems;



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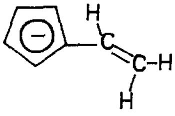

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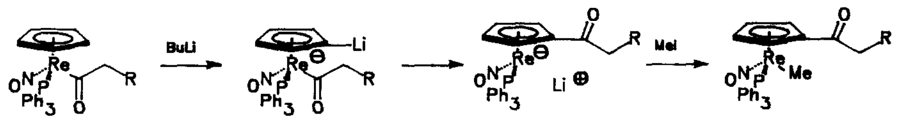
(b) metal-to-ligand shift of the substituent; and

(c) the reaction of acyl-substituted cyclopentadienide reagents such as $Tl[C_5H_4R]$, $Na[C_5H_4R]$, and $Li[C_5H_4R]$ ($R=$acyl) with appropriate transition metal halide fragments. Methods (a) and (b) are related, as it has been postulated that initial attack of an electrophile E^+ in reactions of the type "a" occurs at the metal centre, with subsequent synthesis of a C–E bond and elimination of H^+.

(1) Electrophilic "aromatic" substitution reactions. In 1952, Woodward et al. reported that ferrocene underwent Friedel–Crafts acylation [128,129]. Shortly thereafter, ferrocene was shown to undergo a number of other "aromatic-type" substitution reactions. Many other η^5-cyclopentadienylmetal compounds have since been shown to undergo electrophilic aromatic substitution, but because of the limited scope of these reactions, alternative methods for the synthesis of acyl-substituted η^5-cyclopentadienylmetal compounds have been sought and found [16].

(2) Metal-to-ligand shift reactions. During the course of the shift reaction, the remaining ligand set associated with the metal may undergo rearrangement such that the overall migration reaction occurs with retention or inversion of configuration at the central metal atom.

Gladysz and co-workers have reported recently [130,131] that acylrhenium complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2R)$ (**102**), are preferentially deprotonated by BuLi on the cyclopentadienyl ring, and that the anions thus generated undergo a rapid metal-to-ring migration of the acyl ligand. The resulting rhenium anions were trapped by methyl iodide.



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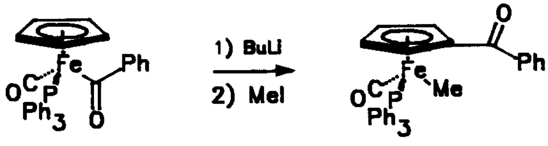
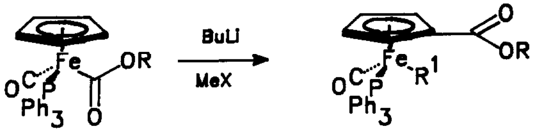
By isotope labelling and stereochemical studies, it could be demonstrated that this migration reaction is intramolecular in nature, and that the migration and subsequent methylation occur with retention of configuration at the rhenium atom. The hydride $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)H$ is also deprotonated at the cyclopentadienyl ring, but hydride migration followed by methylation at the rhenium atom to give $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)Me$ occurs with racemization at the rhenium atom [131].

Davies and co-workers later showed that an equivalent reaction occurs for iron and ruthenium complexes [132]. Treatment of the benzoyliron complex **103** with BuLi in THF at −40°C followed by addition of methyl iodide generated the methyliron complex **104**. The metalla-ester complexes **105** (R = Me, i-Pr, *t*-Bu) exhibit similar reactivity on treatment with BuLi (or BuLi/TMEDA) followed by addition of methanol or methyl iodide to give the iron hydrides **106a** or methyl complexes **106b**, respectively. In contrast to the base migration of acyl ligands, those of the carboxyalkyl ligands are not stereospecific. Similar reactions of the separate diastereomers of the corresponding l-menthyl esters (R–**105**, S–**105**, R = l-menthyl) each give the same 1 : 1 mixture of epimers, indicating that the stereochemistry at iron is scrambled during the transformation of **105** to **106** (R = l-menthyl). Problems can arise with primary alkanoyl complexes (**107**), because deprotonation of the cyclopentadienyl ring competes with enolate formation. At −78°C they undergo clean deprotonation on the acyl ligand to generate stereoselectively the corresponding E-enolates (**108**), which have been utilised in a variety of carbon–carbon bond forming reactions. At



103 **104**



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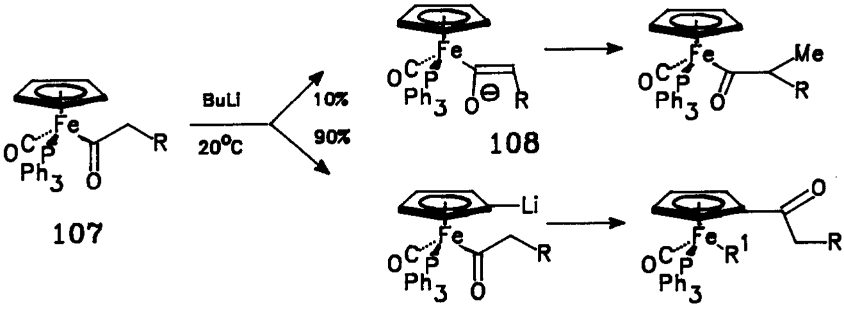
106 a) R^1=H (X=OH)
b) R^1=Me (X=I)



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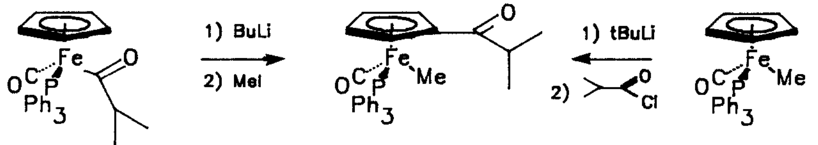
108

109 a) R^1=H
b) R^1=Me

20°C, deprotonation of the cyclopentadienyl ring competes with enolate formation, as evidenced by formation of the iron hydrides (**109a**) or methyliron complex (**109b**) after addition of methanol or methyl iodide respectively. These rearrangements take place with retention of configuration at iron, as shown in experiments using the diastereomeric complexes (**107**) with chiral R (R = 2-hexyl). The isobutyryl complex (**110**) is deprotonated exclusively on the cyclopentadienyl ring by *n*-BuLi at −40°C to give, after methylation, the methyl complex (**111**). This is independently accessible by treatment of **112** with *t*-BuLi followed by 2-methylpropanoyl chloride.



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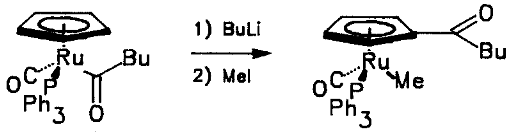
Treatment of the acylruthenium complex (**113**) with *n*-BuLi at −78°C followed by MeI gave the methylruthenium complex (**114**) as the exclusive product [132].

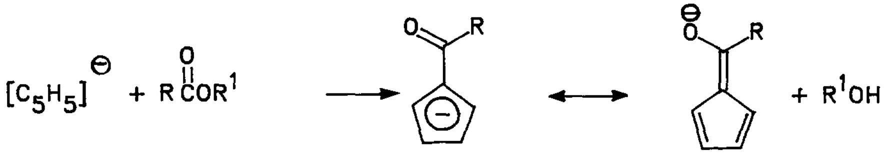


113 114

(3) Use of acyl-substituted cyclopentadienide reagents. Derivatives of sodium cyclopentadienide carrying aldehyde, ketone, or ester functionalities can be synthesised easily following Thiele's method [24]. This procedure has been widely exploited by Hafner et al. [133], Rausch and co-workers [134], and others [135,136(a)].

The reactions of sodium cyclopentadienide with either ethyl formate, methyl acetate, or dimethyl carbonate gave the corresponding sodium compounds of formyl-, acetyl- or carbomethoxycyclopentadienide (**115**), respectively in 60–90% yield. Potassium formylcyclopentadienide has been prepared by the reaction of potassium cyclopentadienide and ethyl formate [136(a)]. Condensation of cyclopentadienide with diethyl oxalate in the presence of sodium ethoxide gave sodium (ethoxycarbonylformyl)cyclopentadienide (**116**) [24,136(b)]. Acetyl- and carbomethoxycyclopentadienide anions (with n-Bu_4N^+ as counter-ion) have also been prepared by cathodic reduction of the corresponding 1,1′-disubstituted ferrocenes [137].

Other important pathways to acyl-cyclopentadienides start from Thiele's acid (**117**), which was originally prepared by Thiele on reaction of gaseous CO_2 with potassium cyclopentadienide suspended in benzene [24]. Variations of the method employ cyclopentadienylmagnesium bromide (from cyclopentadiene and ethylmagnesium bromide) and excess solid CO_2 [136–138].



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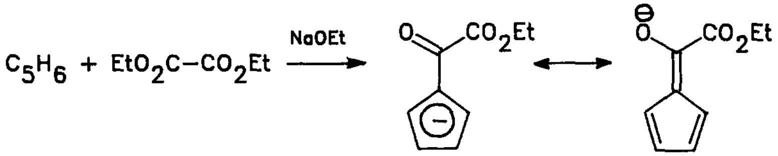

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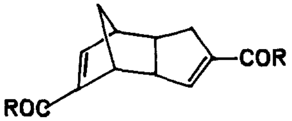


R=OH ("Thiele's acid")

117

Arthurs et al. prepared various esters of thallium(I) cyclopentadienide [136], by esterification of Thiele's acid, and "cracking" and distillation of these esters at 220°C and 18–20 mm Hg directly into an aqueous solution of thallous acetate and KOH. This procedure gives the substituted thallium cyclopentadienides in 60–65% yield. The lithium derivatives of C_5H_5COR (R = Me, *t*-Bu, OMe) have been reported [140(a),(b)]. Alkaline hydrolysis of 6-(dimethylamino)-6-methylfulvene yields $C_5H_4COMe^-$, which after treatment with acid gives C_5H_5COMe [133,139].

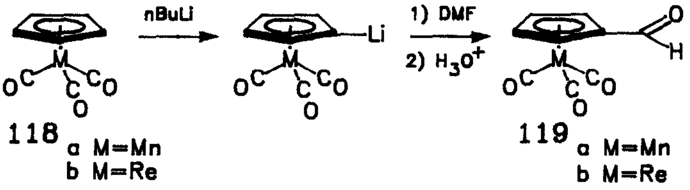
Thallium(I) acetylcyclopentadienide and thallium(I) formylcyclopentadienide were prepared in 90–95% yield by metathesis involving equimolar aqueous solutions of the potassium salts and thallium(I) acetate [136(b)]. The thallium cyclopentadienide can be reacted with RCOI (R = Me, n-C_7H_{15}, i-Pr, *t*-Bu) to give C_5H_5COR in good yield. Reaction with RCOCl proved too slow [141].

Studies have been undertaken on Li[C_5H_4COR] to establish the energy barrier to rotation of the acyl group around the bond connecting the substituent to the cyclopentadienyl ring. By means of ^{13}C NMR spectroscopy it has been possible to establish that rotation is slow for R = Me but more rapid for R = *t*-Bu. The difference in behaviour was ascribed to steric hindrance in the ground state of the complexes [140(b)].

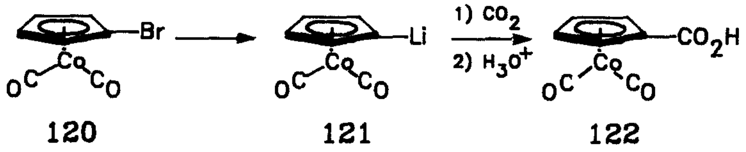
Many of these functionally substituted cyclopentadienide reagents have been used successfully in the syntheses of acylcyclopentadienylmetal complexes. For example, Rausch and co-workers [16,134] have used organosodium reagents to synthesise many new acyl-substituted organometallic compounds.

(4) Acylcyclopentadienylmetal complexes by oxidation of alkylsubstituents on the cyclopentadienyl ring. Carboxy- and 1,1′-dicarboxy-cobalticinium complexes have been prepared by aqueous potassium permanganate oxidation of the methyl groups in the methylcobaltocene cations [142,143].

(5) Metallation of the cyclopentadienyl ring. Formylcyclopentadienyltricarbonylmanganese and -rhenium, (**119a** and **119b**), have been prepared by lithiation of the corresponding unsubstituted complexes **118a** and **118b**, respectively. Reaction of these intermediates with DMF and hydrolytic workup, gave the products in 75% and 91% yield respectively [144].



Metallation of the cyclopentadienyl ring in organometallic complexes may also be achieved by lithium–halogen exchange. An example is the reaction of (η^5-bromocyclopentadienyl)dicarbonylcobalt (**120**) with *n*-BuLi in diethyl ether at −78°C. The organolithium intermediate (**121**), unstable even at this low temperature, reacts with CO_2 to form (after hydrolysis) a carboxylic acid derivative (**122**) [80]. The carboxylic

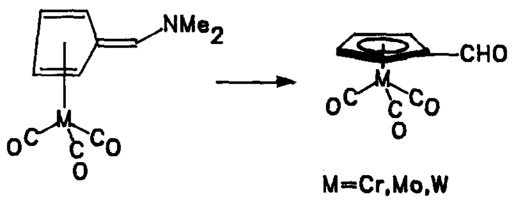


acids of (η^5-C_5H_5)Fe$(CO)_2$R (R = Ph, cymantryl, CH_2Ph) were obtained in high yields via ring metallation with BuLi followed by treatment with CO_2 [145].

(6) Other methods. Formylcyclopentadienyl complexes of Group 6 have been obtained from the corresponding *N*,*N*-dimethylfulvene complexes (**123**) [146].

(e) Syntheses of phenylcyclopentadiene and other arylcyclopentadienes

Most of the procedures described for the syntheses of alkylcyclopentadienes (Sect. C.(ii)(b)) and vinylcyclopentadienes (Sect. C.(ii)(c)) are not applicable for the syntheses of arylsubstituted cyclopentadienes.

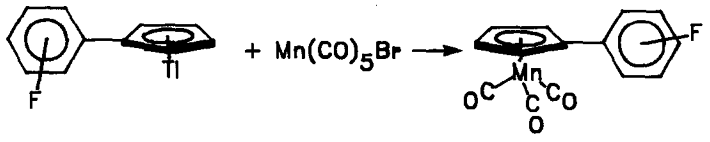


123

M=Cr,Mo,W

Impure phenylcyclopentadiene (**22a**) was prepared for the first time by Pauson [30]. The reaction of phenyllithium with cyclopent-1-en-3-one, followed by dehydration of the intermediate 1-phenylcyclopent-2-en-1-ol yielded the product that was characterised as a substituted ferrocene after reaction with $FeCl_2$. Later, Riemschneider and Nehring [83] were able to obtain pure phenylcyclopentadiene, which mainly exists as the 1-isomer, using the same method (i.e. by addition of PhLi or PhMgBr to cyclopentenone) as well as by the reaction of sodium ethyl acetoacetate with α-bromoacetophenone, followed by reduction of the resulting 1-phenylcyclopent-1-en-3-one.

Anion **22b** and its substituted phenyl derivatives are also accessible by the reaction of iodobenzenes with cyclopentadienylcopper(I) tributylphosphine (Sect. C.(i)(c)) [84] and by anionic (4+2)-cycloreversions of the 7-norbornyl anion [85]. The latter reaction was used to prepare polymer-attached analogs of **22** (see later). Treatment with BuLi, NaH or Na/K alloy yields the Li, Na or K salts, respectively, while treatment with TlOEt yields the thallium derivative [147]. The *m*- and the *p*-fluoro-substituted phenylcyclopentadienes have been prepared by analogy to **22** from the reaction of *m*- (or *p*-) fluorophenylmagnesium bromide and cyclopentenone [147,148]. The latter complex was used in the synthesis of the corresponding substituted cymantrene derivatives (**124**) [147].



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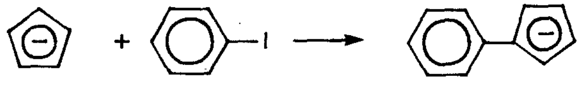
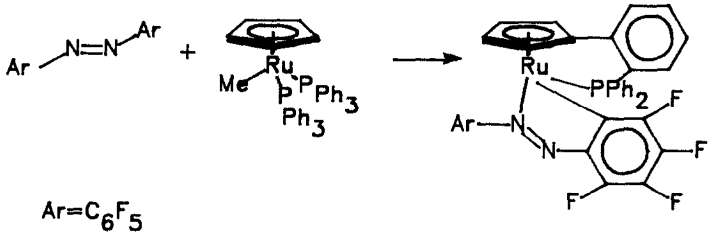
The thallium derivative of unsubstituted phenylcyclopentadiene has also been described recently [136(b)]. An alternative approach to the synthesis of the phenylcyclopentadienyl anion (**22b**) and other arylcyclopentadienyl anions has been investigated, making use of the $S_{RN}1$ coupling reaction between the cyclopentadienide anion and halobenzenes or halonaphthalenes, with moderate success [149(a)].

Many phenyl-substituted cyclopentadienyl complexes have become accessible via a metal-to-cyclopentadienyl migration of the phenyl substituent, similar to the corresponding alkyl migrations (see Sect. C.(ii)(b)).



22b

Finally, a very unusual product (**125**) has been obtained from the reaction of decafluoroazobenzene with (η^5-C_5H_5)Ru(PPh_3)$_2$(Me) [149(b)].



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(f) Cyano-substituted cyclopentadienylmetal complexes

Two novel routes have been used to synthesise metal complexes containing a C_5H_4CN ligand. Reaction of K[C_5H_4CN] with (η^5-C_5H_5)Mn(CO)$_3$ (M = Mn, Re) results in ring exchange and formation of the ring substituted complex [149(c)]. An alternative, and more unusual, reaction involves a ring contraction. Thus, when [(η^6-$C_6H_5N_3$)Mn(CO)$_3$]PF_6 is heated in vacuo, a low yield (22%) of (η^5-C_5H_4CN)Mn(CO)$_3$ is formed [149(d)].

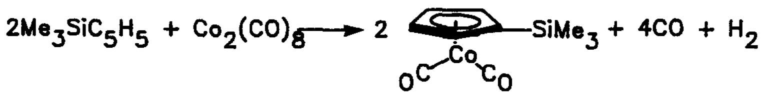
(g) Syntheses of silyl-, germyl-, and stannyl-cyclopentadienyl complexes

The silyl substituent bonded to a cyclopentadienyl ring can, for most purposes, be regarded as being similar to alkyl substituents. Different substituents can be attached to the Si, Ge and Sn ligands but typically the trimethyl substituent has been used. Silyl-substituted cyclopentadienyl complexes have been obtained by various methods.

(a) Reaction of the silyl-substituted cyclopentadienyl anion with metal carbonyls. The carbon–silicon bond appears to be sufficiently stable to resist cleavage in many reactions. On the other hand, silicon is larger than carbon and therefore more easily susceptible to nucleophilic substitution.

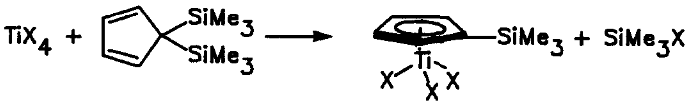
The thermal reaction between trimethylsilylcyclopentadiene and the neutral binary metal carbonyls results in products in which the silicon–ring bond remains intact. For example, cobalt carbonyl and trimethylsilylcyclopentadiene undergo reaction at ca. 40°C to produce **126** in good yield [150]. At higher temperatures, (η^3-trimethylsilylcyclopentenyl)cobalt tricarbonyl appears to be formed as an additional product.

On the other hand, on reaction of trimethylsilylcyclopentadiene with titanium,



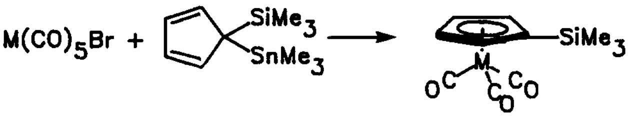
126

niobium and tantalum halides, the silyl group is replaced. This represents a convenient route to (η^5-C_5H_5)$TiCl_3$, (η^5-C_5H_5)$TiBr_3$, (η^5-C_5H_5)TiI_3, (η^5-C_5H_5)$NbCl_4$, and (η^5-C_5H_5)$TaCl_4$ [151]. Routes involving the use of bis(trimethylsilyl)cyclopentadiene have been described for the syntheses of the analogous complexes (η^5-$C_5H_4SiMe_3$)TiX_3 where X = Cl, Br, or I (**127**) [151].



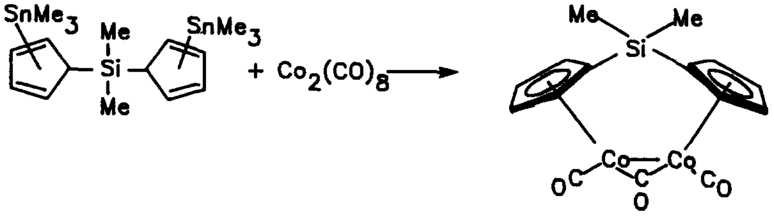
127 (X=Cl,Br,I)

In the reaction of (trimethylsilyl)(trimethylstannyl)-cyclopentadiene with manganese or rhenium pentacarbonyl bromide, exclusive cleavage of the organotin group occurs, yielding **128** (M = Mn, Re) with no trace of the organotin analogue [150].



128 (M=Mn,Re)

The reaction between bis(trimethylstannylcyclopentadienyl)-dimethylsilane and dicobalt octacarbonyl yielded **129**, with $SnMe_3Co(CO)_4$ as byproduct [151].



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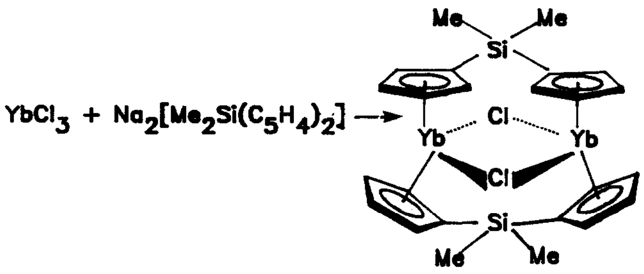
(b) Reaction of the Na, Li, or Tl silyl-substituted cyclopentadienides with metal halides. These reactions follow the same principles as for the alkyl-substituted reagents and need no further discussion here. The method has been extended to the preparation of silylcyclopentadienyl lanthanide complexes, a recent example being the synthesis of **130** [152].

(c) Ring metallation reactions. Two examples of this reaction type, giving **131** and **132**, are shown below [153].



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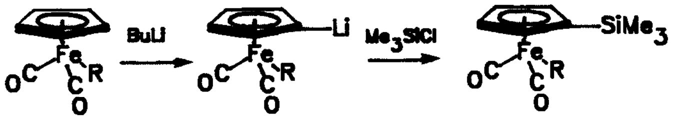
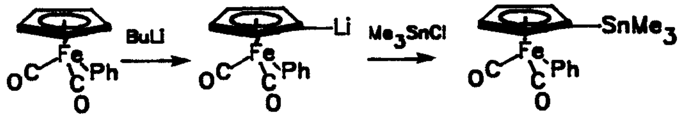


R=Ph,CH$_2$Ph **131**



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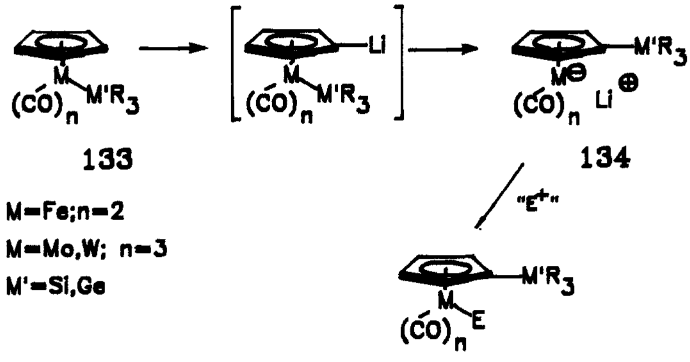
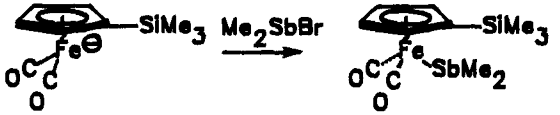
(d) Metal-to-ring shift reactions. Lithiation of the cyclopentadienyl ligand in complexes with a metal–silyl or –germyl bond (**133**) leads to rapid ligand shift and formation of the anionic metal complexes (**134**), which may be intercepted with electrophiles E$^+$ to form **135**.



133 **134** **135**

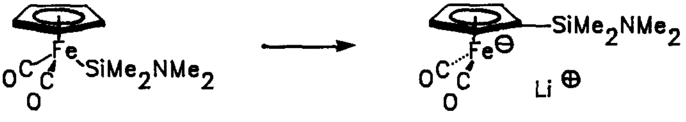
M=Fe;n=2
M=Mo,W; n=3
M'=Si,Ge

$MeSiHCl_2$, Me_2SbBr and RX (R = alkyl) have also been used as electrophiles for the interception of **136**, and yield the corresponding complexes, e.g. **137** [155].

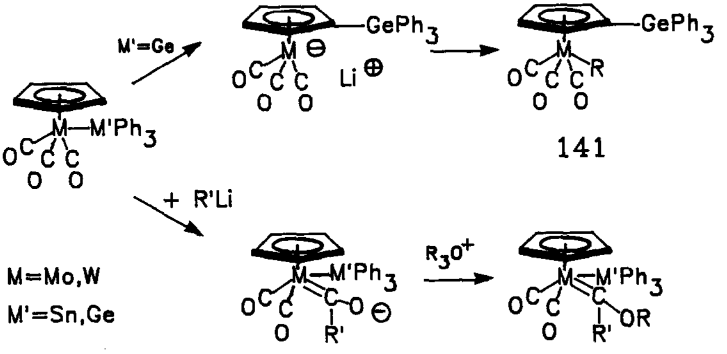


136 **137**

Malisch and co-workers [154] were able to prepare the anionic complex **138** (analogous to **136**) by treating **139** with $LiNMe_2$ in benzene. The migration of the germyl group, corresponding to the silyl migrations, has been observed by Dean and Graham [155]. Reaction of a series of compounds $(\eta^5\text{-}C_5H_5)M(CO)_3M'Ph_3$ (M = Mo, W; M′ = Ge, Sn) with organolithium reagents, followed by alkylation with a trialkyloxonium salt, yielded the corresponding Fischer-type carbene complexes (**140**). The



139 **138**



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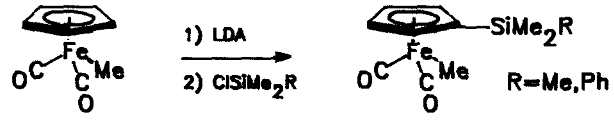
140

reaction took a different course in some instances, and products of formula $(\eta^5\text{-}C_5H_4GePh_3)M(CO)_3R$ (**141**) were obtained. Their formation depends on the central metal and on the organolithium reagent used. The tendency to form ring-substituted products was found to increase with the basicity of the lithium reagent used; also, tungsten complexes seemed to be more prone to yield this type of product than those of molybdenum.

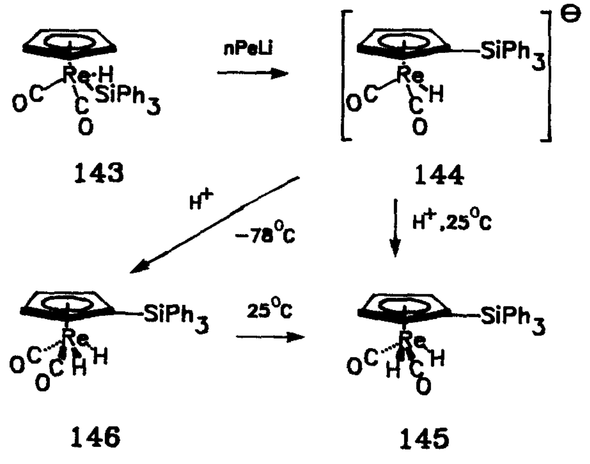
The scope and mechanism of the silyl group migration in complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2R$ have been further investigated by Berryhill et al. [156(a)]. Crossover experiments show the reaction to be intramolecular, and a mechanism involving deprotonation of the cyclopentadienyl ligand followed by silyl group migration utilising a silicon d orbital was presented. A ring-deprotonated species could not be observed or trapped, but an independent experiment with $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ showed that compounds of this type can be deprotonated. Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with LDA followed by TMSCl gave the ring-silylated product (**142**).



142

The regiochemistry of the complexes formed by silyl group migration to a substituted cyclopentadienyl ligand was found to be affected by the size of the substituent. Both 1,2- and 1,3-disubstituted products were obtained when the substituent was methyl, while with bulkier substituents only 1,3-disubstituted products were obtained.

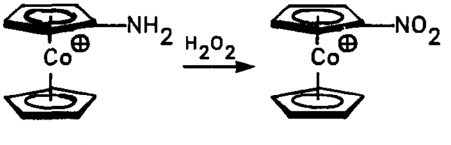
Metal-to-cyclopentadienyl ring migration of a silyl group has also been observed upon deprotonation of *cis*-$(\eta^5\text{-}C_5H_5)Re(CO)_2(SiPh_3)H$ (**143**) by neopentyllithium at −78°C in THF. The deprotonation product was shown by spectroscopic and chemical methods to be $Li[(\eta^5\text{-}C_5H_4SiPh_3)Re(CO)_2(H)]$ (**144**). The formation of **144** was again explained by initial deprotonation of the cyclopentadienyl ligand, followed by an intramolecular silyl-group migration [155]. Protonation of the anion at room temperature gave *trans*-$(\eta^5\text{-}C_5H_4SiPh_3)Re(CO)_2H_2$ (**145**), whereas at −78°C the major product was the corresponding *cis*-isomer (**146**), which isomerises slowly to **145** at room temperature [156(b)].



(h) Syntheses of nitro-cyclopentadienyl complexes

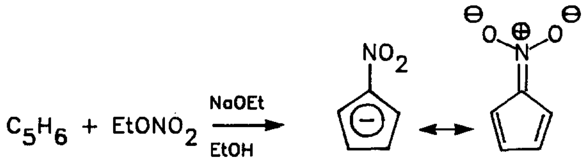
(1) Via electrophilic substitution. Nitroferrocene and nitrocymantrene have been prepared from the parent compounds using multistep procedures involving electrophilic substitution [134].

(2) By oxidation of amino groups. In contrast to aminoferrocene, which is destroyed rapidly by oxidizing reagents (e.g. atmospheric oxygen, nitrous acid) the aminocobalticinium ion (**147**) can be oxidized by hydrogen peroxide to the nitro derivative (**148**) [142].



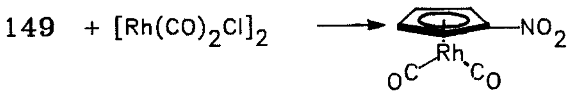
147 148

(3) Syntheses employing nitrocyclopentadienyl derivatives. In 1900, Thiele obtained sodium nitrocyclopentadienide (**149**) (the first cyclopentadienylmetal compound) from the reaction of cyclopentadiene and ethyl nitrate in the presence of sodium ethoxide [24].



149

Compound **149** is accessible by this procedure in yields of 16–21% [157(a)]. The lithium derivative has been prepared analogously from lithium cyclopentadienide and ethyl nitrate in THF [157(b)]. Compound **149** has so far found only very limited application in the synthesis of (η^5-nitrocyclopentadienyl) transition metal complexes, partly owing to the diminished reactivity of Na[$C_5H_5NO_2$] relative to Na[C_5H_5] and Li[C_5H_5]. This diminished reactivity is due to an increased stability of the resonance stabilized anion. Further, introduction of the nitro group results in potential competing redox reactions. For example, attempts to prepare 1,1′-dinitroferrocene by the reaction of **149** with ferrous chloride were unsuccessful [157(c)], and the reaction of **149** with $Cr(CO)_6$ followed by nitrosylation gave a low yield of (η^5-$C_5H_4NH_2$)$Cr(CO)_2NO$ instead of the expected (η^5-$C_5H_4NO_2$)$Cr(CO)_2NO$ [134]. A reaction between $C_5H_5NO_2$ and dichlorotetracarbonyldirhodium did, however, give (η^5-nitrocyclopentadienyl)dicarbonylrhodium (**150**) in 22–30% yield [134], the first and, so far, only η^5-nitrocyclopentadienyl transition metal complex to be synthesised directly from the nitrocyclopentadienide anion.



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(i) Syntheses of amino-substituted cyclopentadienyl complexes

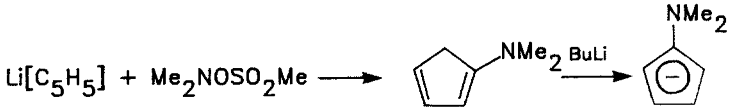
In view of the extraordinary importance of the cyclopentadienyl ligand in organometallic chemistry, it is surprising how few cyclopentadienylamines ($C_5H_5NR_2$) and aminosubstituted cyclopentadienylmetal complexes are known [16]. Basically, three methods are conceivable for the preparation of such complexes:

(a) from cyclopentadienylamines or their anions $(C_5H_4NR_2)^-$;

(b) by conversion of a functionalised cyclopentadienylmetal complex containing N-functionalities or acyl-functionalities to the amino-functional complex; and

(c) direct amination of the unsubstituted cyclopentadienyl ligand.

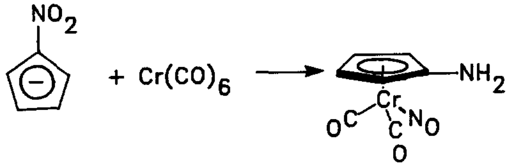
(1) Syntheses employing aminocyclopentadienes or aminocyclopentadienyl anions. *N*,*N*-Dimethylcyclopentadienylamine, mostly existing as the 1,3-cyclopentadienyl isomer (**151a**), is accessible in 47% yield by electrophilic amination of cyclopentadienyllithium with *N*,*N*-dimethyl-*o*-(methylsulphonyl)hydroxylamine in THF at −20°C. Compound **151a** can be metallated with *n*-BuLi almost quantitatively to yield **151b**, the only amino-substituted cyclopentadienide salt known [158].



151a **151b**

(2) Indirect syntheses of amino-substituted cyclopentadienyl complexes. Cyclopentadienyl complexes carrying the primary amino substituent are, in principle, accessible from the corresponding nitro compounds. This route has so far only been used once and then "accidentally". Thus when the synthesis of $(\eta^5\text{-}C_5H_4NO_2)Cr(CO)_2NO$ was attempted in the usual way, by reacting lithium nitrocyclopentadienide first with $Cr(CO)_6$ and then with acetic acid followed by *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide, $(\eta^5\text{-}C_5H_4NH_2)Cr(CO)_2NO$ (**152**) was isolated as the only product from this reaction in 7% yield [134].

A general method for the preparation of ferrocenylamines involves the reactions of ferrocenyl bromide, with the sodium salt of an amine or amide in the presence of



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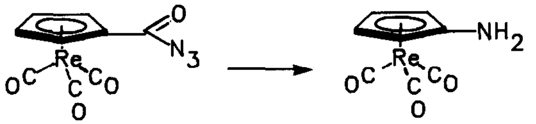
copper(I) bromide/pyridine [158(c),159,160]. The method has, however, not been used so far to synthesise any other amino-cyclopentadienyl complex. The reaction of (η^5-$C_5H_4CCl_3$)$Re(CO)_3$ and NaN_3 in acetone at room temperature gave the azide, which upon heating in benzene–heptane underwent a Curtius rearrangement to the isocyanate, and subsequent hydrolysis with dilute NaOH gave (η^5-$C_5H_4NH_2$)$Re(CO)_3$ (**153**) in 17% yield [161].



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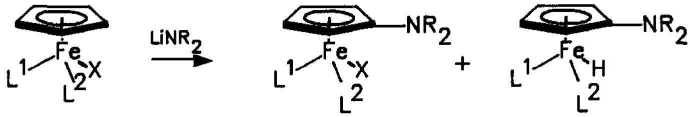
Similarly, the corresponding manganese compound has been prepared by Curtius degradation of (η^5-$C_5H_4CON_3$)$Mn(CO)_3$ (prepared by oxidation of the corresponding hydrazide) in acetic anhydride followed by hydrolysis of the resulting amide [162].

(3) Amination reactions of the coordinated cyclopentadienyl ring. The reaction between lithium dialkylamides and (η^5-C_5H_5)FeL^1L^2X derivatives (**154**) (L^1 = CO, PR_3; L^2 = PR_3; X = Cl, Br, I) yields, among other products, mononuclear complexes **155a** and **155b** aminated in the cyclopentadienyl ring [163–165].



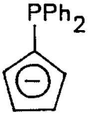
154 **155a** **155b**

Very recently, it has also been shown that the action of LiNHPh and $LiNPh_2$ on cationic cyclopentadienyliron η^2-alkyne complexes also results in amination of the cyclopentadienyl ring [165].

Nucleophilic attack on cationic cyclopentadienylmetal carbonyl complexes are known to occur at either the cyclopentadiene ring, the metal atom, or the carbonyl group. The factors that affect the regioselectivity of this attack remain unclear. Neutral complexes such as **154** may be expected to undergo nucleophilic attack by the amide group, the primary attack most probably occurring on either the metal atom, or the cyclopentadienyl ring. Known examples of base-induced as well as thermally induced metal-to-cyclopentadienyl migrations support the former idea. However a direct *exo*-attack on the cyclopentadienyl ring to produce an intermediate which, after migration of the *endo*-hydride to iron and X^- expulsion, forms **155b**, (or **155a** by liberation of H^- to the medium) is also conceivable.

(j) Phosphorus-substituted cyclopentadienylmetal complexes

(1) P-substituted cyclopentadienyl anions. Mathey and Lampin [166] prepared the phosphine-substituted cyclopentadienide anion (**156**) in situ by reaction of $Tl[C_5H_5]$ with $ClPPh_2$ followed by subsequent deprotonation of the P-substituted cyclopentadiene with *n*-butyllithium.



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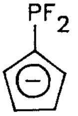
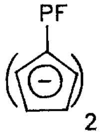


157a



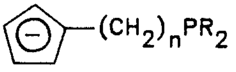
157b

Anion **156** was used in the synthesis of P-substituted fulvenes [166]. Davison and co-workers [167] also generated **156** in situ starting with $Na[C_5H_5]\cdot 2DME$ instead of thallium cyclopentadienide.

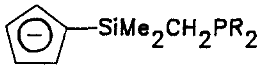
The reaction between $Tl[C_5H_5]$ and polyhalo-phosphines has been used to prepare the fluorophosphine-substituted cyclopentadienyl ligands **157a** and **157b** [168]. The dimethylphosphinocyclopentadienylthallium complex was similarly prepared [169,170(d)].

These ligands, $C_5H_4PR_2^-$, contain two functionalities and hence can coordinate to a metal through either or both of the functionalities. The usual procedure is first to attach a metal to the cyclopentadiene function; but, recently, attachment to the P followed by attachment to the ring has been accomplished [169]. Both homo and heterobimetallic complexes can be synthesised with this ligand [170,171], and this procedure allows two metals to be held in close proximity to each other [172].

This process can also be achieved by linking the C_5H_5 ring to a PR_2 unit via a bridging group [72(b),72(c),173], e.g. as in **158a** and in **158b**. Examples of the use



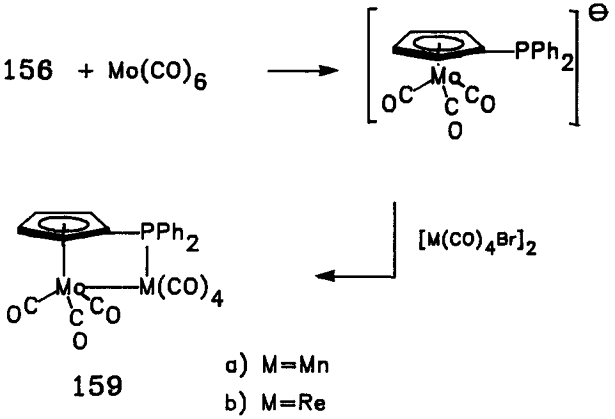
158a



158b

of $C_5H_4(CH_2)_nPR_2$ in the synthesis of some organometallic complexes are given below.

Casey et al. [174(a)] characterised **156** by NMR spectroscopy, and used this compound (as well as the *p*-MeC_6H_4 derivative) for the synthesis of several new heterobimetallic compounds [174(b)]. Thus reaction of **156** with $Mo(CO)_6$ in refluxing THF gave the $(\eta^5\text{-}C_5H_4PPh_2)Mo(CO)_3{}^-$ anion as the major product (85%). The reaction of this anion with $[(CO)_4MnBr]_2$ also gave the heterobimetallic complex (**159a**). The molybdenum–rhenium complex (**159b**) was obtained in an analogous manner.



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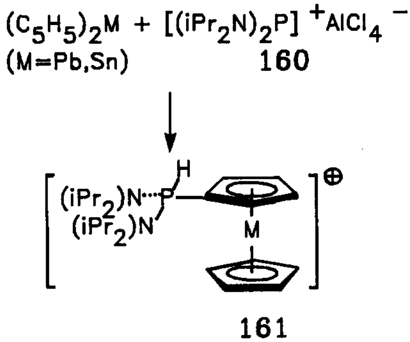
a) M=Mn
b) M=Re

(2) Other methods. The reaction of plumbocene (or stannocene) with the phosphenium ion (**160**) yields the "plumbocenium ions". The reaction may be regarded as an oxidative addition of **160** to a cyclopentadienyl C–H bond. Similar reaction with transition metal complexes may find application in the synthesis of phosphine-substituted complexes. The lead (or tin) complexes (**161**) may also find direct application in organometallic synthesis [175].



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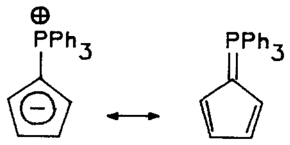
Triphenylphosphoniocyclopentadienide (**162**) has frequently been used in the synthesis of triphenylphosphonio-substituted cyclopentadienyl complexes [176,177].



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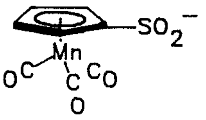
(k) Oxygen- and sulphur-substituted cyclopentadienylmetal complexes

There is a paucity of data available on cyclopentadienyl rings containing O- or S-bonded groups.

(1) S substituents. In the 1960s, numerous $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ complexes were tested as anti-knock agents and this led to the synthesis of a wide range of derivatives, which included the R = sulphonyl group. The parent compound (**163**) was prepared in >90% yield by reaction of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ with H_2SO_4/acetic anhydride in a classic ring sulphonation reaction [178(a)], and subsequent ligand derivatisation produced a range of related complexes [178(b)–(d)].

The $C_5H_4SMe_2$ ligand has been synthesised [178(e)] and provides an alternative procedure for generating $[(\eta^5\text{-}C_5H_4SMe_2)Mn(CO)_3]^+$ (**164**) complexes [178(f)]. The $C_5H_4SMe^-$ ligand has also been stabilized by attachment to a $Mn(CO)_3$ fragment [178(g)].



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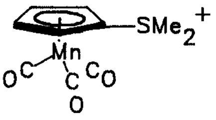

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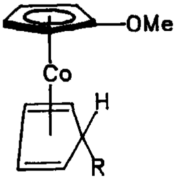
(2) O substituents. To our knowledge, the only "O-C_5H_4" ligands that have been generated have arisen from indirect synthetic strategies [179(a)]. The earliest reported procedure involved oxidation of C_5H_4O with O_2, followed by halogenation with $FeX_2(CO)_4$ to yield $(\eta^5\text{-}C_5H_4OR)Fe(CO)_2X$ (R = H, Me, COMe, COPh; X = Cl, Br) [179(b)]. An alternative procedure starts from cyclopentadienone diethyl ketal; reaction with $Fe_2(CO)_9$ gives $[(\eta^5\text{-}C_5H_4OEt)Fe(CO)_2]_2$ [179(c)]. Finally, it is to be noted that a cobalt sandwich complex also provides a route to the complexes of interest. Thus reaction of $(\eta^5\text{-}C_5H_4OMe)(\eta^5\text{-}C_5H_5)Co^+$ with RLi gives $(\eta^5\text{-}C_5H_4OMe)Co(\eta^4\text{-}C_5H_5R)$ (**165**) as part of a reaction mixture [179(d)].

(l) Syntheses of halogen-substituted cyclopentadienyl complexes

(1) Electrophilic substitution reactions. Indirect halogenation by electrophilic substitution has been reported for ferrocene and cymantrene [16].



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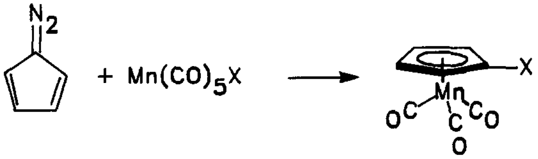
(2) Methods using diazocyclopentadiene. Diazocyclopentadiene can be prepared by the reaction of cyclopentadiene, *p*-toluenesulphonyl azide and a base (e.g. PhLi [180(a)], NEt_2H [180(b)], etc.). Shaver and co-workers [181] reported the syntheses of some halogen-substituted η^5-cyclopentadienylmetal complexes of manganese (e.g. **166**) and rhodium by reaction of diazocyclopentadiene with metal carbonyl halides.



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The same method has been applied by Herrmann and Huber to the syntheses of numerous iron and ruthenium complexes [182].

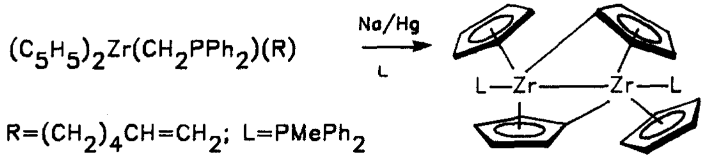
$(\eta^5\text{-}C_5H_4I)Fe(CO)_2I$ has served as starting material for the synthesis of a number of other iron complexes containing the C_5H_4I ligand [182].

(3) Methods using halogen-substituted thallium cyclopentadienides. Conway and Rausch [80] (see also ref. 183) have recently prepared halogen-substituted thallium cyclopentadienides, $Tl[C_5H_4X]$ (X = Cl, Br, I), and used these in the synthesis of halogen-substituted cyclopentadienylmetal complexes. Reaction of thallium cyclopentadienide with *N*-chlorosuccinimide, *N*-bromosuccinimide, or *N*-iodosuccinimide, gave the intermediate halocyclopentadienes. Treatment of the diene with thallous ethoxide, or a basic aqueous Tl(I) solution, gave the corresponding thallium derivatives in yields between 69 and 96%. These organothallium reagents have been used in the synthesis of halogen-substituted cyclopentadienyl complexes by reaction with the appropriate metal halide fragments (see Sect. D).

(m) Transition metal-substituted cyclopentadienyl complexes

Attachment of a metal to a cyclopentadienyl ring bonded to a metal can lead to the formation of bimetallic complexes with or without bonding (or bridging) interaction between the two metals. Examples are shown below.

In the chemistry of the low-valent Group 4 metals, removal of a hydrogen atom from a cyclopentadienyl ring is frequently observed (for reviews, see ref. 184), leading to either the formation of a fulvalene ligand [185] or to the formation of compounds containing a (η^1,η^5-C_5H_4) ligand. Two recent examples (**167** and **168**) [186,187] are given below.



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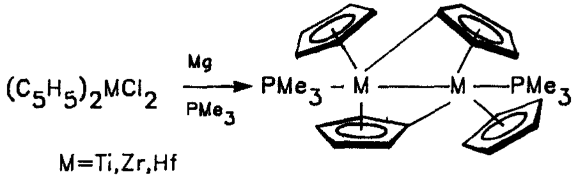

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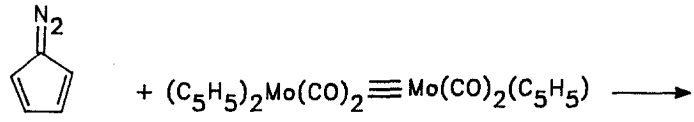
An alternative route to an equivalent complex involves the reaction between diazocyclopentadiene and **169** and leads to the formation of the (η^1,η^5-C_5H_4) complex, **170** [188].



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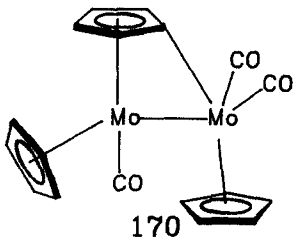

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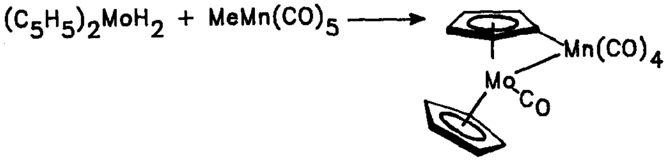
Mixed metal derivatives similar to **169** or **170** are also possible. Thus, the reaction between dicyclopentadienylmolybdenum dihydride and pentacarbonylmethylmanganese in benzene at 80°C leads to the formation of the bimetallic complex **171** [189]. The formation of the bimetallic species **172** has also been detected in the reaction between an iridium complex and tungstenocene/molybdenocene dihydrides [190].



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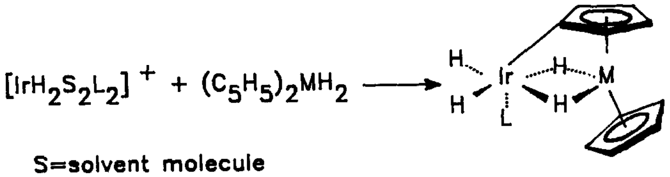


S=solvent molecule
M=Mo,W
L=phosphine

172

The more classical reactions, leading to bimetallic complexes with no metal–metal interaction, have also been reported. A facile method of synthesising these compounds is via reaction of (η^5-C_5H_4Li)ML_m with a metal chloride, $M'ClL_x$. In this way, a wide range of $M'L_x[\eta^5$-$C_5H_4)M(CO)_3]_n$ (M = Mn, Re; n = 1–3) complexes have been synthesised. For example, $M'L_x$ has included (η^5-C_5H_5)$Fe(CO)_2$ (**173**) [191(a),(b),194(g)], (η^5-C_5H_5)$W(CO)_3$ [191(c)],194(i)], $M(CO)_5$ (M = Mn, Re) [194(h)], $Pt(PPh_3)_2Cl$ (**174**) [192(a)], (η^5-C_5H_5)$Ni(PPh_3)$ [192(b)], Cu [193(a)], Ag [193(b)], Ag–Cu [193(c)], $Au(PPh_3)$ [193(d)], SnCl (**175**, n = 3) [194(a)], Bi (**175**, n = 3) [194(b)], Cd (n = 2) [194(c)], Yb and Hg (n = 2) [194(d)], $SmCl_2$ [194(e)], and YbI [194(f)].

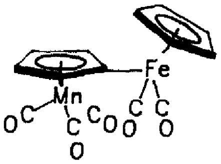
Decarbonylation of the acyl complex (**176**) [195(a)] provides an alternative route to **173**, while thermal demercuration of [η^5-$C_5H_4HgPt(PPh_3)_2Cl]Mn(CO)_3$ provides another route to **174** [195(b),(c)].

An unusual complex involving the coordination of two (gold) atoms to one ring C atom is shown in **177** [195(d)].

The reaction between the two cobalt complexes (**178** and **179**) surprisingly yielded the dinuclear cobalt complex **180** [196].

(n) Deuterium-substituted cyclopentadienyl complexes

Partial or complete [197(a)] deuteration of the cyclopentadienyl ring provides a means of (a) monitoring reactions or (b) yielding spectroscopic information [197(b)]. Deuteration can either be achieved by D addition to the ring prior to attachment to a metal moiety or, in suitable cases, via H/D exchange on the ring–metal complex. This latter procedure is achieved by initially lithiating the ring [197(c)].



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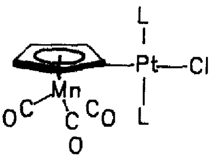
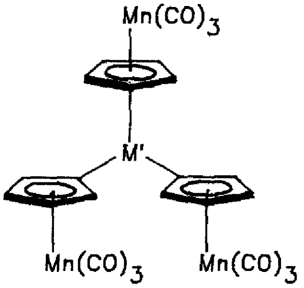
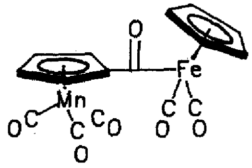


174(L = PPh_3)



175(M' = SnCl,Bi)



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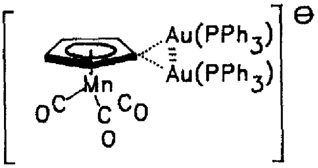

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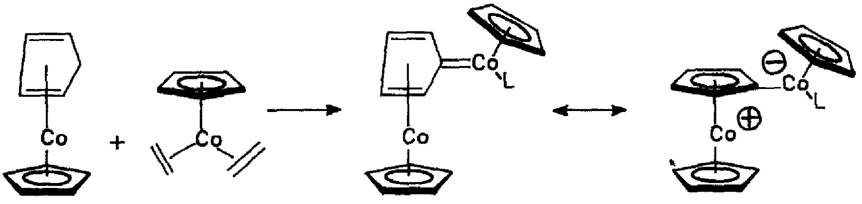
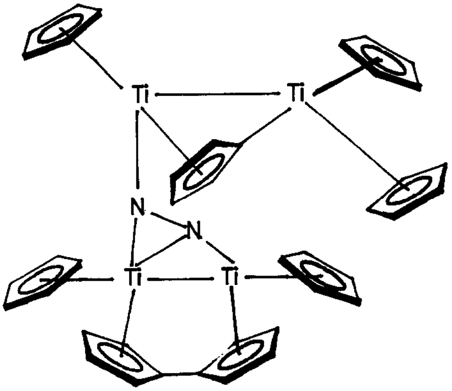


178 **179** **180**

D. SURVEY OF HALF-SANDWICH CYCLOPENTADIENYL TRANSITION METAL COMPLEXES

(i) Titanium, zirconium and hafnium [198–249] (Tables 1–3, pp. 56–59)

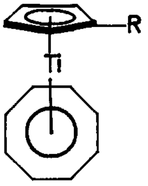
A wide range of Group 4 complexes containing cyclopentadienyl ligands have been synthesised [198], including many complexes containing substituted cyclopentadienyl rings. However, only a limited number of studies are pertinent to this review. Thus, complexes of the type (η^5-$C_5H_4R)_2MX_2$ (M = Ti, Zr, Hf) as well as complexes in which a cyclopentadienyl ring acts as both an η^1- and η^5-ligand to two different metals, such as **181** [187,199], will not be discussed here. It is worth noting, however, that studies on a wide range of $(\eta^5\text{-}C_5H_4R)_2TiCl_2$ complexes, in which the physical and catalytic properties of the complexes have been correlated with the electronic and steric properties of the R group, have been reported [200–202(a)]. In the discussion to follow, Group 4 complexes have been grouped according to the metal oxidation state.



181

(a) *$(\eta^5\text{-}C_5H_4R)M(I)$ complexes*

Substituted cyclopentadienyl complexes of Ti(I) have been prepared from $(\eta^8\text{-}C_8H_8TiCl{\cdot}THF)_2$ and salts of $C_5H_4R^-$ ($R = t$-Bu, $SiMe_3$, Me) [205]. These paramagnetic sandwich complexes (**182**) have been characterised by magnetic moment measurements and mass spectrometry.



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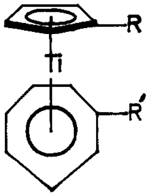

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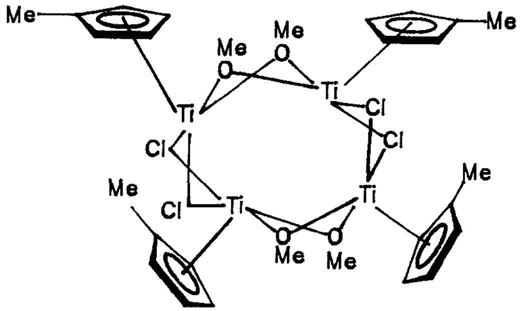
(b) *$(\eta^5\text{-}C_5H_4R)M(II)$ complexes*

The only known complexes of this type contain two cyclic ligands, one of which is a cyclopentadienyl ring. The sandwich complexes $(\eta^5\text{-}C_5H_4R)Ti(\eta^7\text{-}C_7H_6R')$ (**183**) were initially prepared from $(\eta^5\text{-}C_5H_4R)TiCl_3$ [203,204]. The thermally stable, blue, diamagnetic complexes have been fully characterised (Table 1). The substituted complexes can also be synthesised by functionalisation of $(\eta^5\text{-}C_5H_5)Ti(\eta^7\text{-}C_7H_7)$. Depending on the reaction conditions, substitution can be made to occur at the (η^7-C_7H_7) ring [206,207] or both of the rings [208]. For example, use of more than two equivalents of *n*-BuLi/TMEDA with **183** (R, R′ = H) followed by PPh_2Cl gives (η^5-$C_5H_4PPh_2$)Ti(η^7-$C_7H_6PPh_2$). The use of this molecule as a chelating diphosphine ligand has been investigated. No analysis of ring orientation has been undertaken, although X-ray structures confirm that both rings are planar [208].

(c) (η^5-C_5H_4R)M(III) complexes

Although a wide range of Ti(III) complexes have been prepared [209] very few reports have appeared in which half-sandwich, substituted cyclopentadienyl complexes have been synthesised. (It is to be noted that [(η^5-C_5H_4R)$_2$TiX]$_2$ complexes are readily available [210–212].)

Reduction of (η^5-C_5H_4R)$_2MCl_2$ (M = Zr, Hf; R = Me, i-Pr, CH_2SiMe_3) with Na[$C_{10}H_8$] yields "(η^5-C_5H_4R)MCl_2", which was characterised by ESR spectroscopy [213,214]. Similar results were obtained for a series of related Ti complexes [215(a)]. Zinc reduction of (η^5-C_5H_4R)$TiCl_3$ (R = i-Pr, CHMePh), however, yielded isolable (η^5-C_5H_4R)$TiCl_2$ which, on further reaction with sodium diphenolate (O_2R) or dithiolate (S_2R), gave (η^5-C_5H_4R)Ti(O_2R) (brown solid) or (η^5-C_5H_4R)Ti(S_2R) (oil) [215(b)] (Table 2). More recently, [(η^5-C_5H_4Me)$TiCl_3$]$^-$ was synthesised from (η^5-C_5H_4Me)$TiCl_3$ using (η^5-C_5H_5)$_2$Co as reductant [216]. This reaction gave the highly air-sensitive material in 77% yield. Spectral properties reported for the [(η^5-C_5H_4Me)$TiCl_3$]$^-$ complex included ESR and NMR (δ C_5H_4 in CD_2Cl_2 at 30.5 and 29.1 ppm) data. The Ti complex was found to be a poorer oxidant than the analogous, isoelectronic vanadium complex, (η^5-C_5H_4Me)VCl_3. Reaction of (η^5-C_5H_4Me)$_2TiCl_2$ with $ClMgCH_2OCH_3$ yielded (η^5-C_5H_4Me)$_2$TiCl(CH_2OCH_3) which, on thermolysis, gave the Ti(III) complex [(η^5-C_5H_4Me)TiCl(OCH_3)]$_4$ (**184**). The structure of this tetramer was determined by X-ray crystallography [248(a)]. Reduction of (η^5-C_5H_4t-Bu)$_2$$\overline{Zr(CH_2P}Ph_2)_2$ with Na[C_8H_{10}] resulted in loss of a cyclopentadienyl ring and generation of the Zr(III) complex, (η^5-C_5H_4t-Bu)$\overline{Zr(CH_2P}Ph_2$)(CH_2PPh_2). At higher



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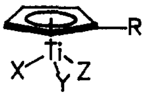
temperatures a further reaction occurs to give $(\eta^5\text{-}C_5H_4t\text{-Bu})\overline{Zr(H)(CH_2P}Ph_2)$. This latter complex was shown to be an olefin hydrogenation catalyst [248(b)].

Irradiation of suitable dicyclopentadienyl complexes $(\eta^5\text{-}C_5H_4R)_2MX_2$ (M = Ti, Zr, Hf) [217], provides an alternative method of producing $(\eta^5\text{-}C_5H_4R)MX_2$ species. Tyler's group [217(b)] has shown that the ligand ejected from the $(\eta^5\text{-}C_5H_4R)_2MX_2$ complex is dependent on X (see Fig. 2), but variation of R (R = CO_2Me, $SiMe_3$) had little effect on the ejection of the ancillary ligand.

(d) $(\eta^5\text{-}C_5H_4R)M(IV)$ complexes

The 4+ oxidation state is a pervasive oxidation state for the Group 4 metals and consequently a wide range of $(\eta^5\text{-}C_5H_4R)MXYZ$ (X, Y, Z = two electron anionic donor ligands) have been synthesised (**185**). Typical synthetic strategies start from the readily available $(\eta^5\text{-}C_5H_4R)_2MX_2$ and MX_4 complexes, e.g.



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(a) $(\eta^5\text{-}C_5H_4R)_2TiX_2 + TiX_4 \rightarrow 2(\eta^5\text{-}C_5H_4R)TiX_3$
(b) $TiCl_4 + C_5H_4R^- \rightarrow (\eta^5\text{-}C_5H_4R)TiCl_3 + Cl^-$
(c) $(\eta^5\text{-}C_5H_4R)_2TiX_2/SO_2Cl_2/SOCl_2 \rightarrow (\eta^5\text{-}C_5H_4R)TiX_3$ [202(b)]
(d) $(\eta^5\text{-}C_5H_4R)TiX_3 + 3Y^- \rightarrow (\eta^5\text{-}C_5H_4R)TiY_3 + 3X^-$

The ligands X, Y, Z in **185** can be the same or different, monodentate or bidentate. Indeed, numerous examples of $(\eta^5\text{-}C_5H_4R)M(A\text{-}B)_3$ (A-B = bidentate ligand) are known, e.g. A-B = carboxylato, xanthato, β-diketonato, quinolinolato (Table 3). In these complexes, the $\eta^5\text{-}C_5H_4R$ ligand can be regarded as occupying

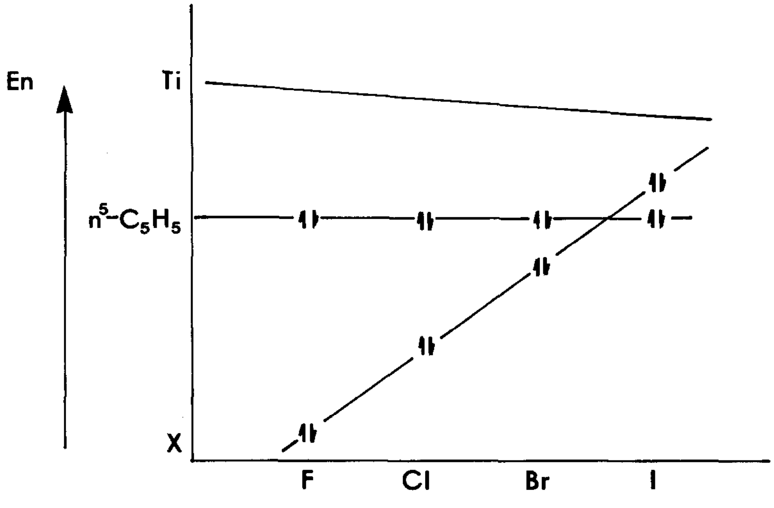
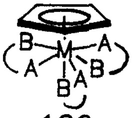


Fig. 2. Variation of the C_5H_5, Ti and X energy levels for a series of $(C_5H_5)_2TiX_2$ complexes.

one coordination site in a distorted pentagonal bipyramid (see, for example, ref. 218) (**186**). In the related (η^5-C_5H_4R)Ti(A-B)$_2$X complex, crystal structure determinations



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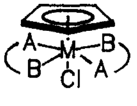

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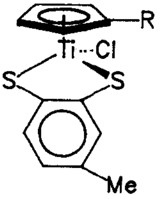
again suggest that the cyclopentadienyl ligand occupies one coordination site in an octahedron with the bidentate ligands bending away from the ring (**187**) (see, for example, ref. 219).

The synthesis of the chelate complexes of Ti(IV) generally involves reaction of (η^5-C_5H_4R)$TiCl_3$ with either the sodium salt of the bidentate ligand, or the bidentate ligand in the presence of a base. An alternative approach has been to use photolytic technqiues which results in displacement of a (η^5-C_5H_4R) ring from (η^5-C_5H_4R)$_2TiX_2$. In the presence of a suitable ligand, Y, the monosubstituted complex (η^5-C_5H_4R)TiX_2Y can be generated. This procedure has been used to synthesise (η^5-C_5H_4R)$TiCl_2X$ where R = CHPh$_2$ or Me and X = acetylacetonato or 8-hydroxyquinolinolato [220].

Disproportionation reactions also represent a viable technique for the synthesis of (η^5-C_5H_4R)TiXYZ, as has been observed by Nesmeyanov et al. [221] (**188**)

$$(\eta^5\text{-}C_5H_4R)TiX_3 + 2(\eta^5\text{-}C_5H_4R)TiY_3 \rightleftarrows 3(\eta^5\text{-}C_5H_4R)TiXY_2 + \eta^5\text{-}C_5H_4R)TiX_2Y$$

Ti(III) complexes can also be used as starting materials for the synthesis of (η^5-C_5H_4R)TiY_3 complexes via facile replacement/oxidation reactions [215(b)]. Using this procedure, three "different" ligands can be added to the metal (see **188**, **189**; R = i-Pr, CHMePh). The C_5H_4R protons are reported as multiplets but no attempt was made to further analyse the ^{1}H NMR spectra. Bridged species such as **190** were also isolated from the reaction.



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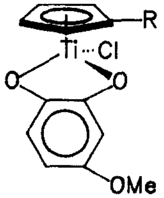

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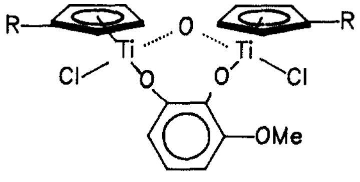

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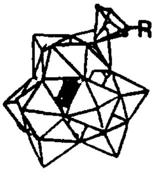
Reaction of $C_5H_4(MMe_n)M'Me_3$ (M, M' = Si, Ge, Sn, As, Sb; $n = 2, 3$) with $TiCl_4$ has permitted the synthesis of a series of substituted derivatives, (η^5-$C_5H_4MMe_n$)$TiCl_3$ [222]. The ability of the groups to displace Cl from $TiCl_4$ followed the sequence $AsMe_2 < SiMe_3 < GeMe_3 < SbMe_2 < SnMe_3$.

Reaction of SO_2 with (η^5-C_5H_5)Ti(OR)$_2$Me leads to the insertion product

(η^5-C_5H_5)Ti$(OR)_2$(μ^2-O_2SMe) and, in the presence of excess SO_2, a ring-substituted product is formed which is tentatively proposed to be (η^5-$C_5H_4SO_2$)Ti$(OR)_2$-(μ^2-O_2SMe) [235].

Keggin and Dawson-type heteropolytungstate ions have been reacted with (η^5-C_5H_4R)Ti$(NMe_2)_3$ [242] to produce complexes **191** and **192**, viz.

$X_7PW_{11}O_{39} + (\eta^5\text{-}C_5H_4R)Ti(NMe_2)_3 \rightarrow X_4[(\eta^5\text{-}C_5H_4R)TiPW_{11}O_{39}]$



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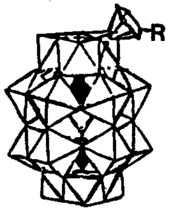
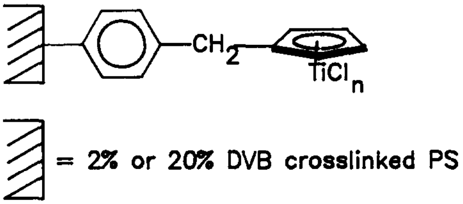


192

where $PW_{11}O_{39}^{7-}$ is the Keggin anion, $X_7 = 7Na^+$ or $(n\text{-}Bu_4^+)_4/(H^+)_3$ and R = $(CH_2)_5CO_2CMe_3$, $(CH_2)_6NH_2$ etc. Similar reactions yielded the Dawson anions, $X_7[(\eta^5\text{-}C_5H_4R)TiP_2W_{17}O_{61}]$.

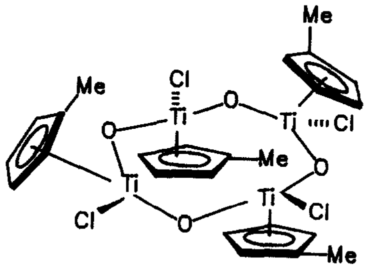
The novel complexes have been completely characterised and the R groups chemically modified to permit binding to substrates. These Ti-heteropolytungstate complexes have been successfully used as label molecules for TEM studies [242(b)].

Polymer-supported cyclopentadienes can readily be synthesised, converted to cyclopentadienyl ions and reacted with suitable metal salts. In this way, a series of supported metal complexes of $TiCl_3$, $TiCl_2$, $ZrCl_3$ and $HfCl_3$ (**193**) have been synthesised, characterised (analysis, electron microscopy) and studied for their behaviour as olefin hydrogenation catalysts [241(a)]. Substituted cyclopentadienyl complexes of Ti containing silyl groups have been attached to silica supports and their catalytic behaviour studied [241(b)].



193

Cathode active materials have been made from the reaction between a divinylbenzene crosslinked polymer support and a cyclopentadienyltitanium complex. The resulting material reacted with Li_2S to give a layered trichalcogenide, of which the precise formulation is unknown but may be of the type (η^5-C_5H_4R)TiS_3 [240].



194

A Ti(IV) tetrameric complex has been prepared by the controlled hydrolysis of (η^5-C_5H_4Me)$TiCl_3$. An X-ray structure determination of **194** has been reported [247(a)]. Reaction of 2-methyl-2-(2-pyridylethylcyclopentadiene) with Mg, and subsequently with $TiCl_4$, followed by recrystallisation from wet CH_2Cl_2, gave a Ti–oxygen-bridged dimer [247(b)].

The most pertinent study relating to this review described the synthesis and NMR characterisation of a series of (η^5-C_5H_4R)$Ti(NMe_2)_3$ complexes [243]. This work is discussed in more detail in Sect. E.

TABLE 1

Complexes of Ti(II): (η^5-C_5H_4R)M(ring)

M	R	Ring	Comments[a]	Ref.
Ti	Me, *t*-Bu, $SiMe_3$	C_7H_7	IR, MS, NMR	203,204
Ti	Me	C_7H_6Me	IR, MS, NMR	203
Ti	PPh_2	$C_7H_6PPh_2$	IR, MS, NMR (^1H, ^{31}P) X-ray, reactions[b]	208

[a] For abbreviations, see p. 3.

[b] For example, reactions of the diphosphine ligand with $Mo(CO)_6$, $Cr(CO)_6$, (η^5-C_5H_5)$Co(CO)_2$ and $Fe_2(CO)_9$.

TABLE 2

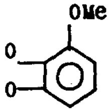
Complexes of M(III): $(\eta^5\text{-}C_5H_4R)M(X)(Y)$ and $(\eta^5\text{-}C_5H_4R)M(X)(Y)_2^-$ (M = Ti, Zr, Hf)

M	R	X	Y	Z	Comments[a]	Ref.
Ti	i-Pr, CHMePh	Cl	Cl	–		215(b)
Ti[b]	Me	μ-OMe	μ-Cl	–	X-ray, NMR	248(a)
Ti	i-Pr		O_2R[c]	–	MS, IR	215(b)
Ti	i-Pr, CHMePh		S_2R[d]	–	MS, IR	215(b)
Ti	COOMe	Br	Br	–	ESR	217(b)
Ti	PS[e]	Cl	Cl	–	Cat, EM	236,237
Ti^-	Me	Cl	Cl	Cl	NMR	216
Zr, Ti	Me, i-Pr, *t*-Bu, C_5H_{11}, C_6H_{11}	Cl	Cl	–	ESR	217(a),217(c)
Zr	*t*-Bu	H, CH_2PPh_2	CH_2PPh_2		ESR	248(b)
Zr	i-Pr, Me	CH_2SiMe_3	CH_2SiMe_3	–	ESR	213,214
Hf	i-Pr	CH_2SiMe_3	CH_2SiMe_3	–	ESR	213,214
Hf	Me, Et, C_3H_7	Cl	Cl	–	ESR	217(a)

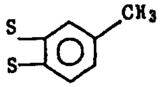
[a] For abbreviations, see p. 3.

[b] See **184**.

[c] O_2R =



[d] S_2R =



[e] PS = 2% or 20% DVB crosslinked polystyrene.

TABLE 3

Complexes of M(IV): (η^5-C_5H_4R)M(X)(Y)(Z) (M = Ti, Zr, Hf)

M	R	X	Y	Z	Comments[a]	Ref.
Ti	Me	Cl, Br	Cl, Br	Cl, Br	IR, MS, PES, NMR (^1H, ^{13}C)	203,224,225,249
Ti	Me	Cl, NMe_2	Cl, NMe_2	$NPPh_3$, NMe_2	IR, NMR, MS	233,239
Ti	Me	Cl	Cl, OEt	Cl, OEt	IR, NMR	226,244
Ti	Me	p-OC_6H_4F	p-OC_6H_4F	p-OC_6H_4F	IR, NMR (^1H, ^{19}F)	245,246
Ti	$SiMe_3$[b]	Cl, Br, I	Cl, Br, I	Cl, Br, I	IR, MS, NMR	151,217(b),222
Ti	$GeMe_3$, $SnMe_3$	Cl	Cl	Cl	IR, NMR	222
Ti	$AsMe_2$, $SbMe_2$	Cl	Cl	Cl	IR, NMR	222
Ti	Et, *t*-Bu, CO_2Me, i-Pr	Cl	Cl	Cl	IR, NMR	215(b),217(b),226
Ti	$(CH_2)_3Si(OMe)_3$	Cl	Cl	Cl	IR, NMR	241
Ti	CH_2Ph, CHMePh	Cl	Cl	Cl	IR, NMR	215(b),227
Ti	$CH_2O\overline{CH(CH}_2)_3$	Cl	Cl	Cl	IR, NMR (^1H, ^{31}P), MS, X-ray	202(b)
Ti	Me, *t*-Bu, $SiMe_3$	Oi-Pr	Oi-Pr	Oi-Pr	IR, RS, NMR(^1H, ^{13}C)	243
Ti	Me, Et, $(CH_2)_3Si(OMe)_3$	OEt	OEt	OEt	IR	226,241,244
Ti	BR_2(R = Cl, Br, Me, OEt)	Cl	Cl	Cl	MS, NMR (^1H, ^{11}B, ^{13}C)	238
Ti	CH_3, $CHPh_2$	Cl	Cl, acac	acac	IR, NMR	220
Ti	CH_3, $CHPh_2$	Cl	HQ[c]	HQ[c]	IR, NMR	220
Ti	$CHMe_2$, CHMePh	Cl	O_2R[d], S_2R[e]	O_2R[d], S_2R[e]	MS, NMR	215(b)
Ti	Me	CF_3COO	CF_3COO	CF_3COO	NMR (^{19}F)	245,246
Ti	i-Pr	OX[f]	OX[f]	OX[f]	–	215(b)
Ti	SO_2[g]	OR	OR	$MeSO_2$	–	235
Ti	Various[h,i]	NMe_2	NMe_2	NMe_2	IR, RS, NMR	242(a),243
Ti	Various[i]	NC_5H_{10}	NC_5H_{10}	NC_5H_{10}	IR, RS, NMR	243
Ti	PPh_3	Cl	Cl	Cl, Cl	–	234
Ti	Me	O[j]	O[j]	Cl	IR, X-ray	247(a)
Ti	PS[k]	Cl	Cl	Cl	Cat, EM	236,237
Ti	PS[k]	S	S	S	–	240
Ti	CMe_2(2-py)	Cl	O[l]	O[l]	X-ray	247(b)

Zr, Hf	PPh_3	Cl	Cl	Cl	–	234
Zr, Hf	PS[k]	Cl	Cl	Cl	Cat, EM	241(a)
Zr, Hf	*t*-Bu	C_9H_6NO	C_9H_6NO	C_9H_6NO	–	229
Hf	$CH_2{=}CH$	I	I	μ-O	–	228
Hf	Et	F	F	F	–	223
Hf	Me	Cl	acac	acac	IR, NMR	229
Zr	Me, *t*-Bu	Cl	acac	acac	IR, NMR	229
Zr	Me	acac	acac	μ-O	–	229
Zr	*t*-Bu	CO_2Me	CO_2Me	CO_2Me	–	230
Zr	Me	S_2CNR_2	S_2CNR_2	S_2CNR_2	IR, NMR	231

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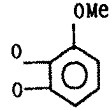
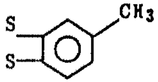
[a] For abbreviations, see p. 3. Note: not all references to all compounds listed are given in this table.

[b] Also isolated $(\eta^5\text{-}C_5H_4SiMe_3)TiCl_3\cdot C_6H_4(AsMe_2)_2$ [151].

[c] HQ = 8-hydroxyquinolate ion.

[d] O_2R = , see **189**.

[e] S_2R = , see **188**.

[f] OX = 8-methoxyquinolate ion; 1.5 ligands per Ti atom in dimer.

[g] Tentative assignment.

[h] Cyclopentadiene ring linked to Keggin and Dawson structural units (see text and structures **191** and **192**) for groups listed in [i], below.

[i] Wide range of complexes investigated, where R = Et, i-Pr, $CHEt_2$, $CHPh_2$, CMe_3, $GeMe_3$, $SiMe_3$, $SiMe_2Ph$ [243] and $(CH_2)_5CHO$, $(CH_2)_2CH{=}CH\text{-}CH{=}CH_2$, $(CH_2)_3O\text{-}C_6H_4CH(OMe)_2$, $(CH_2)_5CO_2t\text{-Bu}$, $(CH_2)_6NH_2$, $(CH_2)_6OTHP$, $(CH_2)_5CH(OMe)_2$, $(CH_2)_5COOH$ [242(a)].

[j] Part of tetrameric structure, see **194**.

[k] 2% or 20% polystyrene crosslinked with DVB, see **193**.

[l] Dimeric structure with O bridges. Ligand also bonds to Ti through the pyridyl N atom.

(ii) Vanadium, niobium and tantalum [250–279] (Tables 4–8, pp. 64–68)

(a) (η^5-C_5H_4R)M(I) complexes

With few exceptions, this group of complexes is dominated by the synthesis and characterisation of (η^5-C_5H_4R)V(CO)$_4$ and its derivatives (Table 4). The only ring-substituted complexes of Nb which have been synthesised contain the Me group viz. (η^5-C_5H_4Me)Nb(CO)$_4$ and its CO-substituted derivatives [266,279]. The first vanadium complex containing a substituted cyclopentadienyl ring to be synthesised was (η^5-$C_5H_4COCH_3$)V(CO)$_4$ [250], which was prepared via the Friedel–Crafts acetylation of (η^5-C_5H_5)V(CO)$_4$. This complex has since been characterised by ^{51}V NMR [254], IR and Raman [251(a),(b)] spectroscopy, as well as by a crystal structure determination [254]. Comparative acetylation studies have shown that (η^5-C_5H_5)V(CO)$_4$ and benzene have the same propensity to be acetylated and consequently little further work has been reported on this approach to ring functionalisation of the vanadium complexes [260(b)]. Other strategies for the synthesis of ring functionalised complexes include:

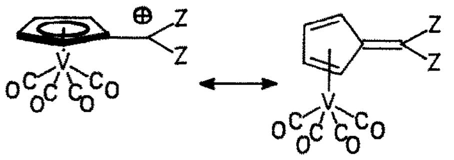
(a) reaction of V(CO)$_6$ with substituted fulvenes [253,257];

(b) reaction of V(CO)$_6$ with substituted cyclopentadienes [254,255,261];

(c) reaction of R_3SnV(CO)$_6$ or R_3SnV(CO)$_5$(PPh$_3$) with substituted fulvenes [257]. This route yields fulvene derivatives (**195**);

(d) reaction of V(NO)(CO)$_5$ with dimethylaminofulvene [257] to give (**196**); and

(e) modification of the ring substituent after formation of (η^5-C_5H_4R)V(CO)$_4$ [254].



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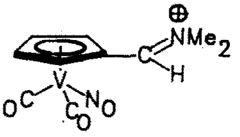

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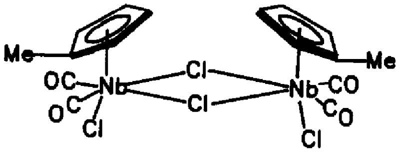
Use of the above techniques, mainly by Rehder and co-workers, has led to the synthesis of the complexes listed in Table 4. The CO-substituted derivatives, which are also listed in Table 4, were prepared by photolytic displacement of CO from (η^5-C_5H_4R)V(CO)$_4$ [252] or by reaction of $C_5H_4CR_2$ with a substituted vanadium carbonyl precursor [259]. The complexes have been fully characterised by NMR spectroscopy (^{51}V, ^{13}C and ^{1}H) [258,260].

The synthesis of (η^5-C_5H_4R)V(CO)$_3$(PEt$_3$) (R = H) from (η^5-C_5H_4R)VCl$_2$(PEt$_3$)$_2$ (via Zn reduction) has been reported and could provide another synthetic route to the required complexes [264].

(b) (η^5-C_5H_4R)M(II) complexes

A rare example of an M(II) complex which contains a C_5H_4R ligand is (η^5-$C_5H_4Me)_2Nb_2(L)_4(\mu$-$Cl)_2$ (L = CO or 1/2 *p*-tolyl acetylene) [269]. The complexes which contain metal–metal bonds were prepared by sodium amalgam reduction of (η^5-$C_5H_4R)_2Nb_2(CO)_4(Cl)_2(\mu$-$Cl)_2$ or (η^5-C_5H_4R)Nb(*p*-tolyl acetylene)Cl_2. The starting materials and products (**197–199**) have been characterised by X-ray crystallography (Table 5).



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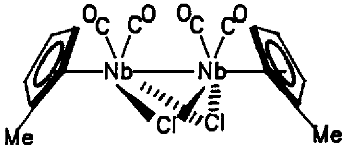

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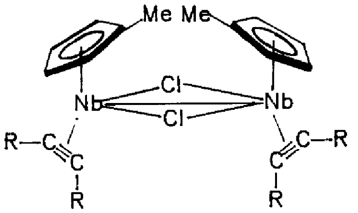

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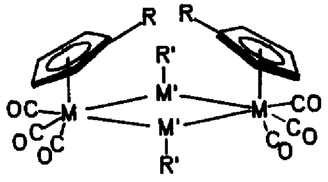
A patent has appeared in which a range of (η^5-$C_5H_4R)_2M_2(CO)_6(\mu$-$M'R')_2$ (M = V, Nb, Ta; M′ = Sn; R, R′ = alkyl) complexes were reported [267]. The structures proposed, if correct, are consistent with the metal being in the 2+ oxidation state (**200**).



200

(c) (η^5-C_5H_4R)M(III) complexes

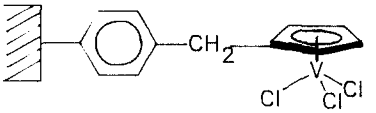
Little is known about this class of complexes. A convenient starting material to the V complexes is $VX_3(THF)_3$ (X = halogen) which has yielded, for example, (η^5-$C_5H_4Me)V(Cl)_2(PMe_3)_2$ after reaction with PMe_3 and subsequently C_5H_4R [264]. This method has not been extended to a wide range of derivatives (Table 6).

The M(III) complexes can also be prepared by reduction of M(IV) complexes.

In this way, $(\eta^5\text{-}C_5H_4Me)VCl_3^-$ has been prepared by $(\eta^5\text{-}C_5H_5)_2Co$ reduction of $(\eta^5\text{-}C_5H_4R)VCl_3$ [265]. Reduction from M(V) can also give $(\eta^5\text{-}C_5H_4R)M(III)$ complexes. Thus, $(\eta^5\text{-}C_5H_4SiMe_3)NbCl_4$ in the presence of suitable ligands is reduced by sodium amalgam to form $(\eta^5\text{-}C_5H_4SiMe_3)NbCl_3L_2$ and $(\eta^5\text{-}C_5H_4SiMe_3)NbCl_2(CO)(L)_2$ ($L = PMePh_2$ or $L_2 =$ dppe) [274]. Alternatively, Al reduction of $(\eta^5\text{-}C_5H_4Me)NbCl_4$ gave $(\eta^5\text{-}C_5H_4Me)Nb$(*p*-tolyl acetylene)$(Cl)_2$ in the presence of *p*-tolyl acetylene, or **197** in the presence of CO [269].

(d) $(\eta^5\text{-}C_5H_4R)M(IV)$ complexes

These complexes are conveniently prepared by reduction of the $(\eta^5\text{-}C_5H_4R)M(V)$ complexes. Thus, reduction of $(\eta^5\text{-}C_5H_4R)NbCl_4$ ($R = Me$, *t*-Bu, CHMePh) with Al or $SnCl_2$ gives $(\eta^5\text{-}C_5H_4R)NbCl_3$ [273(a),274], while in the presence of donor ligands, $(\eta^5\text{-}C_5H_4R)Nb(Cl)_3L_2$ ($R = SiMe_3$, $L = PMe_2Ph$, $L_2 =$ dppe) is formed [274]. A polymer-supported complex of V (**201**) has also been synthesised [277]. The above complexes, including those listed in Table 7, are all paramagnetic and have been characterised by ESR spectroscopy.



201

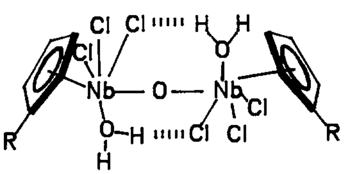
▨ = polystyrene crosslinked with 2% or 20% DVB

Reaction of a cyclopentadiene ligand directly with $NbCl_4$, i.e. Nb(IV), also provides the $(\eta^5\text{-}C_5H_4R)NbCl_3$ complex [273].

(e) $(\eta^5\text{-}C_5H_4R)M(V)$ complexes

The ready availability of MCl_5 provides access to the required complexes by reaction with the appropriate substituted cyclopentadiene ligand. The ligand generally used is $n\text{-}Bu_3Sn(C_5H_4R)$, which contains the good tin–alkyl leaving group [262,270,271]. These complexes can add Lewis bases, L, to form $(\eta^5\text{-}C_5H_4R)MCl_4L$ derivatives [271(a)]. Partial hydrolysis of $(\eta^5\text{-}C_5H_4R)NbCl_4$ ($R = Me$, $SiMe_3$) [271(a),(c),274] gave the μ-O (**202**, $R = Me$) and the μ-O/μ-Cl (**203**) complexes, both of which were characterised by X-ray crystallography [271(c),274(a)]. Reaction of **203** with bidentate ligands has been reported [274(b)].

Very little chemistry has been performed on the $(\eta^5\text{-}C_5H_4R)MCl_4$ complexes, and no comparative studies on the effect of ring substitution on reactivity patterns has been described. Reaction of $(\eta^5\text{-}C_5H_4SiMe_3)TaCl_4$ with the *o*-diphenols $4\text{-}RC_6H_3(OH)_2$ ($R = Me$, *t*-Bu) resulted in substitution of two Cl groups to give $(\eta^5\text{-}C_5H_4R)Ta(Cl)_2(O_2C_6H_3R)$ (**204**), which exists as a dimer in solution [275].



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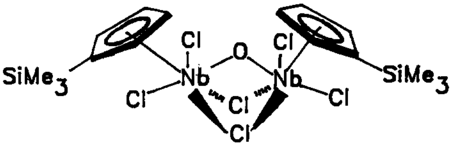

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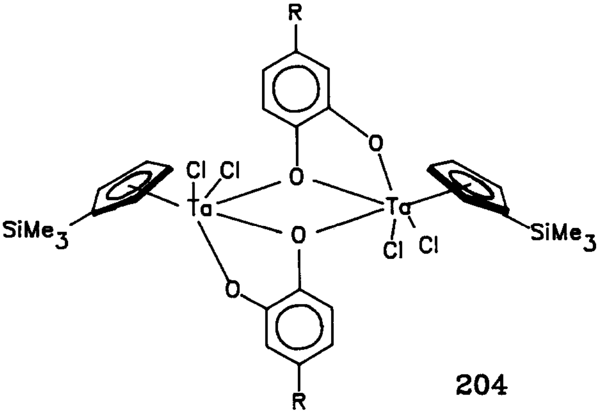

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Reaction of $(\eta^5\text{-}C_5H_4SiMe_3)NbCl_4$ with catechols or OPh^- gave similar Cl displacement reactions as described above for the Ta complexes (Table 8). Interestingly, reaction of **202** ($R = SiMe_3$) with catechol yielded $[(\eta^5\text{-}C_5H_4R)Nb(Cl)_2]_2\text{-}(\mu\text{-}O)(\mu\text{-}O_2C_6H_4)_2$ (**205**) by displacement of both bridging and terminal chloro groups [276] from the starting material.

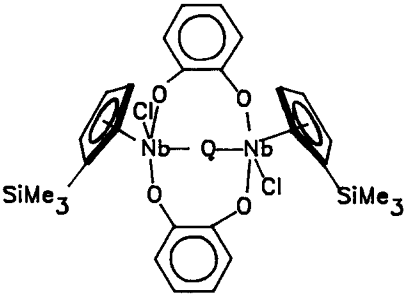

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TABLE 4

Complexes of M(I): (η^5-C_5H_4R)M(W)(X)(Y)(Z) (M = V, Nb, Ta)

M	R	W	X	Y	Z	Comments[a]	Ref.
V	CH_3CO	CO	CO, PMe_3		HCCR (R = H, Ph)	IR, NMR(^1H, ^{13}C, ^{51}V)	252
V	$CR'{=}CH_2$[b]	CO	CO	CO	CO	IR, NMR	253
V	CH_3CO	CO	CO	CO	CO	IR, RS, X-ray, NMR	250,251,254
V	$CR'{=}CHMe$[c]	CO	CO	CO	CO	IR, NMR (^1H, ^{51}V)	253
V	CHR'_2[d]	CO	CO	CO	CO, PPh_3	IR, NMR (^1H, ^{51}V)	255,257,259
V	i-Pr	CO	CO	dppe	dppe	IR, NMR (^1H, ^{51}V)	259
V	*t*-Bu	CO	CO	CO	CO	IR, NMR (^1H, ^{51}V)	263
V	CHR'_2[e]	CO	CO	diphos[f]	diphos[f]	IR, NMR (^1H, ^{51}V)	259
V	Alkyl[g]	CO	CO	CO	CO	IR, MS, NMR (^1H, ^{51}V)	253–255,263
V	$CH{=}C(CH_2)_n$ ($n = 5, 6$)	CO	CO	CO	CO, PPh_3	IR, NMR (^1H, ^{51}V)	253,257
V	XMe_3 (X = Ge, Sn)	CO	CO	CO	CO	IR, NMR (^1H, ^{51}V)	261
V	$SiMe_3$	CO	CO	CO	CO, THF	IR, NMR (^1H, ^{51}V)	256,261
V	$SiMe_3$	CO	CO	CO	N_2H_3R'[h]	IR, NMR (^1H, ^{51}V)	256
V	COPh	CO	CO	CO	CO	IR	254
V	CH(OH)Me	CO	CO	CO	CO	IR	254
V	C(NOH)Me	CO	CO	CO	CO	IR	254
V	$C(NMe_2)H^+$	CO	CO	CO	SnR'_3[i]	IR, NMR (^1H, ^{13}C, ^{51}V)	257
V	$C(NMe_2)_2^+$	CO	CO	CO	SnR'_3[i]	IR, NMR (^1H, ^{13}C, ^{51}V)	257
V	$C(NMe_2)H^+$	CO	CO	NO	–	IR, NMR (^1H, ^{13}C, ^{51}V)	257
V	$C(SCH_2CH_2S)^+$	CO	CO	CO	$SnPh_3$	IR, NMR (^1H, ^{13}C, ^{51}V)	257
Nb	Me	CO	CO	CO, PPh_3	CO, PPh_3	–	266,279
Nb	Me	CO	CO	μ-Nb	μ-Nb	IR, NMR	279
Nb	Me	CO	–		PhC≡CPh	IR, NMR	268

[a] For abbreviations, see p. 3.

[b] R′ = H, Me, Ph.

[c] R′ = Me, Et.

[d] R′ = Ph, *p*-C_6H_6OMe, *p*-$C_6H_4NMe_2$, *p*-C_6H_4Cl.

[e] R′ = Ph, *p*-C_6H_6OMe, *p*-$C_6H_4NMe_2$.

[f] diphos = dppe, dppm, triphos.

[g] alkyl = Me, Et, *n*-Pr, *t*-Bu, Cy, *n*-heptyl, trityl, $CH_2C_5H_5$, $CH_2C_5H_4^-$.

[h] R′ = H, Me, Ph.

[i] R′ = Et, *n*-Bu, Ph, CH_2Ph.

TABLE 5

Complexes of M(II): (η^5-C_5H_4R)M(W)(X)(Y)(Z) (M = V, Nb, Ta)

M	R	W	X	Y	Z	Comments[a]	Ref.
Nb[b]	Me	CO	CO	μ-Cl	μ-Cl	X-ray, NMR (^{1}H, ^{13}C)	269
Nb[c]	Me	μ-Cl	μ-Cl	*p*-Tolylacetylene		X-ray, NMR (^{1}H, ^{13}C)	269
V, Nb, Ta	Alkyl	CO	CO	CO	μ-R[d]	–	267

[a] For abbreviations, see p. 3.

[b] See **198**.

[c] See **199**.

[d] See **200**.

TABLE 6

Complexes of M(III): (η^5-C_5H_4R)M(W)(X)(Y)(Z) (M = V, Nb, Ta)

M	R	W	X	Y	Z	Comments[a]	Ref.
V	Me	Cl, Br	Cl, Br	PMe_3, PEt_3	PMe_3, PEt_3	IR, NMR	264
V^-	Me	Cl	Cl	Cl	–	NMR	265
V, Nb, Ta	Me, Et, *t*-Bu	CO	CO	CO	μ-MR		267
Nb	Me	Cl	2(μ-Cl)	CO	CO	X-ray, NMR (^1H, ^{13}C)	269
Nb	Me	Cl	Cl		*p*-Tolylacetylene	NMR (^1H, ^{13}C)	269
Nb	$SiMe_3$[b]	Cl	Cl	CO	PMe_2Ph, dppe	IR, NMR	274,278
Nb, Ta	PS[c]	Cl	Cl	–	–	Cat	277(b)

[a] For abbreviations, see p. 3.

[b] This is a five-coordinate complex: extra ligand = PMe_2Ph or $\frac{1}{2}$dppe.

[c] 20% polystyrene crosslinked with DVB.

TABLE 7

Complexes of M(IV): (η^5-C_5H_4R)M(X)(Y)(Z) (M = V, Nb, Ta)

M	R	X	Y	Z	Comments[a]	Ref.
V	Me	Cl	Cl	Cl	IR, ESR, X-ray, NMR	265
V^-	Me	Cl	Cl	O	ESR, NMR	265
Nb	Me	Cl	Cl	Cl	ESR	273(a)
Nb	*t*-Bu, $SiMe_3$, CHMePh	Cl	Cl	Cl	ESR	273(a),274
Nb	PS[b]	Cl	Cl	Cl	ESR, Cat	277

[a] For abbreviations, see p. 3.

[b] PS = 20% polystyrene crosslinked with DVB, see **201**.

TABLE 8

Complexes of M(V): (η^5-C_5H_4R)M(W)(X)(Y)(Z) (M = V, Nb, Ta)

M	R	W	X	Y	Z	Comments[a]	Ref.
V	Me	Cl	Cl	O	–	NMR, MS	265
Nb	$SiMe_3$	Cl	Cl	Cl	OPh	IR, NMR	276
Nb	$SiMe_3$	Cl	μ-O		Catecholate[b]	IR, NMR, X-ray	276
Nb	Me, *n*-Bu	Cl	Cl	Cl	OH	–	270
Nb	Me, $SiMe_3$[c]	Cl	Cl	Cl	μ-O	IR, X-ray, NMR	271(a),271(c),274
Nb	Me, *t*-Bu, CHMePh	Cl	Cl	Cl	Cl	–	271(a),273(a),274
Nb	$SiMe_3$	Cl	Cl	Cl	Cl	IR	274
Nb	$SiMe_3$, Me	Cl	Cl	μ-O	2(μ-Cl)[d]	IR, X-ray, NMR	274
Nb	Me	Cl	Cl	$CH(CMe_3)$	–	IR (^1H, ^{13}C)	278
Nb, Ta	PS[e]	Cl	Cl	Cl	Cl	Cat	277(b)
Ta	Me, $SiMe_3$[d]	Cl	Cl	Cl	Cl	IR, NMR	270,271(a),275
Ta	$CH_2{=}CH$	F	F	F	F	–	272
Ta	$SiMe_3$	Cl	Cl		Diphenoxide[f]	IR, OS, NMR (^1H, ^{13}C)	275
Ta	$SiMe_3$	Cl	Cl	Cl	Cl	IR, NMR, OS	275
Ta	Me	Cl	CH_2Ph	CH_2Ph	CH_2Ph	NMR (^1H, ^{13}C)	278

[a] For abbreviations, see p. 3.

[b] See **205**.

[c] Also contains coordinated H_2O (**202**).

[d] See **203**.

[e] 20% polystyrene crosslinked with DVB.

[f] Ligand derived from diphenols 4-$RC_6H_3(OH)_2$ (R = H, Me, *t*-Bu), see **204**.

(iii) Chromium, molybdenum and tungsten [280–404] (Tables 9–20, pp.90–109)

The literature abounds with examples of monosubstituted cyclopentadienyl complexes of chromium, molybdenum and tungsten. The types of cyclopentadienyl substituents include simple alkyl, acyl and vinyl substituents as well as more elaborate chiral groups. There are examples of substituents that act as bridges between the cyclopentadienyl ring and the metal such that the metal is attached to the cyclopentadienyl ring not only via an η^5-bond, but also via the ring substituent. Polymer-supported cyclopentadienyl complexes have also been reported. Fulvene and ylide metal complexes have also been prepared and will be discussed where appropriate.

Apart from monometallic complexes, there are several dimers, trimers and clusters, which contain the substituted cyclopentadienyl ligand. There are also many examples of bimetallic complexes containing bridging cyclopentadienyl ligands, such as fulvalene, where the ligand can bind to two different metal centres.

Examples of studies in which methyl-substituted cyclopentadienyl complexes have been used, are:

(i) The greater solubility of $[(\eta^5\text{-}C_5H_4Me)Mo(CO)_3]_2$ compared with its unsubstituted cyclopentadienyl analogue, permitted photoreactions in hydrocarbon solvents to be performed at low temperatures [295].

(ii) In a study of the reactions of bimetallic dicyclopentadienyl compounds, one metal was bonded to an unsubstituted cyclopentadienyl ligand and the other metal was bonded to a methylsubstituted cyclopentadienyl ligand. Metal–metal cleavage led to a scrambling of cyclopentadienyl ligands, and the cyclopentadienyl rings served as effective metal labels [345].

(iii) The kinetics of carbonyl insertion reactions in complexes of the type $Cp^*Mo(CO)_3(CH_2Ph)$, where $Cp^* = C_5Me_5$ and C_5H_4Me, was compared with that of the analogous unsubstituted cyclopentadienyl derivatives. Results were interpreted on the basis of the electron-donating nature of the methyl substituent, as well as the increased steric size of the cyclopentadienyl ligand with increased ring substitution [346].

Generally, the metals in the cyclopentadienyl half-sandwich complexes are in the 0 to 2+ oxidation states, e.g. $(\eta^5\text{-}C_5H_5)M(CO)_3X$ (X = halide, alkyl), $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ and dimers, e.g. $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$. Only a few substituted cyclopentadienyl compounds containing Mo or W in higher oxidation states have been reported.

(a) $(\eta^5\text{-}C_5H_4R)ML_n$ complexes (M(0), M(I), and M(II))

The chemistry of compounds with metal oxidation states M(0), M(I) and M(II) are interlinked and thus these oxidation states will be treated together. For example, $Na[(\eta^5\text{-}C_5H_4CHO)M(CO)_3]$ formally contains M(0); the metal oxidation state in the related dimer $[(\eta^5\text{-}C_5H_4CHO)M(CO)_3]_2$ is M(I) and in $(\eta^5\text{-}C_5H_4CHO)M(CO)_3CH_3$ is M(II).

(1) Substituted cyclopentadienylmetal complexes derived from fulvene metal complexes. Behrens and co-workers have studied the reactivity of a number of fulvene metal complexes, including tricarbonyl fulvene chromium complexes, which, when reacted with nucleophiles, can be converted into substituted cyclopentadienyl complexes (**206–209**)[280,281].

The reduction of fulvene tricarbonyl chromium has also resulted in the formation of a substituted cyclopentadienyl complex (**210**) [281].

Other workers have also synthesised substituted cyclopentadienylmetal complexes, e.g. **211**, from fulvene metal complexes [282].

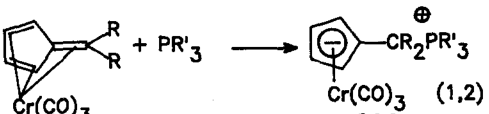
The reactivity of tricarbonyl(formylcyclopentadienyl) metallate anions of chromium, molybdenum and tungsten towards electrophiles was studied [324]. The electrophile can attack either the metal or the oxygen atom of the formylcyclopentadienyl ligand. This can readily be rationalised by the existence of the complex in two possible resonance forms (**212**).

The ylene form will favour attack at the oxygen atom, whereas the ylide form will favour reaction at the metal. Protonation of **212** (M = Mo, W) with acetic acid, leads to the formation of the hydride $(\eta^5\text{-}C_5H_4CHO)M(CO)_3H$, which is subsequently converted to the dimer $[(\eta^5\text{-}C_5H_4CHO)M(CO)_3]_2$ [324]. Dimeric complexes are also formed when $(\eta^5\text{-}C_5H_4CHO)M(CO)_3^-$ (M = Cr, Mo, W) are oxidised with iron(III) nitrate [324]. The electrophiles I_2, $SnMe_2Cl_2$ and $AuPPh_3Cl$ react at the metal centre to form the complexes $(C_5H_4CHO)M(CO)_3X$ (X = I, $SnMe_2Cl$ and $AuPPh_3$) [324]. Reactions occur on the ligand of the chromium complexes when the complex is reacted with the electrophiles RCOCl (R = Me, *t*-Bu, Ph, *p*-Cl-C_6H_4, OEt) to form the η^6-fulvene derivatives (**213**) [324].

However, when acyl chlorides are reacted with formylcyclopentadienyltricarbonyl complexes of molybdenum and tungsten, substituted cyclopentadienyl M(II) derivatives (**214**) are obtained as products [283].

(2) Friedel–Crafts acylation. Rausch has compared the aromatic behaviour of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (cynichrodene) [284] with that of other aromatic-type organometallic compounds, such as metallocenes (ferrocene, ruthenocene, osmocene) and cymantrene.

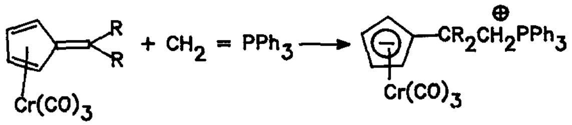
The synthesis of the acetylsubstituted compound $(\eta^5\text{-}C_5H_4COCH_3)Cr(CO)_2NO$ via Friedel–Crafts acetylation, using acetylchloride and $AlCl_3$, was reported in 1961 [285], but initially this method could not be generalised further. NMR studies were used to investigate this problem, and it was found that the order in which the reagents are added together is crucial. Thus, when the Lewis acid ($AlCl_3$) and the acylating reagent are added together first, $RCO^+AlCl_4^-$ forms. If this complex is then added



206

1	R	R'
a	H	CH_3
b	H	C_2H_5
c	H	C_6H_5
d	H	PR'_3 = $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$

2	R	R'
a	CH_3	CH_3
b	CH_3	C_2H_5
c	CH_3	$n{-}C_4H_9$
d	CH_3	PR'_3 = $P(CH_3)_2C_6H_5$
e	CH_3	PR'_3 = $PCH_3(C_6H_5)_2$



R = H,Me

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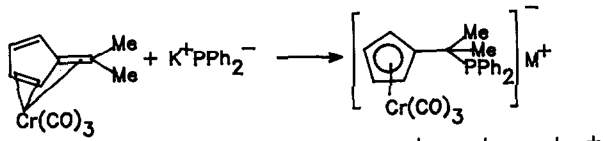
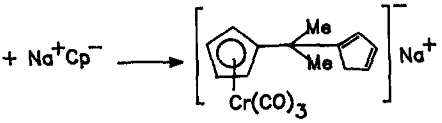


$M = K^+, NEt_4^+, PPh_4^+, Tl^+$

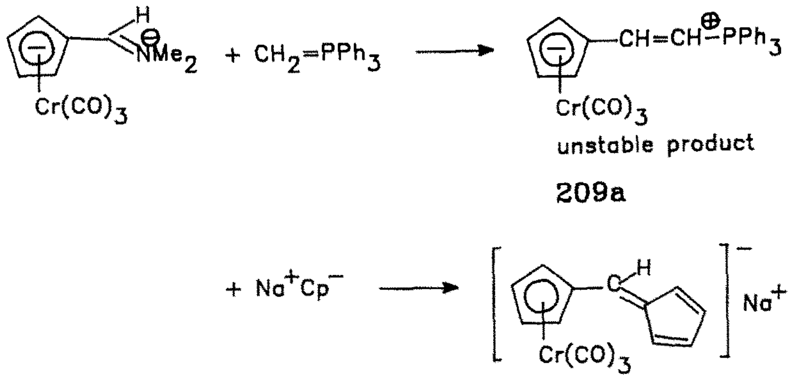
208a



208b

to the cyclopentadienyl complex, ketones and esters can be formed in good yield [284].

(3) Utilisation of substituted cyclopentadienide salts. Sodium, lithium and tetrabutylammonium salts are generally used, and although the use of thallium salts ought to be possible, no notable use has been made of it.



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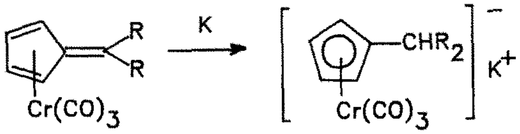

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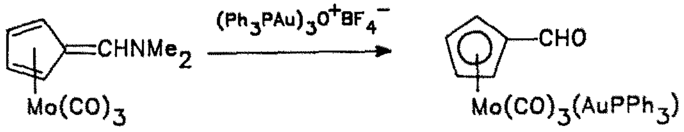

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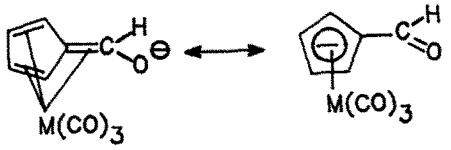

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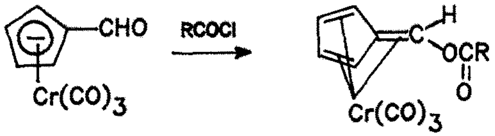

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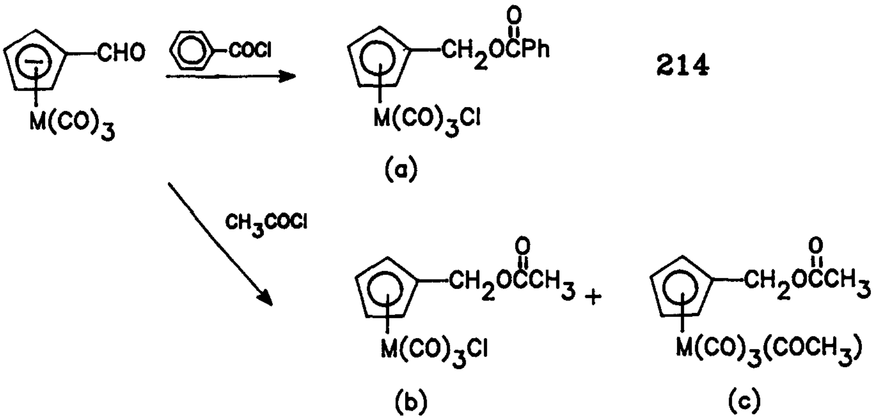


214

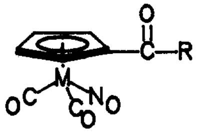
Sodium salts. The Friedel–Crafts acylation ring substitution reactions as described above, were unsuccessful when applied to similar molybdenum and tungsten starting materials [134(a)]. An alternative method for the synthesis of substituted cyclopentadienyl complexes of Mo, W, Cr, as well as Co, Rh and Ir (see later), utilising the sodium salt of the substituted cyclopentadienide was developed:

$$\mathrm{Na^+C_5H_5^- + RCOOR'} \xrightarrow{\mathrm{THF}/\Delta} \mathrm{Na[C_5H_4COR] + R'OH}$$

$$\mathrm{Na[C_5H_4COR] + M(CO)_6} \rightarrow \mathrm{Na[(\eta^5\text{-}C_5H_4COR)M(CO)_3]}$$

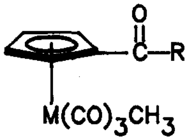
(R = H, OMe, Me; M = Cr, Mo, W [287])

Transformation of this product to nitrosyl (**215**) or alkyl (**216**) complexes can be achieved by standard procedures [134(a),(b),288].



R = OMe; M = Cr,Mo,W
R = H; M = Cr
R = Me; M = Cr,

215



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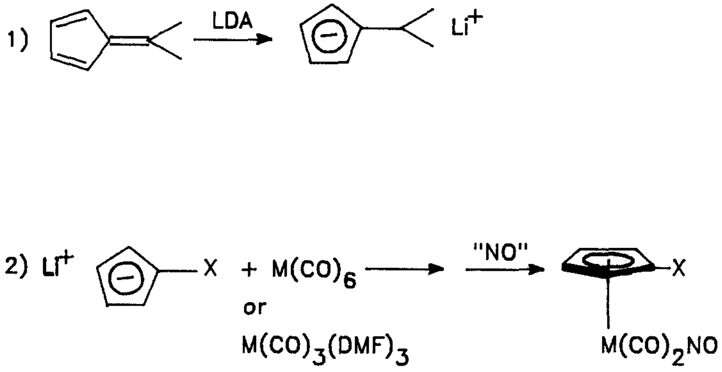
R = OMe; M = Cr,Mo,W
R = H,Me; M = Mo,W

Lithium salts. Another general method has been developed by Rausch and coworkers for synthesising substituted cyclopentadienylmetal complexes. This involves reaction of a metal carbonyl reagent with the lithium salt of the substituted cyclopentadienide [53,69,134(b)] (**217**), which may, for example, have been obtained from the corresponding fulvene.



$X = -CR{=}CH_2$; $R = H, Me$; $M = Mo, W$
$= -CH_2NMe_2$; $M = Mo$
$= NO_2$; $M = Cr$

217

NBu_4^+ salts. An alternative procedure for preparing the ions $CpCOR^-$, the electroreduction of $(\eta^5\text{-}C_5H_4COR)_2Fe$ (R = Me, OMe) in the presence of $[NBu_4^{n+}][PF_6^-]$, has been reported. The cyclopentadienyl ion, with NBu_4^+ as counterion, was reacted with $M(CO)_3L_3$ (M = Mo, W; L = THF, DMF), to form $[(\eta^5\text{-}C_5H_4COR)M(CO)_3]^-$ [137].

(4) Reactions on the substituent of the cyclopentadienyl ring in cyclopentadienylmetal complexes. Once an acyl-substituted cyclopentadienyl complex has been obtained, further reactions can be carried out to alter this substituent, e.g.

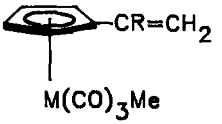
(a) acyl substituted cynichrodene can undergo reductions and substitutions, and form substituents such as –COOH, alcohols, olefins, alkyls and aryls [284];

(b) $(\eta^5\text{-}C_5H_4COR)M(CO)_3Me$ can undergo reactions on the substituent of the cyclopentadienyl ring to form ring substituents such as –CH(OH)Me (M = Mo [288]), –COOH, –COCl (M = W [288]), $-CR{=}CH_2$ (R = H, Me; M = Mo, W [134(a),288–291]. The latter complex (**218**) has been utilised as a monomer in vinyl polymerisation studies.

The analogous $-CH_2OCOCH{=}CH_2$ ring-substituted tungsten complex (**219**) is another useful monomer which has recently been synthesised [290,291].

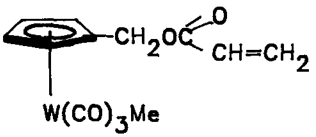
The intramolecular metalloester *trans*-$(\eta^5\text{-}C_5H_4CH_2CH_2OOC)M(CO)_2PR_3$ (**221**), was obtained by treating the alcohol-substituted cyclopentadienyl complex, $[(\eta^5\text{-}C_5H_4CH_2CH_2OH)M(CO)_3PR_3]BF_4$, (**220**), with base (M = Mo, W; R = Ph, *p*-tolyl) [292].

Iodocyclopentadienylmetal complexes have also been converted to ethynylcyclopentadienyl and dicyclopentadienyl mono- and bimetallic complexes (see also Sect. D.(v)(b)) [394].



M = Mo,W; R = H,Me

218



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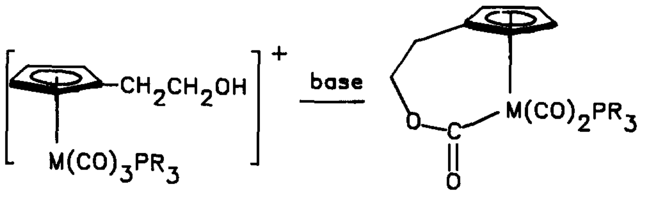
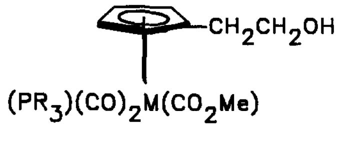


220 **221**

(5) Spirocyclopentadiene as precursor to internally bridged cyclopentadienylmetal complexes. Equilibrium data indicate that the intramolecular metalloester (**221**) is more stable than the corresponding methyl ester (**222**).



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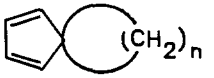
Eilbracht and co-workers have devised a novel way of synthesising intramolecularly bridged compounds by reactions of zero-valent transition-metal carbonyls (M = Cr, Mo, W, Fe, Ni) with spirocyclopentadienes (see Sect. C.(ii)(b)). For example, when M = Mo, Fe and Ni, reactions with spirocyclopentadienes such as **223** have resulted

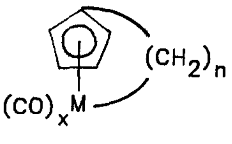


223

in C–C bond cleavage to form alkylene-bridged η^5-cyclopentadienyl-σ-alkyl complexes (**224**). When the C–C bond cleavage is accompanied by carbonyl insertion, the corresponding acyl complexes (**225**) are formed [122(a),293].

To investigate directing effects, similar reactions have also been performed on substituted [293,294] and chiral spirocyclopentadienes [122(c)] (**226**).

Although molybdenum and tungsten complexes of the type $M(CO)_3L_3$ undergo reactions with spirocyclopentadienes, reactions with the analogous chromium rea-



or

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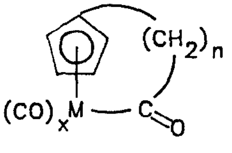

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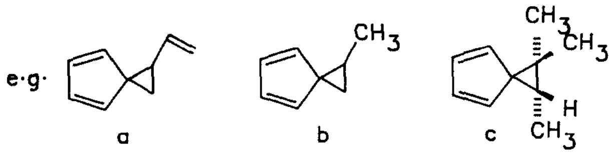
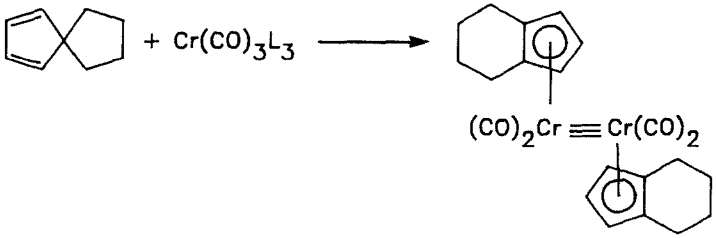


a b c

226

gents have not been successful and other products such as **227** are formed instead [294].



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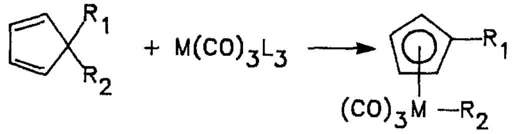
These ring opening reactions have been compared [294] with the reactions of 5,5-dialkylcyclopentadienes with metal carbonyls, where C–C bond cleavage has also been found to occur (in approximately 10% yield) (**228**).



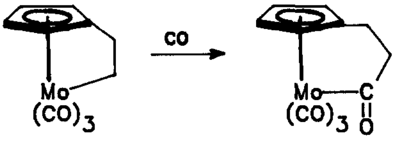
M = Mo; L_3 = diglyme
M = W; L = CH_3CN

	R_1	R_2
a	Me	Me
b	Et	Et
c	Et	Me
d	Me	Et

228

Carbonyl insertion into the molybdenum–carbon bond of the bridging cyclopentadienyl ligand is also possible, leading to a remarkably stable product (**229**) [294].

The steric effect of the chelating ($\eta^{5:1}$-$C_5H_4C_2H_4$) ligand on the bonding to the metal in ($\eta^{5:1}$-$C_5H_4C_2H_4$)$Mo(CO)_2$(η^2-diene) (diene = (E)-1,3-pentadiene, 2-methyl-1,3-butadiene) has been studied [295,296]. The bridge between Mo and the cyclo-



229

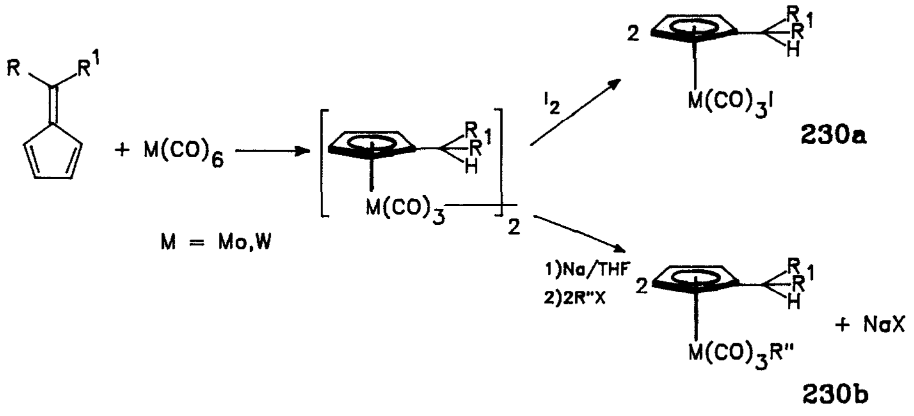
pentadienyl ring is expected to distort the coordination sphere in such a way that the position trans to the attachment point of the bridge is enlarged. This effect would be manifested in (i) the preference shown by coordination to one of the double bonds rather than the other, and (ii) the preferred conformational isomers obtained, with respect to rotation about the single bond which links the two double bonds. The least substituted C=C double bond has been found to be preferentially coordinated to the metal, despite the increased available space. NMR spectroscopy shows no interchange between the free and coordinated C=C bonds. Variable-temperature NMR studies were carried out to probe *syn* and *anti* isomerisation with respect to rotation about the C—C single bond (where the *syn* and *anti* isomers have the free double bond turned towards and away from the cyclopentadienyl ring, respectively) [295,296].

The anticipated enlargement of the coordination sphere around the metal in the complexes $(\eta^{5:1}\text{-}C_5H_4CH_2CH_2)M(CO)_3$ (M = Mo, W), was studied by reacting these complexes photochemically with various olefins to form $(\eta^{5:1}\text{-}C_5H_4CH_2CH_2)M(CO)_2(\eta^2\text{-olefin})$ and, in some cases, $(\eta^{5:1}\text{-}C_5H_4CH_2CH_2)M(CO)(\eta^2\text{-olefin})_2$. A cut-off point was found for the size of olefin that could be accommodated. Rotational isomerism with respect to rotation about the metal–olefin bond was studied by variable-temperature ^1H NMR spectroscopy [297].

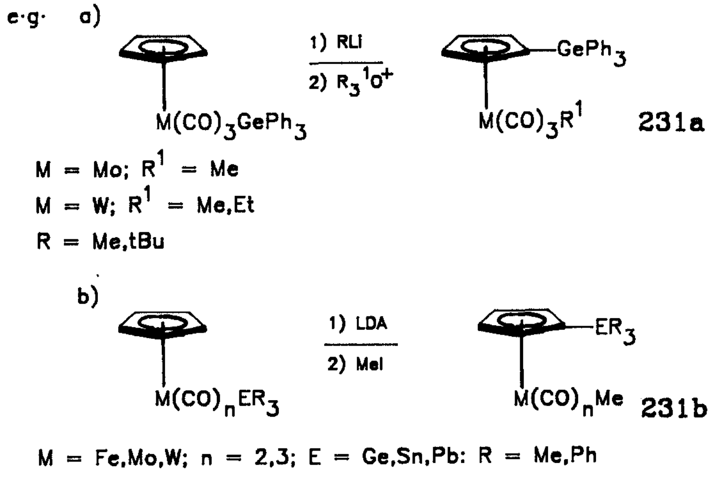
(6) Use of fulvenes to form substituted cyclopentadienylmetal complexes. Dimeric substituted cyclopentadienyl products have been obtained from the reaction between fulvenes and metal carbonyl reagents [41,64,298] and conversion from dimer to mononuclear product (**230**) is facile. The reaction between a fulvene and metal carbonyl complex needs to be carried out in a hydrogen-donating solvent since hydrogen abstraction is involved [41].

Mononuclear products have also been obtained from the reaction between $Mo(CO)_6$ and $Cr(CO)_6$ and 6-dimethylaminofulvene and 6,6-bis(dimethylamino)fulvene [57]. The same fulvenes do not react with $W(CO)_6$, but the reaction proceeds with $(CH_3CN)_3W(CO)_3$ [299].

Fulvenes are useful starting materials for the synthesis of chiral substituted cyclopentadienyl compounds (when $R \neq R'$ in the fulvene C_5H_4RR').



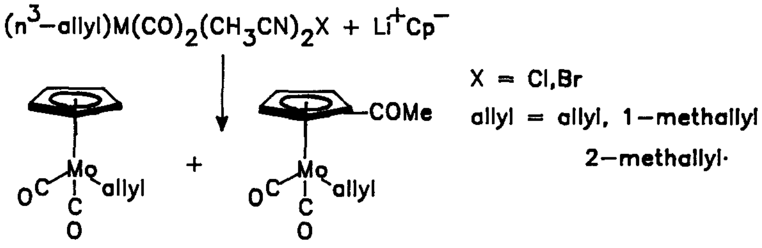
(7) Migration of a group from the metal to the cyclopentadienyl ring. A number of instances of base-induced migration of germyl, stannyl, plumbyl, ethyl and phenyl groups from the metal to the cyclopentadienyl ring have been reported, e.g. to form **231** [112,300,301,400]. However, the phenomenon of ligand migration does not



appear to have been observed to the same extent as with other metal complexes (e.g. iron) and generally occurs as a side reaction.

(8) Unusual methods of obtaining cyclopentadienyl ring substitution. An unusual acetyl substitution of the cyclopentadienyl ring has been reported [302]. In the standard preparation of the allylmolybdenum complexes, (η^5-C_5H_5)Mo(CO)$_2$-(η^3-allyl) from Mo(CO)$_2$(η^3-allyl)(CH_3CN_2)$_2$X and lithium cyclopentadienide, the desired product was obtained. However, an additional product was found in less

than 10% yield, which corresponded to the analogous acetyl-substituted cyclopentadienyl ring analogue (**232**).



232

Further investigation revealed that the acetyl group is derived from attack on the cyclopentadienyl by one of the metal-coordinated acetonitriles of the starting material. This would lead to the formation of an intermediate imine (**233**) which was hydrolysed to form an acetyl group during chromatographic purification [302].

In the reaction of $M[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ with PhCH=CHCOCl, the main product is the result of electrophilic attack on the metal, with acylation of the cyclopentadienyl ring to form **234** occurring as a side reaction [303].

Electrophilic substitution of the cyclopentadienyl ring of $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ in the presence of BF_3 and propanol, to form a propylcyclopentadienyl derivative (**235**), has been reported [304].

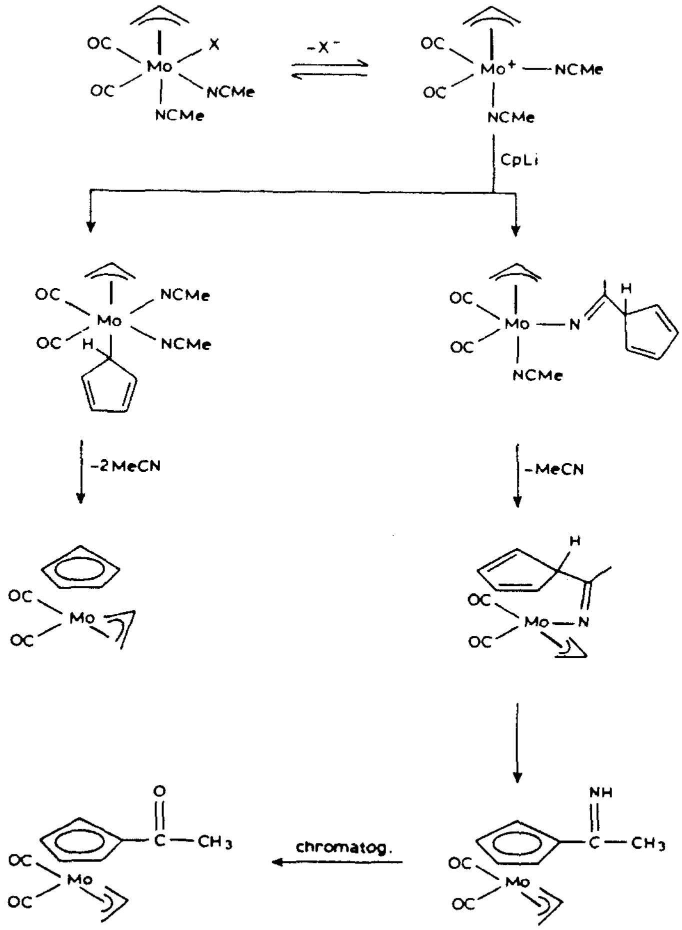
An interesting case of ligand migration [305] has been reported for a chromium-containing cluster. In the reaction, a *t*-butyl group migrated from the thiolate bridge to the cyclopentadienyl ring (**236**).

Treatment of $[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ (M = Mo, W) with $SOCl_2$, at low temperature (−97°C), led to the formation of $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ and a compound which was reported to contain a THF-substituted cyclopentadienyl ligand [392].

(9) Substituted cyclopentadienyl-containing organometallic monomers and polymerisation studies. Rausch has reported the synthesis of a range of organometallic complexes, which include the Cr-, Mo- and W-containing monomers (**237a** and **237b**) [17,69,291,350,365,366]

Radical-initiated reactions that have been carried out with **237a** and **237b** include homopolymerisation and copolymerisation reactions with compounds such as styrene, *N*-vinyl-2-pyrrolidone, vinylcymantrene, acrylonitrile and methyl methacrylate. Reactivity ratios, Alfrey–Price parameters, resonance interaction parameters and kinetic parameters have been determined for some of these reactions. These monomers have all been found to be extremely electron-rich, and resemble aromatic organometallic monomers such as vinylferrocene and vinylcymantrene.

(10) Optically active organomolybdenum compounds. Rausch has reported the synthesis of an optically active organomolybdenum compound (**238**), with the chiral



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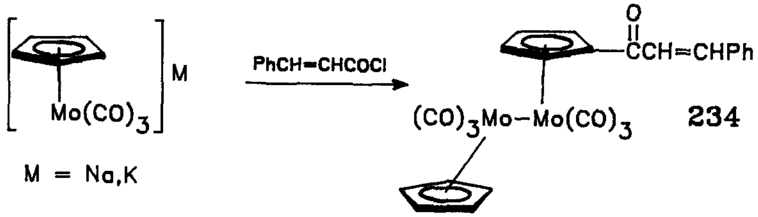

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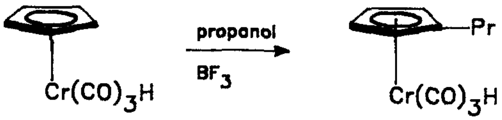

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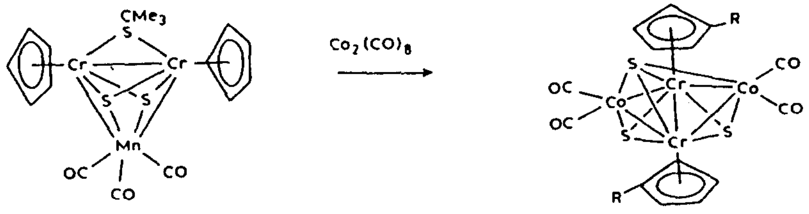

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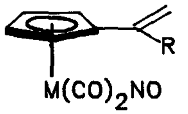
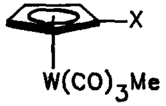


a R = H,Me; M = Cr,Mo,W

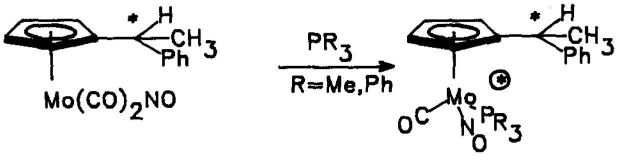


b X = CR=CH$_2$; R = H,Me

X = CH$_2$OCOCH=CH$_2$

237

centre on the cyclopentadienyl ring substituent. The product was obtained from the reaction between molybdenum hexacarbonyl and the optically active cyclopentadienyl salt, Li[C_5H_4CHMePh] (obtained by the asymmetric reduction of 6-methyl-6-phenylfulvene utilising LiAlH$_4$/(−)−quinine) [306]. Substitution of a carbonyl by a phosphine on molybdenum has resulted in the formation of **239**, which contains two chiral centres. The two diastereomers were found in a 50/50 mixture [306].



238 **239**

Faller and co-workers have used a chirally substituted cyclopentadienyl ligand to synthesise neutral or cationic systems of the type (η^5-C_5H_4NM)Mo(NO)(X)-(η^3-allyl), (X = CO, I and NM = neomenthyl).

These compounds have been synthesised according to the following reaction sequence:

(a) Li[C_5H_4NM] + (allyl)Mo(CO)$_2$(CH$_3$CN)$_2$X→(η^5-C_5H_4NM)Mo(CO)$_2$(allyl) X = Cl or Br

(b) $(\eta^5\text{-}C_5H_4NM)Mo(CO)_2(allyl) + NO[PF_6] \rightarrow [(\eta^5\text{-}C_5H_5NM)Mo(CO)(NO)\text{-}(allyl)]PF_6$

(c) Substitution reactions on the metal.

The optically active complexes have been used to study reactions such as:

(a) Stereospecific carbonyl displacement reactions on the metal, e.g. reaction of $(\eta^5\text{-}C_5H_4NM)Mo(NO)(CO)(allyl)$ with X to form $(\eta^5\text{-}C_5H_4NM)Mo(NO)(X)(allyl)$, where $X = CO$, I^- and allyl $= \eta^3\text{-}C_3H_5$, $\eta^3\text{-}2\text{-}CH_3\text{-}C_3H_4$ [307,308].

(b) Reactions on the allyl ligand, e.g.

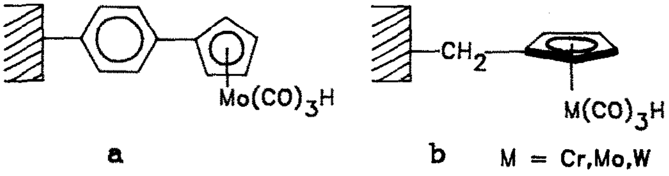
(i) when $X = CO$, nucleophilic attack on the η^3-1,3-dimethylallyl and η^3-cyclooctenyl ligands, to form optically pure allylically substituted olefins and cyclic olefins in high optical yield has been achieved [309,310];

(ii) when $X = Cl$, attack on the ligand η^3-2-methallyl by aldehydes, to give allyl alcohols with extremely good ee values (>97%) was accomplished [311].

The stereochemical outcome of the above reactions is controlled by the chirality at the Mo centre (with its four different groups: cyclopentadienyl, NO, X and allyl). The chiral substituent on the cyclopentadienyl ring, neomenthyl, is responsible for the facile separation of starting material and product diastereomers, and permits the unequivocal determination of the stereochemistry of the product.

Methods that have been used to characterise these compounds include X-ray crystallography, optical rotatory dispersion, circular dichroism and ^1H NMR spectroscopy.

(11) Polymer-supported cyclopentadienylmetal complexes. A few polymer-supported cyclopentadienylmetal complexes have been synthesised [312,313], e.g. **240a** and **240b**.



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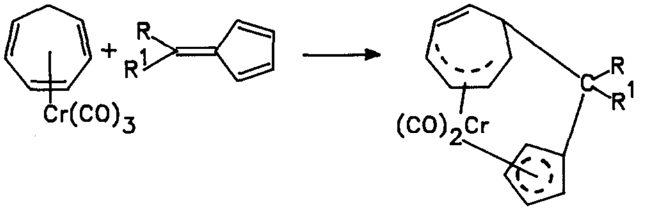
The polymer-supported Cr and Mo compounds (**240b**), when compared with their unsupported $(\eta^5\text{-}C_5H_5)M(CO)_3H$ analogues, show high thermal stability. No loss of H_2 occurs before 180°C, after which point thermal decomposition occurs. Hydrogen loss does not lead to the formation of a dinuclear species (cf. the formation of $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$, which occurs for the unsupported $(\eta^5\text{-}C_5H_5)M(CO)_3H$) [313].

The reactions between several THF-soluble bases and $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ were compared with the same reactions employing the polystyrene-bound analogue (**240a**). It was found that the pKa values of the polymeric and monomeric molybdenum hydrides did not differ significantly [312].

(12) Intramolecular cyclopentadienyl bridging ligands. Cyclopentadienyl ligands that are attached to the metal via a cyclopentadienyl substituent in addition to the η^5-bond have been mentioned previously (Sect. D.(iii)(a)(5)). Kreiter and Kurz have synthesised a number of $\eta^{3:5}$-cyclopentadienyl chelating ligands, which are effectively two ligands: an η^5-cyclopentadienyl ligand and an η^3 ligand joined together. These compounds are obtained from the photochemical reactions between pentafulvenes and $(\eta^6\text{-}C_7H_8)Cr(CO)_3$, $(\eta^6\text{-}C_8H_8)Cr(CO)_3$ or $(\eta^6\text{-}C_{10}H_{12})Cr(CO)_3$ [295,314,315].

When $(\eta^6\text{-}C_7H_8)Cr(CO)_3$ reacts with pentafulvenes, a dicarbonylchromium unit attached to an η^5-cyclopentadienyl ligand, which is further joined together by a —CRR′— group, is formed (**241**).



241

	a	b	c	d	e	f
R	Me	Me	Ph	OMe	H	H
R^1	Me	Ph	Ph	OMe	OCOMe	NMe_2

The resulting compounds are chiral, with the origin of chirality on the ligands. When R ≠ R′, the ligand has *two* chiral centres. When R = R′ = Ph, the above reaction also takes place, forming **242a**, as well as a second reaction with **242b** as the product.

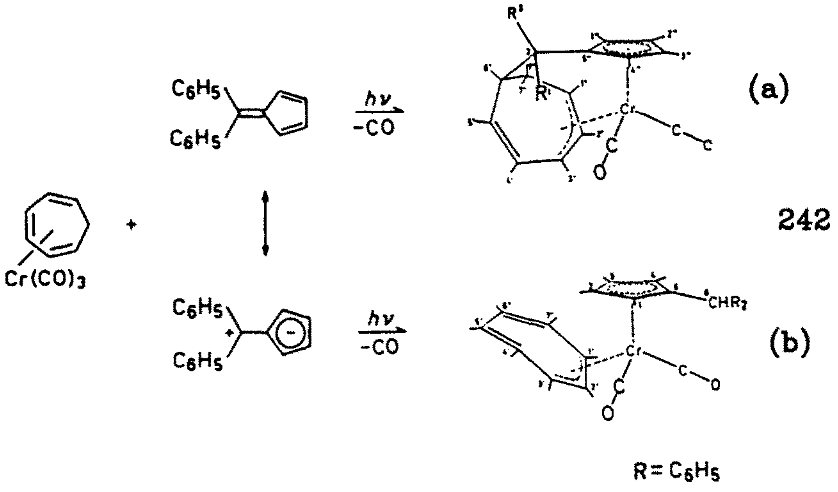
The reaction between $(\eta^6\text{-}C_{10}H_{12})Cr(CO)_3$ and pentafulvenes also leads to the formation of compounds containing $\eta^{3:5}$-cyclopentadienyl chelate ligands. In this case, three different types of compound are possible (**243a–c**) (**243a** R = R′ = Me; R = H, R′ = NMe_2; **243b** R = R′ = Me; R = Me, R′ = Ph; R = H, R′ = NMe_2; **243c** R = Me, R′ = Ph; R = R′ = Ph).

A dicarbonylchromium unit attached to an $\eta^{3:5}$-cyclopentadienyl chelating ligand also results from the reaction between a pentafulvene and $[Cr(CO)_3(\eta^6\text{-}C_8H_8)]$ (**244**). With 6-dimethylaminofulvene, a ring contraction reaction occurs to form **245**.

A photochemical reaction between 6,6-dimethylfulvene tricarbonyl chromium and cycloheptatrienes (C_7H_7R) to form products with various $\eta^{3:5}$-ligands was also documented (**246a–e**).

$$(\eta^6\text{-}C_8H_{10})Cr(CO)_3 + C_7H_7R \rightarrow \underset{\textbf{246a–e}}{(\eta^{3:5}\text{-}C_{15}H_{17}R)Cr(CO)_2} + CO$$

R = H, Me, OMe



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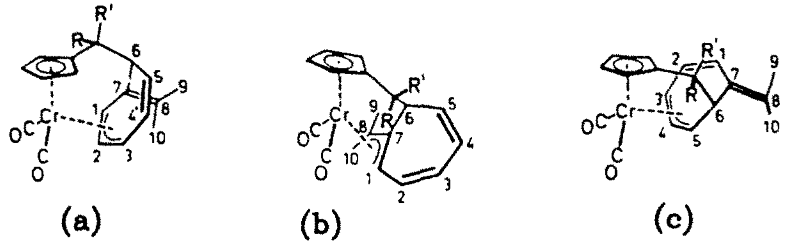
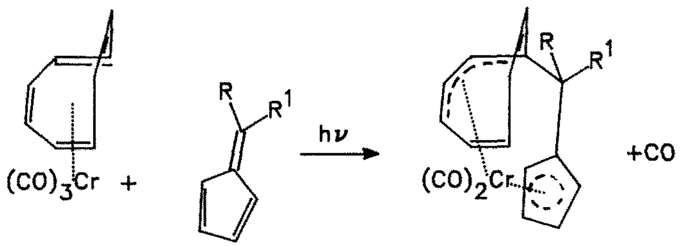


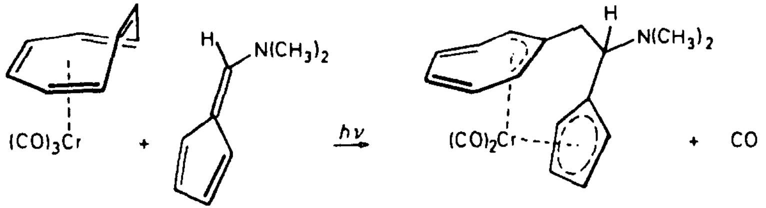
(a) (b) (c)

243



244

	a	b	c	d	e	f
R	Me	Me	Ph	OMe	H	H
R^1	Me	Ph	Ph	OMe	OCOMe	NMe$_2$



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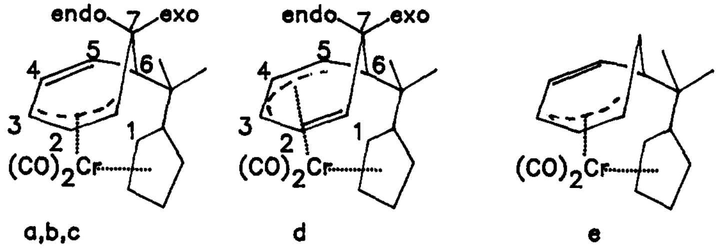
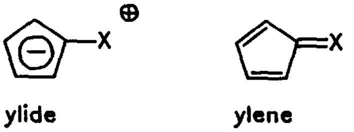


	a	b	c,d
endo	CH_3	OCH_3	H
exo	H	H	OCH_3

246

(13) Fulvene and ylide metal complexes. Although fulvene and ylide metal complexes would appear to fall outside the scope of this review, which is concerned with η^5-bonded cyclopentadienyl complexes, they are pertinent for two reasons. Firstly, fulvenes and ylides can be represented by two extreme resonance structures, the so-called ylide and ylene forms [316], which are η^5- and η^6-bonding respectively (**247**).



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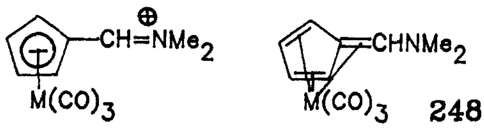
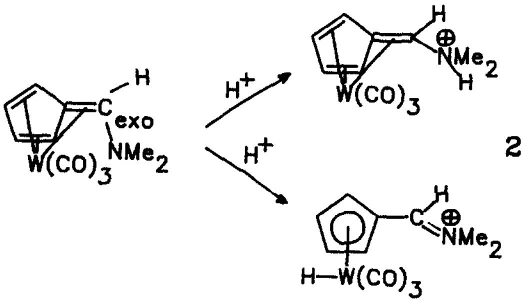
Secondly, when fulvenes are coordinated to metals they can serve as a entry to substituted cyclopentadienylmetal complexes.

As expected, the dipole moments of ylides are larger than those of ylenes [317] and quantum mechanical calculations [317,318] have been performed on some fulvenes and ylides to determine the percentage ylide vs. ylene character. Setkina and co-workers have used a number of methods to distinguish between the ylide and ylene forms in complexes of the type $(C_5H_4X)M(CO)_3$ ($X = SMe_2$, PPh_3, CPh_2, etc; $M = Cr$, Mo, W). They have shown that there is a linear dependence between the mean ^{13}C chemical shift of the cyclopentadienyl ring carbons and the dipole moments of these ligands. The cyclopentadienyl ring carbons are more shielded in the ylides than in the ylenes [316]. The deshielding of the ylides is more evenly distributed amongst the cyclopentadienyl carbons than in the ylenes [316,319]. Variable-temperature ^1H NMR spectroscopy was used to study $(C_5H_4CHNMe_2)M(CO)_3$ (M = Cr, Mo, W), and to establish which one of the two resonance forms shown for **248** best describes the metal carbonyl complex.



248

The barrier to rotation was determined for the C_{exo}—N bond, and was found to depend on the metal (the barrier to rotation increases: W < Mo < Cr) and the solvent (the barrier to rotation increases as the polarity of the solvent increases: acetone < nitromethane < DMF) [320]. Protonation experiments carried out on the above compounds, where M = W [321], have shown that the acidity of the solvent also affects the compound's resonance form. In weakly acidic media, where rotation about C_{exo}—N is increased with respect to the parent fulvene, the N atom is protonated and in strongly acidic media, where rotation about the C_{exo}—N bond is less, the W atom is protonated (**249**).

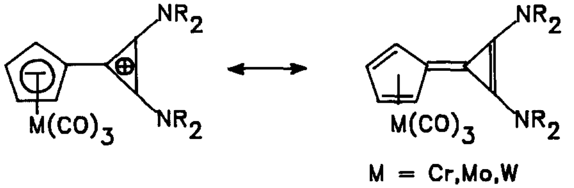


249

It is also possible to deduce whether an $(\eta^5\text{-}C_5H_4X)ML_n$ compound is η^5- or η^6-bonded from X-ray crystallography. Among the distinguishing features are the distance between M and X, cyclopentadienyl C—C bond lengths, the C_{ipso}—X bond length, and displacement of the metal from the centre of the cyclopentadienyl ring. For example, in $(C_5H_4SMe_2)Cr(CO)_3$ [322], the Cr···S distance is of a non-bonding length. The S atom also deviates from the plane of the cyclopentadienyl ring in the direction *away* from the metal and the cyclopentadienyl C—C bond lengths are very similar, indicating an ylide structure. Behrens and co-workers have also determined a number of molecular structures to ascertain the bonding type (η^5- or η^6-) of various metal fulvene complexes. Hence $(\eta^5\text{-}C_5H_4CHNMe_2)Cr(CO)_3$ [323] and $[(\eta^5\text{-}C_5H_4CHO)Cr(CO)_3]PPh_4$ [146] have been shown to contain η^5-bonding cyclopentadienyl ligands, whereas the strong Cr—C_{exo} interaction and the bond lengths in the cyclopentadienyl ring of the compound $(C_5H_4CHOCOC_6H_5)Cr(CO)_3$ [324] indicated η^6-bonding. The molecular structure of (η^5-$C_5H_4PPh_3$)$Cr(CO)_3$ was determined [325] and the data indicate that the $C_5H_4PPh_3$ ligand is in the ylide form.

Interaction between the metal centre and the phosphonium group in complexes of the type (η^5-$C_5H_4PPh_3$)$M(CO)_3$ (M = Cr, Mo, W) could affect the chemistry at the metal centre, and this possibility has been studied [326].

(Diaminocalicene)tricarbonylmetal compounds (**250**) have also been studied in order to determine the contributions of the alternative resonance structures:



250

The position of the C_{ring}—N stretching bands in the infrared region indicate π-electron delocalisation, i.e. the dipolar form, best represents the molecular structure. This is also supported by ^{13}C NMR chemical shift values [328].

The most common method used to synthesise fulvene or ylide metal complexes is:

$$M(CO)_3L_3 + C_5H_4X \rightarrow (C_5H_4X)M(CO)_3$$

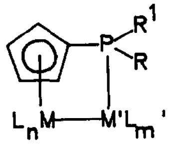
where L_3 can be 3CO [329,330], $3CH_3CN$ [280,298,318,326,331] or diglyme [298].

The following method [146] is used to form a fulvene-like complex, e.g. for X = CHO:

$$M(CO)_3(CH_3CN)_3 + Na[C_5H_4X] \rightarrow Na[(C_5H_4X)M(CO)_3]$$

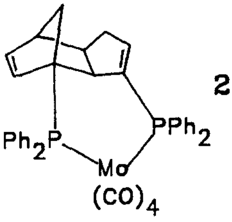
(14) Bimetallic complexes containing bridging cyclopentadienyl ligands. The cyclopentadienyl ring can be used in bimetallic systems to hold the two metals together [332]. Hence bridging cyclopentadienyl-derived ligands are of great interest in the area of heterobimetallic compounds.

One of the cyclopentadienyl ligand types that has been used in this area is cyclopentadienylphosphine [174,286,333], which gives compounds type **251**.



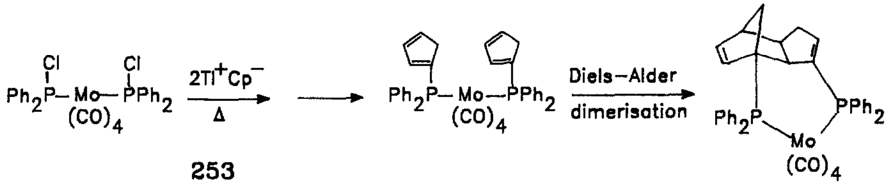
251

An alternative type of reaction for the diphenylphosphino cyclopentadiene ligand has been reported [334]. Reaction between [*cis*-$Mo(CO)_4(Ph_2PCl)_2$] and two equivalents of thallium cyclopentadienide in refluxing toluene yielded the compound **252**.



252

This complex, which has been fully characterised by microanalysis, ^{1}H NMR, IR and mass spectroscopy, as well as by X-ray crystallography, contains a diphosphine ligand in which the two phosphorus atoms are bridged by dicyclopentadiene. The bridging dicyclopentadiene appears to have been formed via intramolecular Diels–Alder dimerisation of two complexed diphenylphosphinocyclopentadienyl ligands (**253**).



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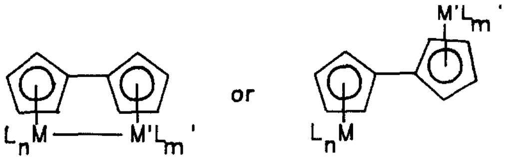
252

Fulvalene has also been used as a bridging ligand and can hold bonded or non-bonded metal centres in hetero- or homometallic systems close together (**254**).

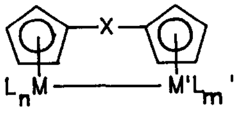


254

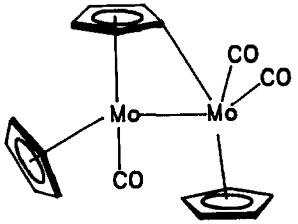
Drage and Vollhardt [332] have shown that, in metal–metal bonded systems bridged by the fulvalene ligand, a bending distortion occurs which results in the metals being pushed further apart and the metal–metal bond being weakened. This in turn may increase the reactivity of the metals relative to unbridged cyclopentadienylmetal dimers.

Other types of bridging cyclopentadienyl ligand have also been used, e.g. **255** (e.g. X = SiMe$_2$) or **256** [188,190(b),335].

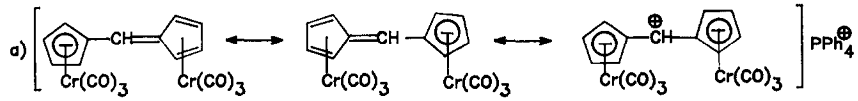
A number of fulvenylcyclopentadienyl bridging complexes (**257**) have also been synthesised [281].



255



256



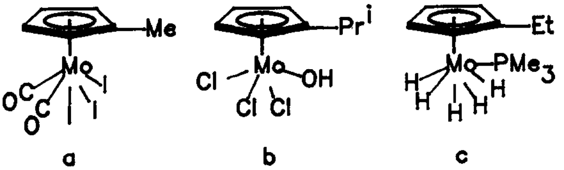
b) $[\{C_5H_4C(NMe_2)C_5H_4\}Cr_2(CO)_6]^{-}PPh_4^{+}$

257

(b) (η^5-C_5H_4R)ML_n complexes (M(III)–M(VI))

Very few substituted cyclopentadienyl complexes containing Group 6 metals in oxidation states other than 0, I and II have been synthesised. The type of chemistry studied in these complexes has not been concerned with the ring substituents.

For example, Green and co-workers [336–343] and others [344] have synthesised a number of substituted cyclopentadienyl-containing complexes with metals in oxidation states III–VI. The novelty of these compounds relate to the other ligands attached to the metal, such as O, S, halogen, H, OH and phosphine (**258**).



258

These compounds have been extensively characterised by NMR studies (^{1}H, ^{13}C, ^{31}P, variable temperature) and X-ray crystallography.

TABLE 9

Group 6 metal complexes of the general formula $[(\eta^5\text{-}C_5H_4R)M(CO)_3]^- \; M'^+$

M	R	M'^+	Comments[a]	Ref.
Cr	$CHMe_2$	K^+	IR	281(a)
Cr	$CHPh_2$	K^+, PPh_4^+	IR, NMR	281(a)
Cr	CHC_5H_4	Na^+, PPh_4^+	IR, NMR	281(a)
Mo	CHC_5H_4	PPh_4^+	IR, NMR (^1H, ^{13}C), X-ray	281(b)
Cr	$CMe_2(C_5H_5)$	Na^+	IR, NMR	281(a)
W	CH_2OH	Na^+	NMR, IR	292
Mo, W	$(CH_2)_nOH$ ($n=2, 3$)	Na^+	NMR, IR	292
Cr	CHO	PPh_4^+	X-ray	146
Cr, Mo, W	CHO	Na^+	IR, NMR	146,324,283,287,292
Cr, Mo, W	COMe	Na^+	–	287
W, Mo	COMe, CO_2Me	NBu_4^+	IR, voltammetry	137
Cr	COMe, CO_2Me	Na^+	–	395
Cr, Mo, W	CO_2Me	Na^+	–	287
Cr	CMe_2PPh_2	K^+, NEt_4^+, PPh_4^+, Tl^+	IR, NMR (^1H, ^{31}P)	281(a)

[a] For abbreviations, see p. 3.

TABLE 10

Group 6 metal compounds of the general formula (η^5-C_5H_4R)M(A)(B)(C)(D)

M	R	A	B	C	D	Comments[a]	Ref.
Mo	Me	CO	CO	CO	HgX X = Cl, Br, I	NMR (^{199}Hg, ^{95}Mo)	347
Mo	Me	CO	CO	CO	$SnPh_3$, HgBr, HgI, HgSCN	–	352
Mo	Me	CO	CO	CO	HgCl	X-ray	352
Mo	Me	CO	CO	$P(OMe)_3$	I	X-ray	353
Mo	Me	CO	CO	$-\overline{CH(CH_2)_3O}-$		X-ray	354
Mo	Me	CO	CO	HgI	$AsPhMe_2$	X-ray	355
Mo	Me	CO	CO	CO	$BiCl_2$	NMR (^{1}H, ^{13}C), IR	356
W	Me	CO	CO	CO	Cl	NMR (^{1}H, ^{13}C), IR	356
Mo	Me	CO	CO	CO	CH_2Ph	–	346
Mo	Me	CO	CO	(η^3-$PhCH_2NCPhNCHMe$- (*p*-X-Ph)) X = H, F, OMe		NMR	376
Mo, W	Me, Et	CO	CO	CO	Me, Et	NMR, IR, UV, MS	294
Mo	Me, COMe, $SiMe_3$	CO	CO	I	$\{-\overline{CO(CH_2)_2C}H_2\}$	–	358
Mo	H, Me, i-Pr	CO	CO	CO	Br	–	393
W	Et	PMe_3	PMe_3	PMe_3	H	NMR, MS	340,341,342
Mo	i-Pr, CHMeEt, $CHEt_2$, CHPhMe, *p*-$MeO\cdot C_6H_4\cdot CH_2^-$, CHMe*m*-Pr	CO	CO	CO	I	IR	41
Mo	i-Pr	CO	CO	CO	Me	NMR (^{1}H, ^{13}C)	357
Mo	i-Pr, $CHEt_2$	CO	CO	CO	Me, I	IR, NMR (^{1}H, ^{13}C)	41
Mo	CHPhMe	CO	CO	CO	Me	IR, NMR (^{1}H, ^{13}C)	41

TABLE 10 (*continued*).

M	R	A	B	C	D	Comments[a]	Ref.
Mo	CHC_5H_4	CO	CO	CO	Me	IR, NMR (^1H, ^{13}C)	281(b)
Cr	Pr	CO	CO	CO	H	–	304
Mo	NM[b,c]	CO	CO	(η^3-C_3H_5)		NMR, IR	307,308
Mo	NM	NO	I	(η^3-C_3H_5), (η^3-C_4H_7)		X-ray	307,308
Mo	NM	CO	CO	(η^3-2-methallyl)		IR	308
Mo	NM	CO	CO	(η^3-1,3-dimethylallyl)		IR, NMR	309
Mo	NM	NO	CO	(η^3-2,2,3-trimethylhex-4-enal)		X-ray	309
Mo	NM	NO	CO	(2,4-Dinitrophenyl) hydrazone derivative of above.		IR, NMR	309
Mo	NM	NO	I	(η^3-2-methylallyl)		IR, NMR	308,311
Mo	NM	NO	($OSO_2C_6H_5$)	(η^3-C_3H_5)		–	308
Mo	NM	CO	CO	(η^3-C_8H_{13})		IR, NMR	310
Mo	NM	NO	Br	(η^3-C_8H_{13})		IR, NMR, X-ray	310
Mo	NM	NO	CO	(η^3-methallyl)		IR, NMR, X-ray	310
Cr	$CHPh_2$	CO	CO	(η^3-C_7H_7)		NMR (^1H,^{13}C), IR	295,314
Mo, W	$CR{=}CH_2$ $R = H$, ME	CO	CO	CO	Me	NMR, IR, MS	134(a)
Mo, W	$CH{=}CH_2$	CO	CO	CO	Me	NMR, IR, MS	288,290
Mo, W	$C(Me){=}CH_2$	CO	CO	CO	Me	NMR, IR, MS	288
Mo, W	$C{\equiv}CH$	CO	CO	CO	Me	IR, NMR (^1H, ^{13}C)	394
W	$C{\equiv}CSnMe_3$	CO	CO	CO	Me	IR, NMR (^1H, ^{13}C)	394
Mo, W	$-\overline{C(t\text{-Bu})C(t\text{-Bu}){=}C}(t\text{-Bu})$	CO	CO	CO	H	–	111
Mo, W	$(CH_2)_nOH$ $n = 1, 2, 3$	CO	CO	CO	H	NMR, IR	292

Mo	$CH(OH)CH_3$	CO	CO	CO	Me	NMR, IR, MS	288,291
W	CH_2OH	CO	CO	CO	Me	–	291
W	$CH(OCH_3)CH_3$	CO	CO	CO	Me	–	291
Mo, W	COR; R = H, Me	CO	CO	CO	Me	NMR, IR, MS	134(a)
W	CHO	CO	CO	CO	Me	NMR, IR, MS	290,291
Mo, W	CHO	CO	CO	CO	Me	NMR, IR, MS	288
Cr, Mo, W	CHO	CO	CO	CO	I	NMR (^1H, ^{13}C)	324
Cr, Mo, W	CHO	CO	CO	CO	$SnMe_2Cl$	NMR (^1H, ^{13}C)	324
Mo, W	CHO	CO	CO	CO	$AuPPh_3$	NMR (^1H, ^{13}C)	324,282(b)
Mo	CHO	CO	CO	CO	$AuPPh_3$	X-ray	282(a)
Cr	CHO	CO	CO	CO	$AuPPh_3$	NMR (^1H,^{13}C), X-ray	282(b),324
Mo	COMe	CO	CO	(η^3-allyl)		IR, MS, NMR (^1H, ^{13}C), X-ray	302
Mo	COMe	CO	CO	(η^3-1-methallyl) (η^3-2-methallyl)		IR, MS, NMR (^1H, ^{13}C)	302
Mo	COMe	NO	CO	(η^2-allylphenylthioether)		IR	302
Mo	COMe	NO	CO	(η^2-dimethyl(allyl)benzylmalonate)		IR, NMR	302
W	$COCH_3$	CO	CO	CO	H	NMR, IR, MS	134(b)
W, Mo	COMe, CO_2Me	CO	CO	CO	Me, I	IR, voltammetry, NMR	137
Cr, Mo, W	CO_2CH_3	CO	CO	CO	Me	NMR, IR, MS	134(a)
W	CO_2CH_3	CO	CO	CO	I	NMR, IR, MS	288
Cr, Mo, W	CO_2CH_3	CO	CO	CO	Me	NMR, IR, MS	288
W	CO_2H	CO	CO	CO	Me	NMR, IR, MS	288
W	COCl	CO	CO	CO	Me	NMR, IR, MS	288
W	$CH_2OCOCH=CH_2$	CO	CO	CO	Me	NMR, IR, MS	290,291
Mo	CH_2OCOCH_3	CO	CO	CO	Cl	IR, NMR	283
W	CH_2OCOCH_3	CO	CO	CO	Cl	IR, NMR X-ray	283
Mo, W	CH_2OCOCH_3	CO	CO	CO	$COCH_3$	IR, NMR	283
Mo, W	$CH_2OCOC_6H_5$	CO	CO	CO Cl		IR, NMR	283

TABLE 10 (*continued*).

M	R	A	B	C	D	Comments[a]	Ref.
Cr	$NHNMe_2$	CO	CO	(η^3-C_7H_7)		NMR (^1H, ^{13}C), IR	315
Cr	$CHPPh_2$	CO	CO	CO	$AuPPh_3$	IR, NMR (^1H, ^{31}P)	281
W	PPh_2	CO	CO	CO	Me	MS, NMR (^1H, ^{13}C, ^{31}P)	286
Mo	PPh_3	CO	CO	CO	CdI_2, $HgBr_2$ HgI_2, $GaBr_3$	IR	326
Mo, W	PPh_3	CO	CO	CO	$HgCl_2$, $InBr_3$	IR	326
Mo	PPh_3	CO	PPh_3	N_2Ar	PF_6	IR	326
Mo	$GeMe_3$	CO	CO	CO	Me	IR	300
W	$GeMe_3$	CO	CO	CO	Me, Et	IR	300
Mo, W	$GeMe_3$	CO	CO	CO	Me	IR, NMR (^1H, ^{13}C)	301
Mo, W	$SnPh_3$	CO	CO	CO	Me	IR, NMR (^1H, ^{13}C)	301
Mo, W	$PbPh_3$	CO	CO	CO	Me	IR, NMR (^1H, ^{13}C)	301
Mo, W	I	CO	CO	CO	Me	–	394
Mo	$(CH_2)_2Fe(\eta^5$-$C_5H_5)(CO)_2$	CO	CO	CO	Me	IR, NMR, MS	97
W	$PPh_2Fe(\eta^5$-$C_5H_5)(CO)(COMe)$	CO	CO	CO	Me	IR, NMR (^1H, ^{13}C, ^{31}P)	286
Mo, W	CMe_2(2-pyridyl)	CO	CO	CO	Me	IR	247(b)

[a] For abbreviations, see p. 3.

[b] NM = neomenthyl.

[c] Enantiomerically pure compounds have been isolated for NM derivatives, but for the sake of simplicity, stereochemical aspects such as enantiomerism, and endo-, exo-isomerism have not been indicated in these tables.

TABLE 11

Group 6 metal compounds of the general formula $(\eta^5\text{-}C_5H_4R)M(A)(B)(C)$

M	R	A	B	C	Comments[a]	Ref.
W	Me	CO	C_2H_2, C_2Me	Me, COMe	NMR (^1H, ^{13}C), IR	359
Mo	Me	Cl	(p-N_2–C_6H_4F)	(p-N_2–C_6H_4F)	X-ray	360
Cr, Mo	Me	CO	CO	NO	NMR, IR, MS	134(b)
Mo	CH(Me)(Ph)	CO	NO	PR_3 R = Me, Ph	NMR, IR	306
Mo	CH(Me)(Ph)	CO	CO	NO	NMR, IR	306
Cr	CH_2R R = Ph, CH_2Ph	CO	CO	NO	NMR, IR, MS	284
Mo	NM[b,c]	NO	CO	(η^2-$C_8H_{13}OH$)	NMR, IR	310
Mo	NM	NO	CO	(η^2-$C_8H_{13}D$)	NMR, IR	310
Mo, W	$-CH{=}CH_2$	CO	CO	NO	NMR, IR, MS	53,69,134(b)
Cr	$-CH{=}CH_2$	CO	CO	NO	NMR, IR, MS	284,290
Mo, W	$-C(CH_3){=}CH_2$	CO	CO	NO	NMR, IR, MS	69,134(b),290
Cr	$-C(CH_3){=}CH_2$	CO	CO	NO	NMR, IR, MS	284
Cr	$-C(Ph){=}CH_2$	CO	CO	NO	NMR, IR, MS	284
Cr	$-C(Cl){=}CHCHO$	CO	CO	NO	NMR, IR, MS	284
Cr	$-C{\equiv}CH$	CO	CO	NO	NMR, IR, MS	284
Cr	NH_2	CO	CO	NO	NMR, IR, MS, X-ray	134(b),381(a)
Mo	$CH(Me)NMe_2$	CO	CO	NO	NMR, IR, MS	134(b)
Cr	CH_2OH	CO	CO	NO	NMR, IR, MS	134(b),284
Cr	CH(OH)R R = Me, Ph, CH_2Ph	CO	CO	NO	NMR, IR, MS	284,290
Cr	C(R)(R′)OH R = R′ = Me, R = R′ = Ph R = Me, R′ = Ph	CO	CO	NO	NMR, IR, MS	284
Cr	CRR′OH, CRR'^+ R = H, R′ = Me, Ph R = Me, R′ = Me, Ph R = R′ = Ph	CO	CO	NO	NMR (^1H, ^{13}C)	349

TABLE 11 (*continued*).

M	R	A	B	C	Comments[a]	Ref.
Cr	CRR'OH, CRR'$^+$ R = H; R' = Ph, *p*-tolyl, p-anisyl R = Me; R' = Ph R = R' = Ph	CO	CO	NO	pK$_{R^+}$ values determined	351
Cr	CHO	CO	CO	NO	NMR, IR, MS, X-ray	134(b),381(a)
Mo	COMe	CO	NO	(η^2-CH_2CHCH_3)	IR	302
Cr, Mo, W	CO_2CH_3	CO	CO	NO	NMR, IR, MS	134(a),134(b)
Cr	$COCH_3$	CO	CO	NO	NMR, IR, MS	134(b),285 290,348
Cr	CO_2H	CO	CO	NO	NMR, IR, MS	134(b)
Cr	COR R = Ph, CH_2Ph, SMe, OH, Me	CO	CO	NO	NMR, IR, MS	284
Cr	CH_2OCOCH_2=CH_2	CO	CO	NO	NMR, IR, MS	134(b)
Mo, W	PPh_3	CO	CO	N_2Ar	IR	326
Cr	CN	CO	CO	NO	X-ray	381(a)
Cr	COX^d, CH_2X^e	CO	CO	NO	X-ray	381(b),(c)

[a] For abbreviations, see p. 3.

[b] NM = neomenthyl.

[c] Enantiomerically pure compounds have been isolated for NM derivatives, but for the sake of simplicity, stereochemical aspects such as enantiomerism, and endo-, exo-isomerism have not been indicated in these tables.

[d] $X = (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$.

[e] $X = (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4CH{=}CH_2)$.

TABLE 12

Group 6 metal compounds of the general formula $[(\eta^5\text{-}C_5H_4R)M(A)(B)(C)(D)]^+M'^-$

M	R	A	B	C	D	M′	Comments[a]	Ref.
Mo	Me	CO	CO	CO	PPh_3	[d]	IR	368
Mo	Me	CO	CO	PPh_3	PPh_3	PF_6	IR	368
Mo	$CHMe_2$	(dmpe)		(dmpe)		PF_6	NMR	343
Mo	NM[b,c]	CO	NO	$(\eta^3\text{-}C_3H_5)$		PF_6	NMR, X-ray	307,308
Mo	NM	CO	NO	$(\eta^3$-1,3-dimethylallyl)		PF_6	NMR, IR	309
Mo	NM	CO	NO	$(\eta^3$-1,3-dimethylallyl)		BPh_4	NMR, IR	309
Mo	NM	CO	NO	$(\eta^3$-2-methallyl)		PF_6	NMR, IR	308
Mo	NM	CO	NO	$(\eta^3\text{-}C_8H_{13})$		BF_4	NMR, IR	310
Mo	NM	CO	NO	$(\eta^3\text{-}C_8H_{13})$		PF_6	NMR, IR	310
Mo, W	$(CH_2)_nOH$ $n = 1, 2, 3$	CO	CO	CO	PR_3 R = Ph, *p*-tolyl	BF_4	NMR (^{31}P, ^1H), IR	292
Mo	COMe	CO	NO	$(\eta^3$-allyl), $(\eta^3$-2-methallyl)		PF_6	NMR	302
Mo	PPh_3	CO	CO	CO	Cl, I	PF_6	IR	326
Mo, W	PPh_3	CO	CO	CO	Br	PF_6	IR	326

[a] For abbreviations, see p. 3.

[b] NM = neomenthyl.

[c] Enantiomerically pure compounds have been isolated for NM derivatives, but for the sake of simplicity, stereochemical aspects such as enantiomerism, and endo-, exo-isomerism have not been indicated in these tables.

[d] $M' = PF_6$, $(\eta^5\text{-}C_5H_4Me)Mo(CO)_3$.

TABLE 13

Group 6 metal complexes where the metal oxidation states are ⩾III

Complex	Comments[a]	Ref.
$[(C_5H_4Me)Mo(CO)_2I_3]$	X-ray	344
$[(C_5H_4Me)MoCl_4]$	NMR, ESR, MS	338
$(C_5H_4Et)W(PMe_3)H_5$	NMR (^1H, ^{13}C, ^{31}P), MS	340–342
$(C_5H_4Et)W(PMe_3)_2H_3$	NMR	340
$(C_5H_4\text{i-Pr})Mo(Cl)_2(PR_3)_2$ $PR_3 = PMe_3, PMe_2Ph$	MS	339
$(C_5H_4\text{i-Pr})Mo(H)_3(PR_3)_2$ $PR_3 = PMe_3, PMe_2Ph$	MS, NMR	339
$(C_5H_4\text{i-Pr})Mo(PMe_3)_2Cl_2$	MS, ESR	343
$(C_5H_4\text{i-Pr})Mo(PMe_2Ph)_2Cl_2$	MS, ESR	343
$[(C_5H_4\text{i-Pr})Mo(dmpe)_2H][PF_6]_2$	MS, ESR	343
$(C_5H_4\text{i-Pr})Mo(dippe)Cl_2$	–	343
$(C_5H_4\text{i-Pr})Mo(PMe_3)_2ClH_2$	NMR (^1H, VT)	343
$(C_5H_4\text{i-Pr})Mo(PMe_3)_2H_3$	NMR	343
$(C_5H_4\text{i-Pr})Mo(PMe_2Ph)_2H_3$	NMR	343
$(C_5H_4\text{i-Pr})Mo(dippe)H_3$	NMR	343
$[(C_5H_4\text{i-Pr})Mo(PMe_3)_2O][PF_6]$	NMR (^1H, VT)	343
$[(C_5H_4\text{i-Pr})Mo(Cl)_2]_2$	NMR, MS, X-ray	339,343
$(C_5H_4R)MoCl_3(OH)$ $R = \text{i-Pr}, n\text{-Bu}$	ESR, NMR, MS	338
$[(C_5H_4R)Mo(\mu\text{-}O)O]_2$ $R = Me, \text{i-Pr}, n\text{-Bu}$	ESR, NMR, MS	338
$[\{(C_5H_4n\text{-Bu})MoCl_2\}_2(\mu\text{-}S_2)]$	–	338
$(C_5H_4PPh_3)MoCl_3(OH)_2$	–	361
$(C_5H_4SiMe_3)WCl_3(CO)_2$	–	362
$[(C_5H_4CHPh_2)Mo(Cl)_2]_2$	NMR	343

[a] For abbreviations, see p. 3.

TABLE 14

Group 6 M(II) intramolecularly bridged compounds with the general formula ($\eta^{5:1}$-C_5H_4\{BXA\})$M(CO)_2L$

M	A–X–B	L	Comments[a]	Ref.
Mo	$-(CH_2)_4-$	CO	–	122(a)
Mo	$-(CH_2)_2-$	CO	–	122(a)
W	$-(CH_2)_2-$	CO	NMR, IR, MS	294
W	$-(CH_2)_4-$	CO	NMR, IR, MS	294
Mo	$-CH_2CH(CH_3)-$	CO	NMR, IR, MS	294
Mo	$-CH(CH_3)CH_2-$	CO	NMR, IR, MS	294
W	$-CH_2CH(CH_3)-$	CO	NMR, IR, MS	294
Mo	$-CH(CH_3)CH_2-$	CO	NMR, IR, MS	294
Mo	$-CH_2C(CH_3)_2-$	CO	NMR, IR, MS	122(c)
Mo	$-C(CH_3)_2C(CH_3)_2-$	CO	NMR, IR, MS	122(c)
Mo	$-CH(CH_3)CH(CH_3)-$	CO	NMR, IR, MS	122(c)
Mo	$-CH_2CHCHCH_2-$	CO	NMR, IR	293
Mo	$-COC(CHCH_3)CH_2-$	CO	NMR, IR	293
W	$-CO(CH_2)_2-$	CO	MS, IR	294
W	$-COCH_2CH(CH_3)-$	CO	NMR, IR, MS	294
W	$-COCH(CH_3)CH_2-$	CO	NMR, IR, MS	294
Mo	$-CO(CH_2)_2-$	CO	NMR, IR, MS	294
Mo, W	$-CO_2(CH_2)_2-$	PR_3 R = Ph, *p*-tolyl	NMR, IR, MS	292
W	$-CO_2(CH_2)_2-$	PPh_3	X-ray	292
Mo, W	$-CO_2(CH_2)_2-$	PR_3 R = Ph, *p*-tolyl	NMR (^1H, ^{31}P), IR	292
Mo	$-(CH_2)_2-$	η^2-olefin[b]	NMR, IR	297
W	$-(CH_2)_2-$	η^2-olefin[c]	NMR, IR	297
W	$-(CH_2)_2-$	(η^2-olefin)$_2^{d}$	NMR, IR	297
Mo	$-C(SMe)_2C_5H_4C(SMe)_2CO$	CO	IR, NMR, X-ray	398

[a] For abbreviations, see p. 3.

[b] Ethylene, propene, 1-butene, Z-2-butene, E-2-butene, 2-methylpropene, 2-methyl-2-butene, styrene, allene.

[c] Ethylene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, 2,2-dimethylcyclopropene.

[d] One of the CO groups has been replaced by an olefin, olefin = ethylene.

TABLE 15

Group 6 M(II) intramolecularly bridged compounds of the general formula ($\eta^{3:5}$-X)M(CO)$_2$

M	X	Comments[a]	Ref.
Cr	C_8H_8RR'[b]	IR, NMR (^{1}H, ^{13}C)	295,314,315
Cr	$C_{14}H_{14}RR'$[c]	IR, NMR (^{1}H, ^{13}C)	295
Cr	$C_{15}H_{17}R$[d]	IR, NMR (^{1}H, ^{13}C)	295
Cr	$C_{16}H_{16}RR'$[e]	IR, NMR (^{1}H, ^{13}C)	295
Mo	$C_5H_4C(SMe)_2C_5H_4C(SMe)_2$	IR, NMR, X-ray	398

Identities of R and R′

	A	B	C	D	E	F	G
R	Me	Me	Ph	OMe	H	H	$S(CH_2)_2S$
R′	Me	Ph	Ph	OMe	OCOMe	NMe_2	

[a] For abbreviations, see p. 3.

[b] RR′: combinations A–G.

[c] RR′: combinations A–F.

[d] RR′: combinations A–C.

[e] RR′: combinations A, B, C, F.

TABLE 16

Group 6 ylide and fulvene metal compounds of the general formula $(C_5H_4R)M(CO)_3$

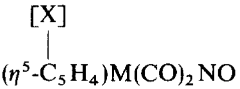
M	R	Comments[a]	Ref.
Cr	SMe_2	X-ray	316,322,329,363
Mo		PMR, IR, MS	316,318,329,363
W		–	316,329
Cr	PPh_3	X-ray	316,325,330,396
Mo		–	316,330,363,396
W		–	316,330,396
Cr	$CHNMe_2$	X-ray, NMR (^{13}C)	319,320,323,281,57,299
Mo			320,363,57,299
W			320,321
Cr, Mo		–	364
Cr, Mo	$(CH)_5N(Me)(Ph)$	IR, NMR	281(a)
Cr	$CHCHPPh_3$	IR	281(a)
Cr, Mo, W	$-CHC\{N(CHMe_2)_2\}=C\{N(CHMe_2)_2\}$		328
Cr	$CH_2PR'_3$ $PR'_3 = PMe_3, PEt_3,$ $PPh_3, PPh_2(CH_2CH_2PPh_2)$	NMR (^1H, ^{31}P), IR	280
Cr	$CMe_2PR'_3$ $PR'_3 = PMe_3, PBu_3,$ $PMe_2Ph, PMePh_2$	NMR (^1H, ^{31}P), IR	280,281(a)
Cr	CMe_2PEt_3	NMR (^1H, ^{31}P), IR, X-ray	280
Cr	$CH_2CH_2PPh_3$	NMR (^1H, ^{31}P), IR	280
Cr	$CMe_2CH_2PPh_3$	NMR (^1H, ^{31}P), IR	280
Cr, Mo	$C(NMe_2)_2$	IR, UV, VIS, NMR	57,299

[a] For abbreviations, see p. 3.

TABLE 17

Group 6 metal polymeric complexes

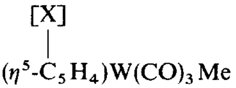
A. General formula of the monomer



$$\overset{[X]}{(\eta^5\text{-}C_5H_4)}M(CO)_2NO$$

[X]	M	Ref.
$[CH_2CH(Ph)CH_2\underset{\mid}{CH}]$	Cr	350
$[CH_2-\underset{\mid}{CH}]$	Cr	350
$[CH_2CH(\overline{NCOCH_2CH_2C}H_2)CH_2\underset{\mid}{CH}]$	Cr	350
$[CH_2CH\{(\eta^5\text{-}C_5H_4)Mn(CO)_3\}CH_2CH]$	Cr	350
$[(CH_2CH)_x-(CH_2CH(Ph))_y]$	Mo	69

B. General formula of the monomer

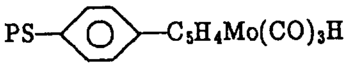
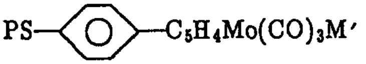
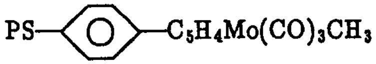
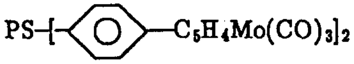


$$\overset{[X]}{(\eta^5\text{-}C_5H_4)}W(CO)_3Me$$

[X]	Ref.
$[CH_2\underset{\mid}{CH}]$	291,365,366
$[CH_2\underset{\mid}{CH}CH_2CH(CN)]$	291,366
$[CH_2\underset{\mid}{CH}CH_2(CH_3)(CO_2CH_3)]$	291,366
$[CH_2\underset{\mid}{CH}CH_2CH(\overline{NCOCH_2CH_2C}H_2]$	291,366
$[CH_2\underset{\mid}{CH}CH_2CH(Ph)]$	291,366
$[CH_2CH(CO_2\underset{\mid}{CH_2})]$	291
$[CH_2CH(CO_2\underset{\mid}{CH_2})CH_2CH(CO_2CH_3)]$	291
$[CH_2CH(CO_2\underset{\mid}{CH_2})CH_2CH(Ph)]$	291

TABLE 17 (*continued*).

C. Polymer-supported cyclopentadienyl metal complexes

Complex	Comments[a,b]	Ref.
PS–$CH_2C_5H_4M(CO)_3H$ M = Cr, Mo, W	IR	313
PS–CH_2–$C_5H_4Cr(CO)_2NO$	IR	313
PS–CH_2–$C_5H_4Cr(CO)_3Cl$	IR	313
PS–CH_2–$C_5H_4CrCl_2$	IR	313
PS–CH_2–$C_5H_4Cr(NO)_2Cl$	IR	313
	IR	312
 M′ = Li, Na	IR	312
	IR	312
	IR	312

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[a] For abbreviations, see p. 3.
[b] PS = polystyryl.

TABLE 18

Group 6 bimetallic complexes with non-bridging substituted cyclopentadienyl ligands

Complex	Comments[a]	Ref.
$[(\eta^5\text{-}C_5H_4Me)Mo(CO)_3]_2$	IR, NMR (^1H, ^{95}Mo, ^{199}Hg), MS, UV, hplc	345,347,367,368,370,371
$[(\eta^5\text{-}C_5H_4Me)Mo_2(CO)_6(\eta^5\text{-}C_5H_5)]$	IR, NMR, MS, UV, hplc	345,370
$[(\eta^5\text{-}C_5H_4Me)Cr(CO)_3]_2$	–	371,372,373
$[(\eta^5\text{-}C_5H_4Me)W(CO)_3]_2$	–	371
$[(\eta^5\text{-}C_5H_4Me)W(CO)_2]_2$	NMR (^1H, ^{13}C)	399
$[(\eta^5\text{-}C_5H_4Me)Mo(CO)_2]_2$	IR, NMR (^1H, ^{13}C), MS, UV, hplc	345,370,399
$[(\eta^5\text{-}C_5H_4Me)Mo_2(CO)_4(\eta^5\text{-}C_5H_5)]$	IR, NMR, MS, UV, hplc	345,370
$[(\eta^5\text{-}C_5H_4Me)Cr(CO)_2]_2$	NMR (^1H, ^{13}C)	374,399
$[(\eta^5\text{-}C_5H_4Me)Cr(CO)_2L]_2$[b]	–	372
$[(\eta^5\text{-}C_5H_4Me)Mo(O)(\mu\text{-}S)]_2$	NMR (^{95}Mo)	375
$[(\eta^5\text{-}C_5H_4Me)Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$	NMR (^{95}Mo)	375
$[(\eta^5\text{-}C_5H_4Me)Mo(\mu\text{-}S)(\mu\text{-}SEt)]_2$	NMR (^{95}Mo)	375
$[(\eta^5\text{-}C_5H_4Me)Mo_2(\mu\text{-}S)(\mu\text{-}SMe)(\mu\text{-}SCH_2S)]I$	NMR (^{95}Mo)	375
$[(\eta^5\text{-}C_5H_4Me)Mo(\mu\text{-}S)]_2(\mu\text{-}SCH_2S)$	NMR (^{95}Mo)	375
$[(\eta^5\text{-}C_5H_4Me)Mo(\mu\text{-}SMe)]_2(\mu\text{-}SCH_2S)$	NMR (^{95}Mo)	375
$[(\eta^5\text{-}C_5H_4Me)_2Mo_2(\mu\text{-}SC_2H_2S)(\mu\text{-}SC(S)S)]$	NMR (^{95}Mo)	375
$[(\eta^5\text{-}C_5H_4Me)_2Mo_2(\mu\text{-}SC_2H_2S)(\mu\text{-}SCH_2S)]$	NMR (^{95}Mo)	375
$[(\eta^5\text{-}C_5H_4Me)Mo(\mu\text{-}SC_2H_2S)]_2$	NMR (^{95}Mo)	375
$[(\eta^5\text{-}C_5H_4Me)Mo(CO)_3]_2Hg$	–	352
$[(\eta^5\text{-}C_5H_4Me)M(CO)_3]_2BiCl$	IR, NMR (^1H, ^{13}C)	356
$M = Mo, W$		
$[(\eta^5\text{-}C_5H_4Et)Mo(CO)_3]_2$	IR	378,400
$[(\eta^5\text{-}C_5H_4CHMe_2)Mo(CO)_3]_2$	–	64
$[(\eta^5\text{-}C_5H_4i\text{-}Pr)Mo(\mu\text{-}SMe)_2]_2$	NMR (^{95}Mo)	375
$[(\eta^5\text{-}C_5H_4t\text{-}Bu)MoCl_2]_2S_2$	–	379
$[(\eta^5\text{-}C_5H_4R)M(CO)_3]_2$[c]	IR	41
$[(\eta^5\text{-}C_5H_4Ph)Mo(CO)_3]_2$	–	112
$[(\eta^5\text{-}C_5H_4Ph)Mo_2(CO)_6(\eta^5\text{-}C_5H_5)]$	–	112
$[(\eta^5\text{-}C_5H_4Ph)W_2(CO)_6(\eta^5\text{-}C_5H_5)]$	–	378
$[(\eta^5\text{-}C_5H_4CH_2Ph)M_2(CO)_6(\eta^5\text{-}C_5H_5)]$	–	378
$M = Mo, W$		
$[(\eta^5\text{-}C_5H_4CH_2Ph)M(CO)_3]_2$	–	378

$[(\eta^5\text{-}C_5H_4CH_2Ph)Cr(CO)_2]_2$	–	374
$[(\eta^5\text{-}C_5H_4CH_2Ph)M(CO)_3]_2$ $M = Cr, Mo, W$	General preparation method	371
$[(\eta^5\text{-}C_5H_4CMe{=}CH_2)Mo(CO)_3]_2$	–	64
$[(\eta^5\text{-}C_5H_4CHR_2)M(CO)_3]^{d}$	IR, NMR (^1H, ^{13}C)	298
$[(\eta^5\text{-}C_5H_4(CH_2)_2OH)Mo(CO)_3]_2$	–	377
$[(\eta^5\text{-}C_5H_4(CH_2)_3OH)Mo(CO)_3]_2$	–	377
$[(\eta^5\text{-}C_5H_4COR)M(CO)_3]_2{}^{e}$	Voltammetry, IR	137
$[(\eta^5\text{-}C_5H_4COCHCHPh)Mo_2(CO)_6(\eta^5\text{-}C_5H_5)]$	–	303
$[(\eta^5\text{-}C_5H_4PPh_3)Mo(CO)_3]_2X_2{}^{f}$	IR	326
$[(\eta^5\text{-}C_5H_4R)Cr(CO)_3]_2$ $R = COMe, CO_2Me$	IR, NMR	395
$[(\eta^5\text{-}C_5H_4R)Cr(CO)_3]_2Hg$ $R = COMe, CO_2Me$	IR, NMR	395
$[(\eta^5\text{-}C_5H_4CHO)M(CO)_3]_2$ $M = Cr, Mo, W$	IR, NMR	324
$[(\eta^5\text{-}C_5H_4R)_2W_2Cl_4(C_2Me_2)_2$ $R = Me$, i-Pr	NMR (^1H, ^{13}C), X-ray	401
$[(\eta^5\text{-}C_5H_4R)_2W_2Cl_2(O)(\mu\text{-}C_4Me)_4$ $R = Me$, i-Pr	NMR (^1H, ^{13}C), X-ray	401
$[(\eta^5\text{-}C_5H_4\text{i-Pr})_2W_2Cl_2(\mu\text{-}Cl)_2(\mu\text{-}C_2R_2)$ $R = SiMe_3$, Et	NMR (^1H, ^{13}C)	401
trans-$[(\eta^5\text{-}C_5H_4\text{i-Pr})W_2Cl_4(\mu\text{-}(1,2)\text{-}C_4Me_2Et_2)]$	NMR	401
$[(\eta^5\text{-}C_5H_4R)WCl_2]_2$ $R = Me$, i-Pr	X-ray, NMR	402
$[(\eta^5\text{-}C_5H_4Me)W_2Cl_2(\mu\text{-}Cl)_2(dmpe)]$	X-ray, NMR	402
$[(\eta^5\text{-}C_5H_4\text{i-Pr})WCl_2(\mu\text{-}H)]_2$	NMR	402

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[a] For abbreviations, see p. 3.

[b] $L = PPh_3$, $P(OMe)_3$, $P(OEt)_3$.

[c] $M = Mo$, R = *n*-Pr, i-Pr, CHMeEt, $CHEt_2$, CHMe*n*-Pr, CHPhMe, $CHPh_2$, *p*-MeO $\cdot C_6H_4 \cdot CH_2$, cyclohexyl $M = W$, R = i-Pr, $CHEt_2$.

[d] $M = Mo$, R = Ph, 4-Me-OPh, 4-ClPh; $M = W$, $R = Ph$.

[e] $M = Mo$, W; $R = Me$, OMe.

[f] $X = SbCl_6$, ClO_4, PF_6.

TABLE 19

Group 6 bimetallic complexes containing bridging cyclopentadienyl ligands

A.1 Compounds with the general structure $\{(\eta^{5:1}C_5H_4P(p\text{-}Me\text{-}C_6H_4)_2)Mo(CO)_3ML^1L^2\}$

M	L^1	L^2	Comments[a]	Ref.
Rh	$L^1L^2 = [(p\text{-}Tol)_2PCH_2]_2$		IR, NMR (^1H, ^{13}C, ^{31}P)	333
Rh	CO	CO	IR, NMR (^1H, ^{13}C, ^{31}P)	333
Rh	$P(p\text{-}Tol)_3$	CO	IR, NMR (^1H, ^{13}C, ^{31}P)	333
Rh	PMe_3	CO	IR, NMR (^1H, ^{13}C, ^{31}P)	333
Ir	CO	CO	IR, NMR (^1H, ^{13}C, ^{31}P)	333
Ir	PMe_3	CO	IR, NMR (^1H, ^{13}C, ^{31}P)	333
Ir	PPh_3	CO	IR, NMR (^1H, ^{13}C, ^{31}P)	333

A.2 Compounds with the general structure $\{(\eta^{5:1}C_5H_4PR_2)Mo(CO)_3M(CO)_4\}$

M	R	Comments[a]	Ref.
Mn	Ph	NMR (^1H, ^{13}C, ^{31}P), IR, X-ray	174(a),(b)
Mn	p-Tol	NMR (^1H, ^{13}C, ^{31}P), IR	174(a),(b)
Mo	p-Tol	NMR (^1H, ^{13}C, ^{31}P), IR	174(a)

B. Fulvalene bimetallic complexes (Fv = fulvalene = η^5, η^5-$C_{10}H_8$)

Complex	Comments[a]	Ref.
$FvMo_2(CO)_6$	X-ray, UV, VIS, NMR, IR, MS	332,380, 382,403
$FvMo_2(CO)_4(RC{\equiv}CR)$	UV, VIS, NMR, MS, IR	332
$FvMo_2(CO)_3(RC{\equiv}CR)_2$	UV, VIS, NMR, MS, IR, X-ray	332
$FvMo_2(CO)_6^{2-}$	UV, VIS, NMR, MS, IR	332
$FvMo_2(CO)_6H_2$	UV, VIS, NMR, MS, IR	332
$FvMo_2(CO)_6R_2$ R = Me, CH_2Ph, CH_2OMe	UV, VIS, NMR, MS, IR	332,382
$FvMo_2(CO)_6(CH_2OCH_3)(=CH_2)^+$	NMR	332
$FvMo_2(CO)_6(C_2H_4)^{2+}$	–	332,383
$FvMo_2(CO)_5(=\overline{C(CH_2)_3O})$	X-ray	332
$FvMo_2(CO)_5(=\overline{C(CH_2)_4O})$	–	332
$FvMo_2(CO)_5(PMe_3)_2$	NMR (^1H, ^{31}P), IR, MS	384
$FvMo_2(CO)_5((CH_3)_2PCH_2P(CH_3)_2)$	NMR (^1H, ^{31}P), IR, MS, X-ray	384
$FvCr_2(CO)_6$	NMR, IR, MS	380,403
$FvW_2(CO)_6$	NMR, IR, MS	380,385,403
$FvMoRu(CO)_5$	NMR, IR, MS	380
$FvFe(\eta^5\text{-}C_5H_4COCH_3)W(CO)_3CH_3$	NMR, MS	386
$FvFeW(CO)_5^{2-}$	Electrochemistry	386
$FvFe(\eta^5\text{-}C_5H_4COCH_3)W(CO)_3I$	NMR, MS	386
$FvMo_2(CO)_5(PMe_3)_2$	–	387
$FvMoCr(CO)_5(PMe_3)_2$	–	387

TABLE 19 (*continued*)

Complex	Comments[a]	Ref.
$FvRuCr(CO)_4(PMe_3)_2$	–	387
$FvRuMo(CO)_4(PMe_3)_2$	–	387
$FvRuW(CO)_4(PMe_3)_2$	–	387
$FvMnMo(CO)_5(PMe_3)_2$	–	387
$FvMnMo(CO)_4(PMe_3)_2(CH_3)$	–	387
$FvMo_2(CO)_4\{C_2(CO_2Me)_2\}$	IR, NMR, MS	380
$FvMo_2(CO)_3\{C_2(CO_2Me)_2\}_2$	IR, NMR, MS, X-ray	380
$FvW_2(CO)_5(C_2Ph_2)$	IR, NMR, MS	380
$FvW_2(CO)_3(C_2Ph_2)_2$	IR, NMR, MS	380
$FvMM'(CO)_6$ $MM' = MoCr, MoW, WCr$	–	387
$FvMnW(CO)_6Me$	–	387

C. Compounds with the general structure $(\eta^5,\eta^5\text{-}C_5H_4XC_5H_4)M_2Ln$

X	M_2Ln	Comments[a]	Ref.
$SiMe_2$	$W_2(CO)_6H_2$	NMR (^{31}P, ^{183}W, ^1H, 2D)	388,389
$SiMe_2$	$W_2(CO)_4P(Me)_2H$	NMR (^{31}P, ^{183}W, ^1H, 2D)	388
$SiMe_2$	$W_2(CO)_3(PMe_2)_2$	NMR (^{31}P, ^{183}W, ^1H, 2D)	388
$SiMe_2$	$W_2(CO)_6$	NMR	389
$SiMe_2$	$Mo_2(CO)_6$	NMR	389
$SiMe_2$	$Cr_2(CO)_6$	NMR	389
$SiMe_2$	$W_2(CO)_6Cl_2$	NMR	389
$SiMe_2$	$W_2(CO)_6H_2$	NMR	389
$SiMe_2$	$Mo_2(CO)_6Cl_2$	NMR	389
$SiMe_2$	$Mo_2(CO)_6H_2$	NMR	389
$SiMe_2$	$M_2(CO)_6Na_2$ $M = Mo, W$	NMR, IR	390
$SiMe_2$	$Mo_2(CO)_6(AsMe_2)_2$	NMR, IR	390
$SiMe_2$	$Mo_2(CO)_6(AsMe_3)_2I_2$	NMR, IR	390
$SiMe_2$	$Mo_2(CO)_6(PMe_3)_2$	NMR, IR	390
$SiMe_2$	$M_2(CO)_6Me_2$ $M = Mo, W$	NMR, IR	390
CH_2	$Mo_2(CO)_6$	Catalysis	391(b)
CH(Me)OCH(Me)	$W_2(CO)_6Me_2$	–	291
$CH_2C_6H_4CH_2$	$Mo_2(CO)_6$	IR, NMR	327,391(a)
$CH_2C_6H_4CH_2$	$W_2(CO)_6$	–	391(a)
$CH_2C_6H_4CH_2$	$M_2(CO)_6^{2-}$ $M = Mo, W$	IR, NMR	327
$CH_2C_6H_4CH_2$	$Mo_2(CO)_2X_2Y_2$[b]	IR, NMR	327
$CH_2C_6H_4CH_2$	$W_2(CO)_3X$ $X = Me, Et$	IR, NMR	327
–C≡C–	$Mo(CO)_3MeML_n$[c]	IR, NMR (^1H, ^{13}C)	394
–C≡C–	$W(CO)_3MeML_n$[d]	IR, NMR (^1H, ^{13}C)	394
–C≡C–	$W(CO)_3MeMn(CO)_2PPh_3$	IR, NMR (^1H, ^{13}C), X-ray	394

TABLE 19 (*continued*)

D. Bridging fulvenylcyclopentadienyl complexes

Complex	Comments[a]	Ref.
$[(C_5H_4CHC_5H_4\}Cr_2(CO)_6]$	IR, NMR	281(a)
$[\{C_5H_4C[NMe_2]C_5H_4\}Cr_2(CO)_6]$	IR, NMR	281(a)
$[(C_5H_4CHOCO(CH_2)_6CO_2CHC_5H_4)Cr_2(CO)_6]$	IR	324

E. η^5-, η^1-bridging cyclopentadienyl ligand metal complexes

Compound	Comments[a]	Ref.
$(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}, \eta^1\text{-}C_5H_4)Mo_2(CO)_3$	X-ray	188
$(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}, \eta^1\text{-}C_5H_4)_2Mo_2$	–	335(b)
$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}, \eta^1\text{-}C_5H_4)MoMn(CO)_5$	X-ray	335(c),(d)
$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}, \eta^1\text{-}C_5H_4)MIr(\mu^2\text{-}H)_2H(PEt_3)_2$ $M = Mo, W$	–	335(a),190(b)

[a] For abbreviations, see p. 3.

[b] $X = CO$, $Y = H$, Me, Et, I; $X = PPh_3$, $Y = Me$.

[c] $MLn = Fe(CO)_2Me$, $W(CO)_3Me$, $Mn(CO)_3$, $Re(CO)_3$.

[d] $MLn = Fe(CO)_2Me$, $Mn(CO)_3$, $Re(CO)_3$.

TABLE 20

Clusters containing Group 6 metal-substituted cyclopentadienyl units

Cluster	Comments[a]	Ref.
$[Mo(\eta^5\text{-}C_5H_4CHMe_2)(\mu^3\text{-}S)]_4^{n+}$ $n = 0, 1, 2$	X-ray	336
$[C]^{n+}[A]^{n-}$ $C = [Mo_4(C_5H_4i\text{-}Pr)(\mu^3\text{-}X)_4]$ X = S, Se $[Fe_4(C_5H_4Me)(\mu^3\text{-}S)_4]$ $[Cr_4(C_5H_4Me)(\mu^3\text{-}X)_4]$ $A = [Fe_4(NO)_4(\mu^3\text{-}S)_4]$ $[Os_6(CO)_{18}]$ $[Mo(S_2C_2(CF_3)_2)_3]$ [TCNQ] [TCNE]	Synthesis, solid-state properties	337
$[\eta^5\text{-}C_5H_4W(CO)_3R]_3SiMe$ $R = Me, CH_2Ph$	NMR (^1H, ^{13}C), IR	369
$\{Bi[Mo(CO)_3(\eta^5\text{-}C_5H_4Me)]_3\}$	IR, NMR (^1H, ^{13}C)	356
$[(\eta^5\text{-}C_5H_4i\text{-}Pr)Mo(\mu_3\text{-}S)]_4$	NMR (^{95}Mo)	375
$[(\eta^5\text{-}C_5H_4t\text{-}Bu)(\eta^5\text{-}C_5H_5)Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4]$	X-ray	305
$\{(\eta^5\text{-}C_5H_4R)MoO_2\}_4$ R = Me, i-Pr, *n*-Bu	ESR, NMR, MS	338
$MeSi(\eta^5\text{-}C_5H_4)W(CO)_3R$ $R = Me, CH_2Ph$	IR, NMR (^1H, ^{13}C)	404
$[(\eta^5\text{-}C_5H_4Me)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2M$ M = Mn, Fe	X-ray	397
$(\eta^5\text{-}C_5H_4R)Mo(CO)_2Te_2XFe(CO)_3$[b]	IR, NMR (^1H, ^{125}Te), MS X-ray	393
$[(\eta^5\text{-}C_5H_4i\text{-}Pr)MoFeTe_2(CO)_5]_n$	IR, NMR, MS	393
$[(\eta^5\text{-}C_5H_4Me)MoFeTe_2IrCl(PPh_3)_2(CO)_6]SbF_6$	IR, NMR (^1H, ^{31}P)	393

[a] For abbreviations, see p. 3.

[b] R = Me; X = SbF_6, SC(S)NEt_2, S_2CNEt_2.
R = i-Pr; X = Br, SC(S)NEt_2.

(iv) Manganese and rhenium [405–436]

The cyclopentadienyl protons in $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ have been shown to be acidic [405] and, consequently, the organic chemistry of the C_5H_5 ring in this complex has been extensively explored. This has resulted in the synthesis of a wide range of $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ complexes via Friedel–Crafts acylation and alkylation, lithiation reactions, etc. The sheer volume of papers and patents that have described the chemical and physical properties of these complexes precludes an extensive analysis of all this information in this review. Further, much of this work relates to the interconversion of one organic fragment attached to the cyclopentadienyl ring into another organic fragment by classical organic chemistry methodology [14].

It is still possible to give an overview of this area of chemistry, especially as it relates to the theme of the review and this has been done below. The overview is not comprehensive. Further, no tabulated data are included with this section. The ring substitution chemistry of cymantrene, $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$, must rather await a review of its own.

Of the voluminous amount of material that has been published on the half-sandwich complexes of the Group 7 metals, most relates to the complexes of Mn and little information is available on compounds containing technetium [406]. Much of the manganese work has been generated by the pioneering studies of Nesmeyanov and his co-workers in Russia.

An interesting reaction involving an η^5 to η^0 ring slippage has been reported. Reaction of $(\eta^5\text{-}C_5H_4COMe)Re(CO)_3$ with PMe_3 did not yield the CO-substituted product but rather $Re(CO)_3(PMe_3)_2(OCMeC_5H_4)$, i.e. a Re(I) complex containing an enolate substituent [434].

(a) (η^5-C_5H_4R)M(I) complexes

The following strategies have been employed for the preparation of monosubstituted Mn and Re half-sandwich complexes:

(a) Friedel–Crafts-type electrophilic substitution on the cyclopentadienyl ring;

(b) metallation of the ring, followed by reaction with an electrophile;

(c) reaction of $M(CO)_5X$ (M = Mn, Re; X mostly Br) with a suitable cyclopentadienyl precursor; and

(d) transformation of the ring substituent.

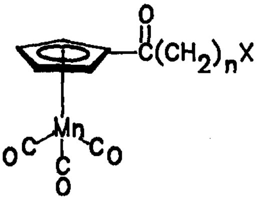
(1) Friedel–Crafts reactions.

Acylation. Cyclopentadienylmanganese tricarbonyl, as well as the corresponding Re and Tc compounds, undergo Friedel–Crafts acylation reactions [406]. The acyl substituents in these derivatives can undergo the organic reactions characteristic of these functional groups. These reactions will not be discussed in detail in this review; some of this chemistry has been reviewed previously [14,407]. Examples are given below for illustration.

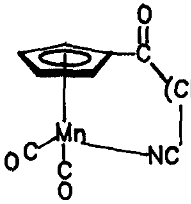
Friedel–Crafts reaction of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ with $ClCO(CH_2)_nCl$ ($n = 2, 4, 6$) gives **259a**. Treatment of **259a** with KCN gives **259b**, which, on UV-irradiation in hexane, gives **260** by intramolecular coordination of the nitrile group [408]. By this procedure, the ring substituent coordinates to both the ring and the metal.

Friedel–Crafts acylation of cyclopentadienylmanganese tricarbonyl yields the trifluoroacetyl and perfluorobutyryl derivatives **261** and **262** when $AlCl_3$ and the respective acid chloride are treated with cymantrene in dichloromethane [409]. Reaction of cymantrene with substituted succinic anhydrides gives succinoylated cymantrenes (**263**) [410].

A similar application of the Friedel–Crafts reaction occurs during the acetyla-



259a X=Cl
b X=CN



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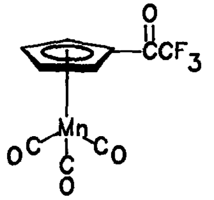

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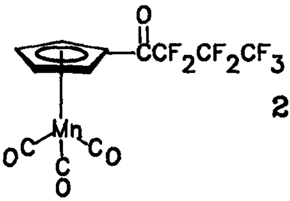

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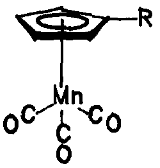


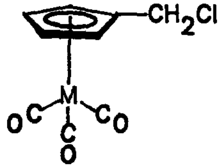
$R{=}COCH_2CR^2CR^3COOR^4$

$R{=}COCR^2CR^3CH_2COOR^4$

263

tion of the ring in (η^5-C_5H_5)Mn(CO)$_2$PPh$_3$ in the presence of acetylchloride/AlCl$_3$ to give (η^5-C_5H_4COR)Mn(CO)$_2$PPh$_3$ [411].

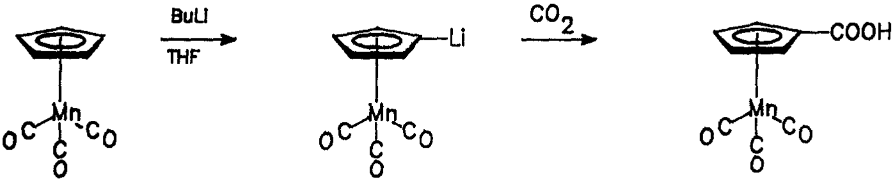
Alkylation. Friedel–Crafts alkylation is a less preferred method for functionalising cymantrene [14]. Chloromethylation has been affected using HCl, ZnCl$_2$, and formaldehyde, or bis(chloromethylether). The product (**264a**) is an important intermediate in the preparation of many other cymantrene derivatives [14]. Preparation of the corresponding Re compound (**264b**) has been achieved by treating cyclopentadienylrhenium tricarbonyl with methylchloromethylether and AlCl$_3$ [412].



264a M=Mn
b M=Re

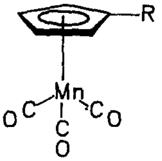
(2) Metallation reactions. Chloromercurated cyclopentadienylmanganese tricarbonyl has been obtained in a number of ways, e.g. by direct chloromercuration of cymantrene with mercuric acetate in the presence of alcoholic calcium chloride [14], or by treatment of the sulphinic acid with mercuric chloride in ethanol [14]. The product is an important intermediate in the synthesis of many other monosubstituted cymantrene derivatives.

Metallation of cymantrene with BuLi in THF at −40 to −45°C gives the lithium derivative (**265**). This intermediate has been carbonated to yield carboxycyclopentadienylmanganese tricarbonyl (**266**) [413], or reacted with metal halides to give metal-substituted cyclopentadienyl rings (Sect. C.(ii)(m)).



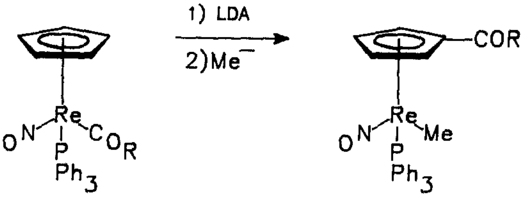
265 **266**

Cyclopentadienylrhenium tricarbonyl has been similarly metallated [407]. Lithiated cyclopentadienylmanganese or -rhenium tricarbonyl has been used in numerous synthetic studies [407]. For instance, lithiated cyclopentadienylmanganese tricarbonyl gave, on treatment with DMF in THF at −70°C followed by treatment with NH_4Cl at −10°C, the aldehyde **267a**. Reduction of **267a** with $LiAlH_4$ in Et_2O at 0°C gave the alcohol **267b** in quantitative yield [414].



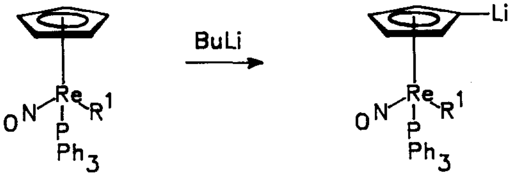
267a R=CHO
b R=CH_2OH

Suitable cyclopentadienylmanganese or -rhenium complexes give metal-to-ring migration of substituents on deprotonation with strong bases. Thus, (η^5-C_5H_5)Re(NO)(PPh_3)COR (**268**) (R = Me, Ph, CH_2Ph) has been lithiated with LDA and methyl-



268

ated to give (η^5-C_5H_4COR)Re(NO)(PPh_3)Me by acyl migration [130]. Lithiation and bromination of **268** (R = CH_2Ph) gave (η^5-C_5H_4COR)Re(NO)(PPh_3)Br. On the other hand, lithiation of (η^5-C_5H_5)Re(NO)(PPh_3)R′ (R′ = CH_2Ph, Me) with BuLi/TMEDA at −78°C gave the ring-metallated product (η^5-C_5H_4Li)Re(NO)(PPh_3)R′ (**269**), which did not rearrange on warming to room temperature. Methylation of **269**



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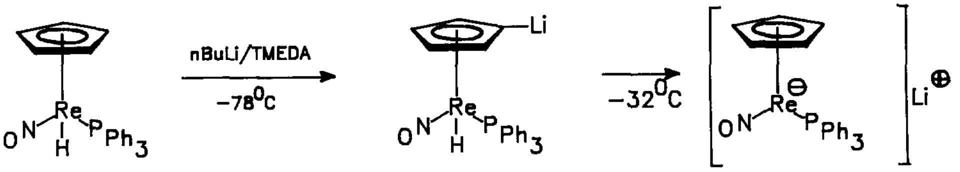
(R′ = CH_2Ph) occurred at the ring, as did acylation [130]. Similarly, the reaction of cyclopentadienylrhenium halide complexes, (η^5-C_5H_5)Re(NO)(PPh_3)(X) (X = Cl, Br, I), with BuLi/TMEDA gives ring metallation (as shown by NMR spectroscopy) and subsequent methylation of the ring [415]. Metallation of the hydride complex (η^5-C_5H_5)Re(NO)(PPh_3)(H) with BuLi/TMEDA (THF, −78°C) also gives ring metallation to give **270** as shown by NMR spectroscopy and methylation reactions. At −32°C, rearrangement to the Re anion (**271**) by an intramolecular hydrogen shift takes place [197(c)].

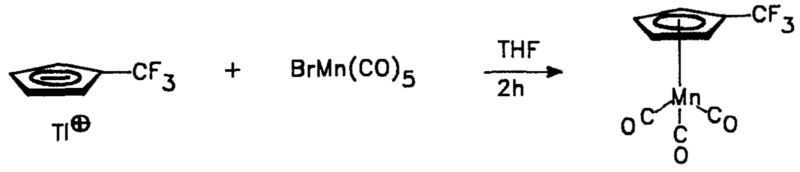


270 **271**

Similarly, lithiocyclopentadienyl silyl complexes undergo metal-to-carbon silatropic shifts. For example, when (η^5-C_5H_5)Re(CO)(NO)$SiMe_3$ is treated with BuLi, the $SiMe_3$ group migrates to the ring. Treatment of the anion with $PhCH_2Cl$ gives (η^5-$C_5H_4SiMe_3$)Re(CO)(NO)CH_2Ph [416].

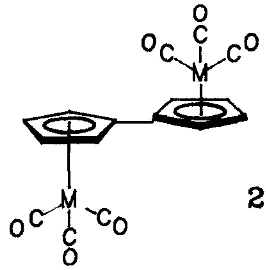
(3) Syntheses based on reaction of M(CO)₅X with a cyclopentadienyl precursor. The syntheses of (η^5-C_5H_5)Mn$(CO)_3$ or (η^5-C_5H_5)Re$(CO)_3$ from M$(CO)_5$X (M = Mn, Re; X = Cl, Br, I) and a cyclopentadienyl precursor, can also be used for the preparation of substituted derivatives. Thus, reaction of thallium(I) (trifluoromethyl)-cyclopentadienide with Mn$(CO)_5$Br for 2 h at room temperature gave **272** [89].

Similarly, the reaction of thallium(I) (tricyanovinyl)cyclopentadienide with Mn$(CO)_5$Br yielded [η^5-$C_5H_4C(CN)C(CN)_2$]Mn$(CO)_3$ [417]. The reaction of Mn$(CO)_5$Br or Re$(CO)_5$Br with fulvalenedithallium gave the fulvalene complexes



272

273 [79], and the reaction of $Mn(CO)_5Br$ with $(C_5H_4X)Tl$ (X = Cl, Br, I) gave (halocyclopentadienyl)tricarbonylmanganese (halocymantrene) [80].



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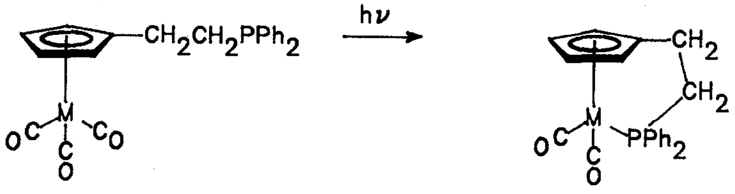
Diazocyclopentadiene was found to insert into the metal–halogen bond of manganese pentacarbonyl halides at room temperature, and gave the same halogen-substituted (cyclopentadienyl)tricarbonylmanganese derivatives, as above, in quantitative yield [181(b)]. The corresponding Re compounds were obtained in an analogous manner [182(b)].

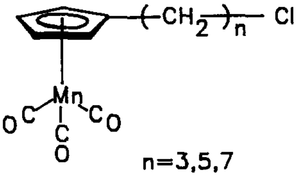
The organotin intermediate, (trimethylstannyl)(trimethylsilyl)cyclopentadiene, has been reacted with the appropriate metal carbonyl halides to afford $(\eta^5\text{-}C_5H_4SiMe_3)M(CO)_3$ (M = Mn, Re) by elimination of the organotin halide [150]. Complex **274** was obtained by employing a similar procedure, which, after photochemical irradiation, gave the intramolecularly bridging complex **275** [173].



274 **275**

A cyclopentadienyl ring can also act as a leaving group. This was shown by the reaction of potassium cyanocyclopentadienide with cyclopentadienylmanganese and -rhenium tricarbonyl in THF, which gave nitrilocyclopentadienyltricarbonylmanganese and -rhenium, respectively [418].

(4) Transformation of a ring substituent. Some examples of this well-documented approach are given below. Treatment of formylcymantrene with $CHCl_3$ under phase-transfer catalysis conditions (e.g. using $[PhCH_2NEt_3]Cl$), gave α-cymantrenylglycolic acid and additionally 1,3-dicymantrenyl-1-propen-3-ones [419]. Compounds **276** are quaternised with Me_3N at 80–90°C in ethanol to give **277**, which act as cationic surfactants [420].



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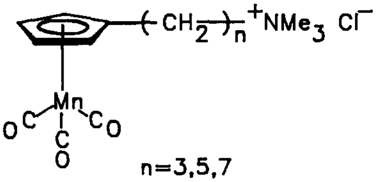

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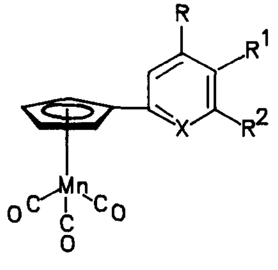
Cyclisation of $(\eta^5\text{-}C_5H_4COCH_3)Mn(CO)_3$ with $RCH{=}CR^1COR^2$ in CH_3COOH in the presence of $HClO_4$ gave **278** (R,R^2 e.g. Ph, R^1 e.g. H; $X{=}O^+$ ClO_4^-) which, on treatment with NH_3 or $PhNH_2$, gave **278** ($X{=}N$, $[PhN]ClO_4$, respectively) [421].



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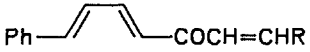
Grignard reaction of trimethylsilylpropargylbromide with CH_3COR ($R{=}(\eta^5\text{-}C_5H_4)Mn(CO)_3$) as electrophile gave the acetylenic product $Me_3SiC{\equiv}CCH_2C(OH)RMe$. No propargyl rearrangement products were formed [422].

Reaction of $(\eta^5\text{-}C_5H_4COCH_3)Mn(CO)_3$ with $[(Ph_3PAu)_3O]BF_4$ in THF in the presence of NaH gave α-aurated acetylcymantrene, $(\eta^5\text{-}C_5H_4\text{-}COCH_2AuPPh_3)Mn(CO)_3$ [423].

The reaction of either **279** or **280** with $Fe_3(CO)_{12}$ gave **281** and **282** ($R{=}(\eta^5\text{-}C_5H_4)Mn(CO)_3$) [424].

Unsaturated ketones, $RCH{=}CHCOR'$ ($R{=}(\eta^5\text{-}C_5H_4)Mn(CO)_3$), were prepared by treating RCHO with R'Ac [425].

An unusual Os–Mn complex (**283**), characterised by X-ray crystallography, has been prepared by reaction of $(\eta^5\text{-}C_5H_4COOH)Mn(CO)_3$ with $HOs_3(OH)(CO)_{10}$. In



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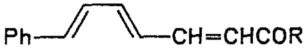

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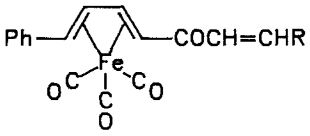

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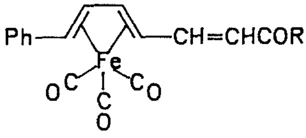
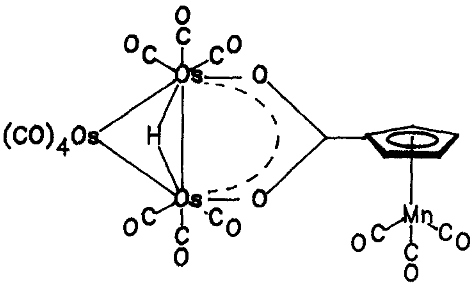


282

this complex, the ring substituent is coordinated to a metal cluster via two oxygen atoms [426].



283

The motivation for the synthesis of a wide range of ring-substituted cymantrene complexes has been the expectation that these complexes may have some commercial use. In this respect, cymantrene and its derivatives have been thoroughly investigated as potential anti-knock agents in fuels [427]. The complexes have also been investigated for catalytic activity [428]. Radical-initiated homopolymerisations, as well as copolymerisations of vinylcymantrene [350(a),(b),366,429,430], have been undertaken and the reactions have produced metallo-polymers. Finally, it should be noted that $Mn(CO)_3$ moeities have been used as markers in immunoassay studies [431].

(b) (η^5-C_5H_4R)M(II) complexes

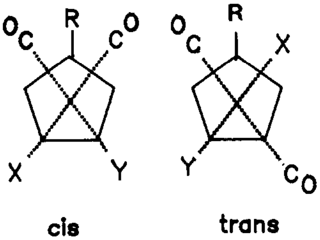
Removal of an electron from a stable (η^5-C_5H_4Me)$Mn(CO)_3$ complex by chemical or electrochemical means produces the unstable 17-electron (η^5-C_5H_4Me)$Mn(CO)_3^+$ species. The 17-electron species undergoes rapid ligand substitution reactions and provides a means of introducing substituents onto the otherwise unreactive 18-electron compounds [432].

Dimeric halide-bridged Mn(II) complexes, $[(\eta^5\text{-}C_5H_4R)MXL]_2$ (R = Me, $SiMe_3$;

L = PEt_3; X = I), have been prepared from $(C_5H_4R)_2M$, MX_2 and L. The novel 17-electron dimers have been characterised by NMR spectroscopy and magnetic measurements and the data indicate that the dimers have five unpaired electrons per Mn atom [433].

(c) (η^5-C_5H_4R)Mn(III) complexes

Studies have been carried out on two types of M(III) complex, (η^5-C_5H_4R)Re$(CO)_2$(X)(Y) and (η^5-$C_5H_4SiR_3$)Mn$(CO)_2$(SiR'_3)(H). These complexes can exist as both *cis* and *trans* isomers (**284**). The Re complexes are synthesised by oxidative addition of XY (X,Y = H, halide) to (η^5-C_5H_4R)Re$(CO)_3$ (R = Me, COOMe) [435]. Characterisation of these complexes has included mass spectral studies [436].



284

A metal-to-ligand shift reaction on a Re(III) complex has also provided a route to ring-substituted Re(III) complexes [156(b)], viz.

$$(\eta^5\text{-}C_5H_5)Re(CO)_2(SiPh_3)(H) + n\text{PentLi} \rightarrow Li[(\eta^5\text{-}C_5H_4SiPh_3)Re(CO)_2(H)]$$

$$\downarrow$$

$$\textit{trans-}(\eta^5\text{-}C_5H_4SiPh_3)Re(CO)_2(H)(H) \xleftarrow{\Delta} \textit{cis-}(\eta^5\text{-}C_5H_4SiPh_3)Re(CO)_2(H)(H)$$

A comprehensive investigation of the photoelectron spectra of a series of, formally Mn(III), complexes of the type (η^5-C_5H_4R)Mn$(CO)_2$(SiR'_3)(H), has been reported and these studies are discussed in Sect. E.

(v) Iron, ruthenium, and osmium [437–536] (Tables 21, p. 122, and 22–39, pp. 149–170)

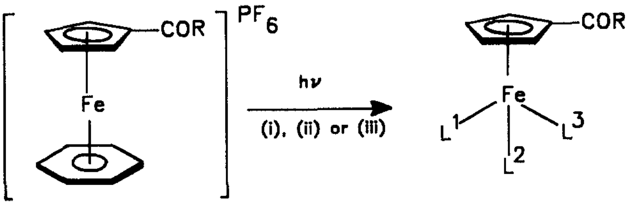
Numerous reports of the synthesis and study of monosubstituted cyclopentadienyl complexes of iron and ruthenium have appeared in the literature, but to date no reports on osmium have been recorded. The types of cyclopentadienyl substituents that have been reported include groups attached via carbon, halogen, nitrogen, phosphorus, boron, silicon and oxygen. They will be dealt with according to synthetic procedures, types of compounds and types of studies. The complexes have not been divided according to the oxidation states of iron and ruthenium, since most of the compounds reported formally belong to the M(I) or M(II) formal oxidation states, e.g. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (M(I)) and $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (M(II)).

(a) Synthetic procedures

A large variety of synthetic procedures have been used to obtain substituted cyclopentadienyliron and -ruthenium complexes and they are discussed below.

(1) From metallocenes. A number of reactions involving the exchange of an aryl or cyclopentadienyl ligand for other ligands, in sandwich compounds, have been reported. For example, diacetylferrocene was reduced and further reacted with carbon monoxide and other ligands to form acetylcyclopentadienyldicarbonyliron derivatives. A radical of the type $(\eta^5\text{-}C_5H_4COMe)Fe\cdot$ was proposed as a possible intermediate in the reaction [437].

Half-sandwich complexes of the general type **286** were obtained by the photochemical reaction of the metallocenes $[(\eta^5\text{-}C_5H_4COR)Fe(\eta^6\text{-}C_6H_6)]PF_6$ (**285**) with ligands such as $P(OMe)_3$, CH_3CN, CO and dppe. The electron-withdrawing acyl substituent on the cyclopentadienyl ring makes the arene ring more photolabile compared with the corresponding complexes containing the unsubstituted or alkyl-substituted rings [438].



285

R = Me, Ph

286

Conditions

(i) $P(OMe)_3$ / CH_2Cl_2

(ii) $P(OMe)_3$ / CH_3CN

(iii) $Ph_2P(CH_2)_2PPh_2$ / CH_3CN

Product 286

(a) $L^1 = L^2 = L^3 = P(OMe)_3$

(b) $L^1 = L^2 = P(OMe)_3$, $L^3 = CH_3CN$

(c) $L^1L^2 = Ph_2P(CH_2)_2PPh_2$, $L^3 = CH_3CN$

Attempts were made to remove the cyclopentadienyl ring rather than the aryl ring in $(\eta^5$-cyclopentadienyl)Fe$(\eta^6$-aryl) complexes. It was thought that electron-withdrawing substituents on the cyclopentadienyl ring would make this more likely, but when the complexes $(\eta^5\text{-}C_5H_4R)Fe(\eta^6\text{-}C_6H_6)$ (R = H, Me, Et, COMe, Cl, CO_2R') were reacted with phosphites, $P(OR')_3$ (R' = Me, Et, Ph), the *aryl* group was replaced in each case, affording $[(\eta^5\text{-}C_5H_4R)Fe\{P(OR')_3\}_3]^+$ complexes as products [439].

(2) Reaction between a substituted cyclopentadiene and metal carbonyls and halides.

Metal carbonyls. The product from the reaction between a substituted cyclopentadiene, C_5H_5R, and an iron carbonyl, $Fe(CO)_5$ or $Fe_2(CO)_9$, is the iron dimer, $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$. This dimer can readily react either by Fe–Fe bond cleavage or by replacing the CO ligand with other ligands. This method of introducing the substituted cyclopentadienyl ring into a metal complex is also the most popular one for synthesising metal dimers containing two linked cyclopentadienyl ligands, including fulvalenes. Examples are:

$C_5H_5R + Fe_n(CO)_m \rightarrow [(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$

$Fe_n(CO)_m = Fe(CO)_5$; R = $SiMe_3$[440], $SiMe_2OEt$[441], $Si(OMe)_3$[441].

$Fe_n(CO)_m = Fe_2(CO)_9$; R = $Si(Me)(CH_2)_3$[442], *t*-Bu[443(a)], CHPhMe[444].

$C_5H_5XC_5H_5 + Fe(CO)_5 \rightarrow X[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$

X = $SiMe_2$, CH_2, etc. (see, for example, refs. 445–452).

When ruthenium carbonyl, $Ru_3(CO)_{12}$, was reacted with menthyl or neomenthyl cyclopentadiene, the corresponding dicyclopentadienyldirutheniumtetracarbonyl complexes formed as products [453(c)].

Metal halides. $(\eta^5\text{-}C_5H_4R)Ru(PPh_3)_2Cl$ was formed from the reaction between a substituted cyclopentadiene, C_5H_5R, ruthenium trichloride and PPh_3 in refluxing ethanol (R = COMe [454(a)], $CH_2C_4H_3S$ [455]).

(3) Thallium cyclopentadienides as precursors. Thallium cyclopentadienides were used to form phenyl- and benzyl-substituted cyclopentadienylruthenium complexes [81]:

$Tl[RC_5H_4] + [Ru(CO)_3Cl_2]_2 \rightarrow [(\eta^5\text{-}C_5H_4R)Ru(CO)_2]_2 + (\eta^5\text{-}C_5H_4R)Ru(CO)_2Cl$

R = Ph, CH_2Ph.

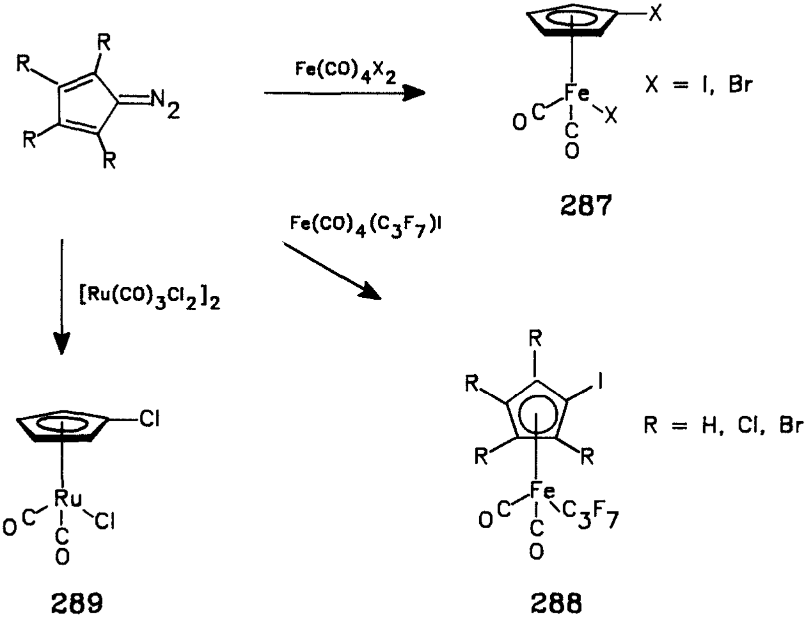
Thallium cyclopentadienides were also used to form linked cyclopentadienylmetal dimers [451]:

$CH_2[C_5H_4Tl]_2 + Fe(CO)_4Br_2 \rightarrow CH_2[(\eta^5\text{-}C_5H_4)Fe(CO)_2Br]_2$

$CH_2[C_5H_4Tl]_2 + [Ru(CO)_3Cl_2]_2 \rightarrow CH_2[(\eta^5\text{-}C_5H_4)Ru(CO)_2Cl]_2 + CH_2[(\eta^5\text{-}C_5H_4)\text{-}Ru(CO)_2]_2$

(4) Diazocyclopentadienes as precursors. The halogens are one of the most difficult types of substituent to introduce onto the cyclopentadienyl ring in cyclopentadienylmetal complexes. For example, the metal cyclopentadienides $M[C_5H_{5-n}X_n]$ (X =

halogen, M = Na, Li, MgBr, Tl) can not be used since they are generally unobtainable or very unstable. Use of the diazocyclopentadienyl precursor has made the synthesis of monohalocyclopentadienyl and multiply substituted cyclopentadienyl complexes readily accessible. Diazocyclopentadienes have been used as building blocks for a range of metal complexes, including those containing iron and ruthenium. To form the substituted cyclopentadienyl iron and ruthenium half-sandwich complexes, the diazocyclopentadiene was reacted with $Fe(CO)_4X_2$ (X = Br, I), $Fe(CO)_4(\sigma\text{-}C_3F_7)I$, or $[Ru(CO)_3Cl_2]_2$ to give the respective products **287**, **288**, and **289**. During the reaction, nitrogen was eliminated from the cyclopentadienyl ring and its exact position was taken up by a halogen which had migrated from the metal. Hence, in multiply substituted cyclopentadienyl rings it is possible to determine the ring substituent positions at the starting material stage [182(a),456].



(5) Benzvalenes. Reaction between benzvalenes and $Fe_2(CO)_9$ yield substituted cyclopentadienyl bimetallic complexes (Sect. C.(i)(f)) (**50**–**52**, **54**) [103,104].

(6) Reactions between iron or ruthenium carbonyls and fulvenes. In 1962, Weiss and Hübel [457] were the first to report reactions between a range of substituted fulvenes and iron carbonyls. The fulvenes they used included $C_5Ph_4CH_2$ and $C_5H_4CR_2$, where R = Me, Ph, $p\text{-Cl}{-}C_6H_4$ and $R_2 = {-}CH_2(CH_2)_3CH_2{-}$, and the iron carbonyls were $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. When $Fe(CO)_5$ was used as reagent, the

reaction required vigorous conditions (sealed tube at 150°C), whereas the reactions with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ were carried out under milder conditions (40°C).

The outcome of the above reactions was expected to be similar to that obtained for the reaction between molybdenum and tungsten carbonyls and fulvenes [41], where the major products were dimeric substituted cyclopentadienylmetal carbonyl complexes. However, a far more complicated situation arose with the reactions utilising iron carbonyls. The number of product *types* that were obtained were as numerous as the number of reactions that were attempted! Examples of fulvenes used and products characterised are (**290–318**), summarised in Table 21. As far as it is possible to generalise, it can be said that, under vigorous conditions using $Fe(CO)_5$, hydrogen abstraction can occur and substituted cyclopentadienylmetal carbonyl complexes are formed as products, e.g. **309a**. The use of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, which, by contrast, require milder reaction conditions, resulted in the formation of various types of fulvene metal carbonyl complex, e.g. **303**, **305**. Complexes containing bridging cyclopentadienyl ligands were also obtained, e.g. **304a–c**, **308a**.

Reactions between some of the above products with acids and iodine to give monometallic compounds was also described [457]. Weiss and Hübel [457] also reported the conversion of 6,6-diphenylfulvene iron tricarbonyl (**303a**) into substituted cyclopentadienyliron complexes in the presence of various acids, with different acids and reaction conditions leading to different products. Products ranged from $[(\eta^5\text{-}C_5H_4CHPh_2)Fe(CO)_3]Y$, ($Y = BPh_4$ and PF_6) by reaction of **303a** with HCl in benzene, to $[(\eta^5\text{-}C_5H_4CHPh_2)Fe(CO)_2Cl$, formed by reaction with HCl in acetone, to the binuclear product $[(\eta^5\text{-}C_5H_4CHPh_2)Fe(CO)_2]_2$ by reaction with acetic acid. The authors also reported a novel product from the reaction of **303a** with methanol, and assigned it structure **310**, a bridging cyclopentadiene iron compound. Approximately 20 years later, the reaction between **303a** and methanol/methoxide was shown to lead to nucleophilic attack of carbon monoxide and protonation of the fulvene to form a substituted cyclopentadienyliron metalloester, $(\eta^5\text{-}C_5H_4CHPh_2)Fe(CO)_2\text{-}CO_2Me$ [458], which was suggested to be the real identity of the compound originally synthesised by Weiss and Hübel.

The work that followed in subsequent years extended the range of fulvenes used (see **290–302** for the types of fulvene used) and also extended these studies to include reactions with ruthenium carbonyl ($Ru_3(CO)_{12}$). The products obtained were various and crystal structures have been reported for several of these complexes. The variety of products that form can be explained by the formation of a diradical (**319**) as intermediate, which can combine with many different substances, e.g. $Fe_2(CO)_9$, other diradicals, or abstracted protons to give the various products [459].

Table 21 summarises the reactions between metal carbonyls and fulvenes that have been carried out by various workers. The discussion that follows will deal with only some aspects of this work.

In 1964, King and Bisnette [57(a)] reacted iron pentacarbonyl with 6-dimethylaminofulvene and obtained the linked dimer **308b**. Despite the vigorous conditions

TABLE 21

Products obtained from the reactions between fulvenes and metal carbonyls

Fulvene[a]	Metal carbonyl	Products[b]	Ref.
290	$Fe_2(CO)_9$	**317b**(X)	398
290	$Fe_2(CO)_9$	**309f**	465
290	$Fe_2(CO)_9$	**304f**(X)[c]	466
291	$Fe(CO)_5$	**308a**	457,461
291	$Fe(CO)_5$	**309c**	460(a)
291	$Fe_2(CO)_9$	**304b, 306b, 307a**	457
291	$Fe_2(CO)_9$	**317a**(X)[d]	467,459
291	$Ru_3(CO)_{12}$	**312**(X)[e]	462
292	$Fe_2(CO)_9$	**317c**(X)	398
292	$Fe_2(CO)_9$	**309g, 313b**	459
292	$Ru_3(CO)_{12}$	**314**	462(b)
293	$Fe(CO)_5$	**303a, 309a**	457
293	$Fe(CO)_5$	**309a**	460(a)
293	$Fe_2(CO)_9$	**303a, 305a, 311b, 310**	457
293	$Fe_2(CO)_9$	**311b**(X)	467,459
293	$Ru_3(CO)_{12}$	**311a**(X)	462
294	$Fe_2(CO)_9$	**303b, 305b**	457
295	$Fe_2(CO)_9$	**304g**	58
296	$Fe(CO)_5$	**308b**(X)	57(a),460
296	$Fe_2(CO)_9$	**316**(X)	468,459
297	$Fe_2(CO)_9$	**303c, 304a, 306a, 309b**	457
297	$Ru_3(CO)_{12}$	**309e**	462
298	$Fe_3(CO)_{12}$	**304c**	457
299	$Fe_2(CO)_9$	**304d, 315a**	469
299	$Ru_3(CO)_{12}$	**308c, 315b**	469
300	$Fe_2(CO)_9$	**304e**	465
301	$Fe(CO)_5$	**309d**	460(a)
302	$Fe(CO)_5$	**309h**	460(a)

[a] See **290–302** for the structures of the fulvenes.

[b] See **303–318** for the structures of the products. Yields are not indicated. (X) indicates that the crystal structure has been determined.

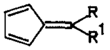
[c] The same compound has been synthesised from $Fe_3(CO)_{12}$ and acetylene [470].

[d] Compounds **307a** and **317a** have the same empirical formula and have been synthesised by the same method, which probably means that they have the same structure, that indicated by **317a**.

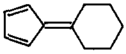
[e] The structure was first thought to be **313a** [462(a)], but the crystal structure determination showed it to be **312** [462(b)].

(135°C, 24 h) no hydrogen abstraction occurred, but this could be ascribed to the charge delocalisation effect of the amino group. Two isomers, (**308bi,ii**), possibly *cis–trans* stereoisomers with respect to the relative positions of the two H and NMe_2 groups in this rigid system, were obtained in 46 and 3% yield. It could not be ascertained which one of the two possibilities corresponded to the major product.

Fulvenes:



290 R=R^{1}=H
291 R=R^{1}=Me
292 R=R^{1}=Et
293 R=R^{1}=Ph
294 R=R^{1}=p–Cl–C_6H_4
295 R=H, R^{1}=OMe
296 R=H, R^{1}=NMe_2
301 R=Me, R^{1}=Ph
302 R=Me, R^{1}=Et



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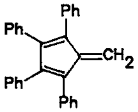
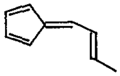


298



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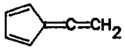
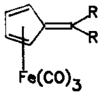
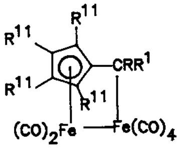


300

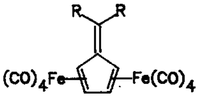
Products obtained from the reactions between fulvenes and metal carbonyls:



303 a R=Ph
b R=p–Cl–C_6H_4
c R_2=–$(CH_2)_5$–



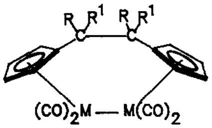
304 a RR^{1}=–$(CH_2)_5$–; R^{11}=H
b R=R^{1}=Me; R^{11}=H
c R=R^{1}=H; R^{11}=Ph
d R=R^{11}=H, R^{1}=Pr^{n}
e CRR^{1}= C=CH_2; R^{11}=H
f R=R^{1}=R^{11}=H
g R=R^{11}=H; R^{1}=OMe
h R=H; R^{1}=Ph; $(R^{11})_4$=(Ph_2H_2)



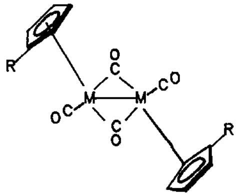
305 a R=Ph
b R=p–Cl–C_6H_4

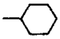
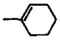
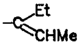
$(C_5H_4CR_2)_2Fe(CO)_2$
306 a R_2=$(CH_2)_5$
b R=Me

$(C_5H_4CR_2)_2Fe_2(CO)_5$
307 a R=Me

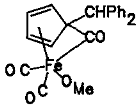


308 a M=Fe; R=R^{1}=Me
b M=Fe; R=H; R^{1}=NMe_2
c M=Ru;R=H; R^{1}=–$CHCHCH_3$
d M=Fe; R=R^{1}=Et
e M=Fe; R=R^{1}=Ph



309 a M=Fe; R=–$CHPh_2$
b M=Fe; R= 
c M=Fe; R=–$CHMe_2$
d M=Fe; R=CHMePh
e M=Ru; R= 
f M=Fe; R=Me
g M=Fe; R= 

h M=Fe; R=CHMeEt



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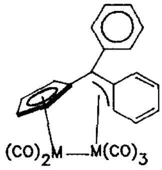
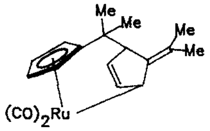
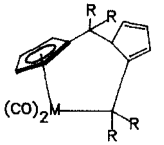


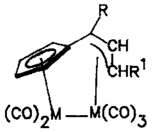
311 a M=Ru
b M=Fe



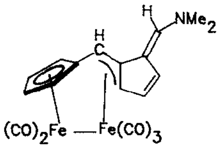
312



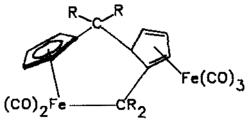
313 a M=Ru; R=Me
b M=Fe; R=Et



314 M=Ru; R=Et; R^1=H
315 a M=Fe; R=H; R^1=Me
b M=Ru; R=H; R^1=Me

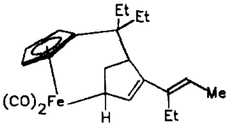


316



a R=Me
b R=H

317



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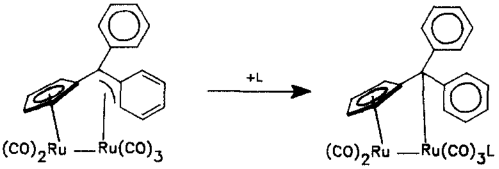
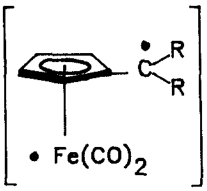


311a

318
L=CO,PMe$_3$,SbPh$_3$,etc



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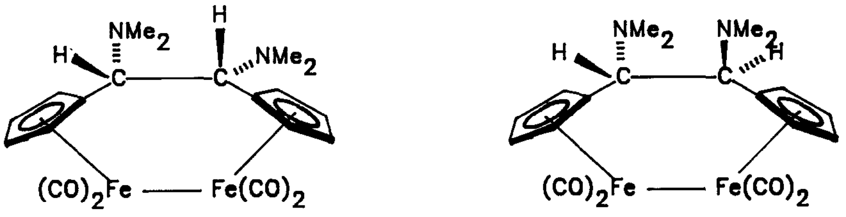


(i) (ii)

308b

Iron–iron bond cleavage reactions were carried out (e.g. treatment of the dimer with sodium amalgam, followed by the addition of MeI; or reaction with a halogen such as I_2) and the products obtained confirmed the identity of the dimer.

The linked metal dimers (**308a** and **308b**) reported by Weiss and Hübel, and King and Bisnette stimulated the interest of McArdle and Manning [460], who saw these compounds as useful models in their IR studies of the *cis–trans* isomerisation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. McArdle and Manning were unable to synthesise bridged dimers such as **308a**, **308d**, and **308e**, and obtained dimeric substituted cyclopentadienyliron carbonyls instead. This failure to synthesise the bridged compounds is not surprising since **308a** was reported by Weiss and Hübel [457] in only 3.6% yield as the only product isolated from that reaction. McArdle and Manning did, however, synthesise and determine the molecular structure of **308b** [460(b)]. Cotton et al. later modified Weiss and Hübel's method, and obtained **308b** in better yield (8%) and undertook IR and ^{13}C NMR studies to investigate fluxional processes in these compounds [461].

Behrens and Weiss extended these studies to ruthenium compounds [462], by reacting $Ru_3(CO)_{12}$ with various fulvenes. Once again, the reactivity patterns were not simple and different products were obtained for the different fulvenes. Compounds **311a**, **312**, **309e**, and **314** were obtained from the fulvenes $C_5H_4CR_2$, where $R = Ph$ (**311a**), Me (**312**), Et (**314**) and $R_2 = -CH_2-$ (**309e**). Crystal structures of **311a** and **312** were determined and showed that the real structure of **313** is that represented by **312** and not **313** as originally proposed [462(b)].

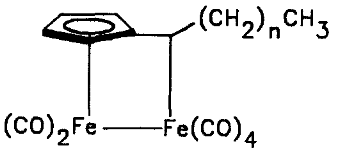
A number of interesting bimetallic complexes with bridging $\eta^{5:3}$-cyclopentadienyl ligands have also been obtained, e.g. **311a** and **314**. In **311a**, the aromaticity of the phenyl ring appears to have been disturbed and the ring has become incorporated into an η^3-allyl ligand. In **314**, one of the ethyl groups has lost two H atoms to form an allyl group. Complex **311a** can undergo addition reactions, which restore the aromaticity to the phenyl ring, so that the ring substituent changes from an η^3-ligand (**311a**) to an η^1-ligand (**318**) [463].

(7) Spirocyclopentadienes as precursors to substituted cyclopentadienylmetal complexes. In Sect. C.(ii)(b) reactions between metal carbonyls and spirocyclopentadienes

were discussed. The spirocyclopentadienes that have been reacted with iron carbonyls are based on two types: spiro[4.4]nona-1,3-diene (**76a**) and spiro[2.4]hepta-4,6-diene (**76b**). Various derivatives of **76b**, such as the spironorcaradiene (**87**) and substituted analogues such as (**226**) were also used.

Hallam and Pauson [123(b)] reacted $Fe(CO)_5$ with **76a** and **76b**) and obtained polymeric products as well as the dimers $[(\eta^5\text{-}C_5H_4Et)Fe(CO)_2]_2$ (from **76b**) and $[(\text{tetrahydroindenyl})Fe(CO)_2]_2$ (from **76a**).

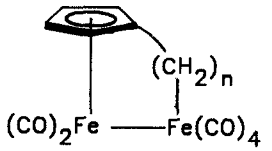
When Eilbracht reacted $Fe_2(CO)_9$ with **76a**, **79** (40%) and a small amount of **80** (2%) were obtained [122(a)]. (These yields were improved to 72% and 6%, respectively, by utilising $Fe(CO)_5$ in the presence of trimethylamine-*N*-oxide [471(c)].) Further additions of $Fe_2(CO)_9$ to **79** led to the formation of more **80**, as well as **320a**,



320

a n=2

b n=0



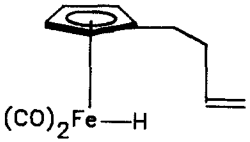
321

a n=4

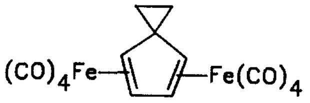
b n=2

via the postulated intermediate **321a**. The following reaction sequence appeared to take place by sequential addition of $Fe_2(CO)_9$ with heating: **76a**→**79**→**80**→**321a**→**320a** [471(b),(c)].

Photolysis of **80**, in a matrix at low temperature, has been reported to form the iron hydride **322** [184(b), 472].



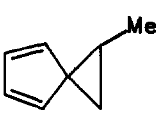
322

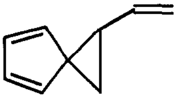


323

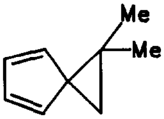
Eilbracht and co-workers observed that the reaction between $Fe_2(CO)_9$ and **76b** gave not only **83** [122(a)] and **320b** [124], but also the unstable compounds **323** and **321b** [471(b)]. An analogous reaction sequence can be postulated for **76b** as for **76a**, where sequential addition of $Fe_2(CO)_9$ results in **76b**→**83**→**321b**→**320b**.

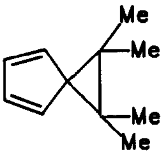
Substituted analogues of **76b** such as **324a,b** [471(d)], **325a,b,c** [122(c)] and spironorcaradienes, e.g. **87** [123(a)] were also reacted with $Fe_2(CO)_9$. The reactivity of substituted analogues of **76b** is greatly influenced by the methyl substituents, and the reaction solvent. For example, the reaction between **325b** and $Fe_2(CO)_9$ [122(c)] gives **326** (analogous to **83**), as well as **327** and **328** (analogous, respectively, to **79**

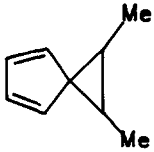




a **324** b

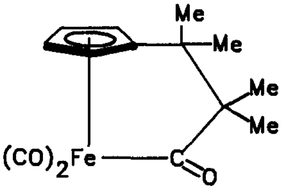






c **325** b c

and **80** obtained from **76a**). These types of products could not be isolated for the unsubstituted spiro[4.2]cycloheptadiene **76b**.



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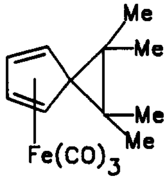

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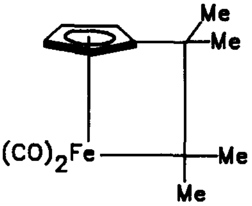

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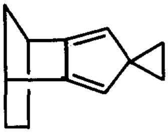
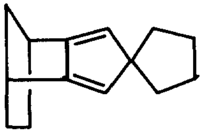
The spironorcaradiene **87** and its dimethylated derivative were reacted with $Fe_2(CO)_9$ under various conditions (see Sect. C.(ii)(b)) [123(a)]. The sterically more demanding derivatives of **76a,b**, the spirocyclic isodicyclopentadienes **329a,b** were also reacted with iron carbonyls [473].





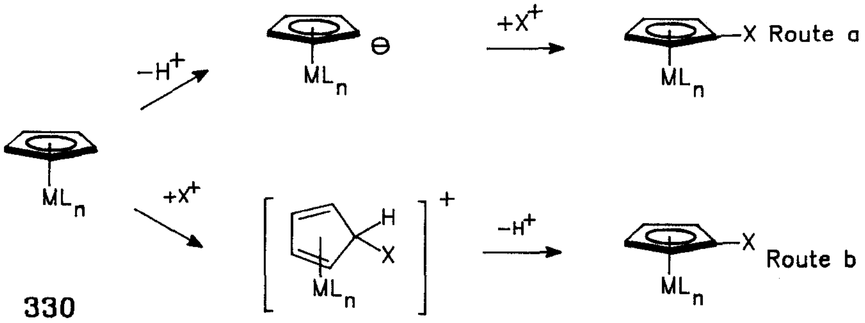
a **329** b

To permit an understanding of the mechanism of the reactions between $Fe_2(CO)_9$ and spirocyclopentadienes, $Fe_2(CO)_9$ was reacted with the less reactive 5,5-dialkylsubstituted cyclopentadienes (**228**). The reactions yielded products corresponding to those of the reaction sequence of **76a**, except that the dinuclear products that were obtained were of the general type $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ [471(c)]. Low-temperature matrix photolysis reactions were also carried out on 5,5-dialkylcyclopentadiene iron complexes [472].

Spiro[2.4]hepta-4,6-diene (**76b**) and its methylated derivatives (**324a, 325a**) can be reacted with Na[(η^5-C_5H_5)Fe(CO)$_2$] to form substituted cyclopentadienes (**49**), which have been used to form numerous organometallic complexes, e.g. ferrocenes [97].

Gladysz and co-workers have cocondensed various metals with organocyclopropanes and spirocycles, including **76a,b**, and produced a range of substituted ferrocenes in the presence of the cocondensed iron atoms [474].

(8) Modification of the cyclopentadienyl ring in cyclopentadienylmetal complexes. The modification of the unsubstituted cyclopentadienyl ring which is already part of a metal complex (**330**) has been thoroughly studied. Substitution of one of the cyclopentadienyl hydrogens by another group can occur either by first deprotonating the ring followed by subsequent electrophilic attack (route a), or by "direct" substitution (route b). This second route, where deprotonation only occurs *after* attachment of the electrophile, goes via an η^4-cyclopentadiene intermediate (see, for example, refs. 492–496), which is subsequently converted back to an η^5-cyclopentadienyl complex by deprotonation.



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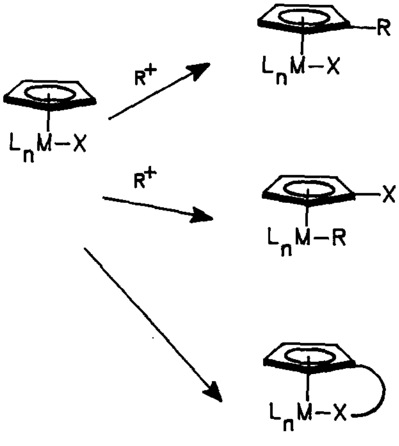
Substitution of the ring may be achieved by an external reagent to yield **331**. It can also occur via an intramolecular process, either by ligand transfer from the metal to the ring to yield **332** or by linkage to a ligand attached to the metal (without metal–ligand bond cleavage) to form a cyclic structure (**333**). This is illustrated diagrammatically in the figures below.

Many groups containing acyl, silyl (including polysilane), germanium, lead and boron (including carboranyl) functionalities have been found to migrate from the metal to the ring. The outcome of the ring-substitution reactions is generally very sensitive to the reaction conditions employed since competitive reactions are always possible. For example, deprotonation of acyl ligands and metal–ligand bond cleavage compete with ring deprotonation. Reaction variables include temperature, type of base used (size, basicity) and the type of metal complex used, e.g. (η^5-C_5H_5)Fe(CO)$_2$R



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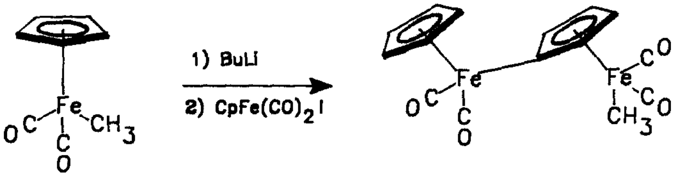
versus (η^5-C_5H_5)Fe(CO)(PPh_3)R. Of the Group 8 metals, iron has been the most extensively studied, and indeed only a few ring modification reactions have been reported for ruthenium.

Ring deprotonation studies and reactions with external electrophiles. Orlova et al. were the first to study systematically the substitution reactions of the cyclopentadienyl ring in complexes of the type (η^5-C_5H_5)Fe$(CO)_2$R [153].

In EtOD/EtONa, they found that hydrogen exchange occurred for [(η^5-C_5H_5)Fe$(CO)_2$]$_2$ and (η^5-C_5H_5)Fe$(CO)_2$R, R = Ph, CH_2Ph [153], R = –(η^5-C_5H_4)Mn$(CO)_3$ [145]. The acidity of the cyclopentadienyl ring protons was high and only those cyclopentadienyl rings that were π-bonded to iron underwent hydrogen exchange. They were also able to metallate these (η^5-C_5H_5)Fe$(CO)_2$R complexes, using ^{n}BuLi in THF at –78°C. Treatment of the metallated cyclopentadienyliron complex Li[(η^5-C_5H_4)Fe$(CO)_2$Ph] with electrophiles such as D_2O, $SiMe_3Cl$, Me_3SnCl, MeI and EtBr led to the formation of substituted cyclopentadienyliron, (η^5-C_5H_4R)Fe$(CO)_2$Ph, R = D, $SiMe_3$, $SnMe_3$, Me and Et [153]. Treatment of (η^5-C_5H_5)Fe$(CO)_2CH_2$Ph with BuLi followed by RR′CO (R = R′ = Ph; R = H, R′ = Ph) or Me_2NCHO led to the formation of (η^5-C_5H_4X)Fe$(CO)_2CH_2$Ph, X = C(OH)RR′ or CHO [475]. The carboxylic acids (η^5-C_5H_4COOH)Fe$(CO)_2$R, R = Ph, CH_2Ph, –(η^5-C_5H_4)Mn$(CO)_3$ were formed after treatment of the corresponding unsubstituted complexes with BuLi followed by CO_2. These carboxylic acids are very acidic and are 2–4 times stronger than ferrocene carboxylic acid [145]. The carboxylic acid group was modified to form the corresponding acyl chloride by using PCl_5 in benzene (R = CH_2Ph) [475].

Metallation reactions were used to form bimetallic complexes with η^1,η^5-cyclopentadienyl bridging groups (**334**) [476]. Cyclopentadienyl-bridged dimers, e.g. **334**, can undergo further metallation reactions, leading, for example, to substitution of the non-bridging cyclopentadienyl ligand by trimethylsilane (**335**), or the formation



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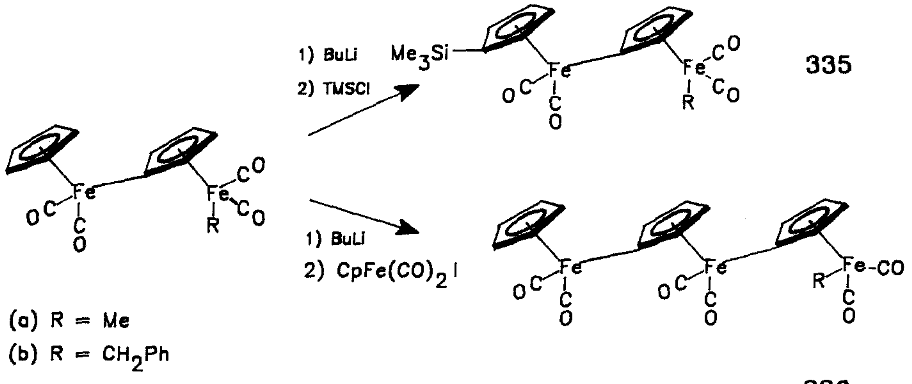

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of a trimer (**336**) when metallation is followed by reaction with (η^5-C_5H_5)Fe(CO)$_2$I [477].

Metal acyl complexes. The (η^5-C_5H_5)Fe(CO)$_2$COR system. Deprotonation/metallation studies were extended to metal acyl complexes. When the acyl ligand contains a hydrogen α to the carbonyl group, deprotonation at this position occurs competitively with deprotonation of the cyclopentadienyl ring. In the Fp–acyl systems, (Fp = (η^5-C_5H_5)Fe(CO)$_2$), the resulting regiochemistry of the products depends on the base that is used. For instance, addition of LDA causes deprotonation at the cyclopentadienyl ring and acyl group transfer to the deprotonated site followed by electrophile attachment to the metal. The use of LiN(SiMe$_3$)$_2$, however, leads to exclusive deprotonation of the acyl ligand to form an enolate, which is quenched by addition of an electrophile to form a substituted acyl ligand [478].

In another study, the activity of the bases NaH, *n*-BuLi, LDA and LiN(SiMe$_3$)$_2$ were compared by addition of the base to FpCOCH$_3$ followed by MeI addition [479]. NaH did not react at all, *n*-BuLi gave an unidentified green paramagnetic product and LDA and LiN(SiMe$_3$)$_2$ both gave reactions at the acyl ligand. With LDA, acyl migration also occurred (ratio of acyl : ring deprotonation was 72 : 28).

Reaction of FpCOCHRR′ (R = H, R′ = Me; R = R′ = Me) with LDA caused deprotonation exclusively at the ring, followed by migration of the acyl group to the ring. Use of $LiN(SiMe_3)_2$ as base resulted in reaction at the acyl group exclusively when R = H, R′ = Me, but no reaction occurred for R = R′ = Me [479]. These results have been interpreted on steric grounds. The cyclopentadienyl ring protons are more acidic than the acyl protons, but the cyclopentadienyl ring is in a sterically less accessible environment, forcing bulky bases to attack at the more accessible acyl protons [479].

The acetyl group has also been introduced onto the cyclopentadienyl ring by treating the dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with boron trifluoride and acetic anhydride, a reaction which results in substitution of one of the two cyclopentadienyl rings [480].

Metal acyl complexes. The $(\eta^5\text{-}C_5H_5)Fe(CO)(L)COR$ *(L = phosphines and phosphites) system.* Deprotonation studies with BuLi were also conducted on the above system, in which one of the CO groups of the Fp system has been replaced by a PPh_3 ligand. The complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COX)$ (X = Ph, OMe, O-i-Pr, O-*t*-Bu) which do not contain α-acyl protons, underwent ring deprotonation with BuLi. Acyl group migration then occurred, with retention of configuration at iron for the COPh-complex, but with scrambling at iron for the esters [132].

Acyliron complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2R)$, R = Me, Pr, which contain α-acyl protons, could be deprotonated selectively by BuLi by varying the temperature. At −78°C, enolate formation takes place exclusively and at 20°C, deprotonation occurs preferentially at the ring (90% compared with 10% enolate formation) [132].

Metal-to-ring migration, with retention of configuration at iron, takes place when the more substituted acyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCHMe_2)$ is treated with BuLi at −40°C, followed by MeI addition. The complex $(\eta^5\text{-}C_5H_4COCHMe_2)Fe(CO)(Me)PPh_3$ was also synthesised by treating the analogous unsubstituted cyclopentadienyl complex, $(\eta^5\text{-}C_5H_5)Fe(CO)(Me)PPh_3$ with *t*-BuLi followed by $Me_2CHCOCl$ [132].

The acyl group of the ruthenium complex $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(COBu)$ migrates from the metal to the ring when treated with BuLi followed by MeI at −78°C [132].

The behaviour of these $(\eta^5\text{-}C_5H_5)M(CO)(PPh_3)(COX)$ complexes can also be rationalised in terms of the steric arguments presented above for the FpR complexes. Here, the PPh_3 ligand introduces increased steric constraints at the acyl group. However, the acyl group is still sterically more accessible than the cyclopentadienyl ligand in the iron complexes so that, at low temperatures, the acyl group deprotonates preferentially. However, with a more bulky acyl moiety, e.g. $COCHMe_2$, ring deprotonation is relatively more facile and, at higher temperatures, where thermodynamic factors dominate, the more acidic cyclopentadienyl ring is deprotonated preferentially. With the larger ruthenium metal (and longer metal–cyclopentadienyl distances) the cyclopentadienyl ring is sterically less restricted and is attacked preferentially at −78°C.

In a study aimed at producing the corresponding enolate from $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_3$, the base LDA was also used. Formation of the enolate rather than an acyl migration product was brought about by slowly adding the iron complex in THF to the LDA at −42°C [481].

Migration of the acyl group occurred when $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OMe)_3]COCH_3$ was treated with LDA and MeI [482].

Metal silanes. Reaction of $FpSiMe_2R$ with a base could lead to two possibilities: either reaction at the ring, or reaction at silicon.

When $FpSiMe_3$ was reacted with LDA or BuLi followed by RX, the product, $(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2R$, resulted from trimethylsilane group migration from the metal to the ring [483]. An intermediate in this reaction sequence was identified by infrared spectroscopy as $Li[(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2]$ [156(a),483].

The reactivity of these iron silanes was compared with that of the similar iron alkyl, FpMe. Under similar reaction conditions, no migration products were formed in the latter complex. Only unreacted starting material, ferrocene, FpEt and polymeric non-carbonyl material was obtained [483].

The product of the migration reaction, $(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2R$, undergoes reactions typical of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ system such as carbonyl insertion and β-hydride elimination [483].

Fp compounds containing the silicon groups $SiMe_2R$ (R = Me, Ph and *n*-Pr) were also studied, and a reaction mechanism for silyl migration was proposed [156(a)]. Crossover experiments were carried out which showed that the reaction was intramolecular. Hence, after deprotonation of the cyclopentadienyl ring, the negatively charged cyclopentadienyl moiety can coordinate to silicon via its empty d-orbitals to form a five-coordinate silicon intermediate. The Fe–Si bond then breaks to give $Li[(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2$ [156(a)].

Reaction of the substituted cyclopentadienyl compounds, $(\eta^5\text{-}C_5H_4R)Fe(CO)_2SiMe_3$, R = Me, $SiMe_3$ and $SiMe_2Ph$, with base, followed by addition of an electrophile, resulted in migration of the trimethylsilyl group from the metal to the ring. Ring substitution depended on the steric size of the original ring substituent. The effect was manifested in two ways; firstly the reaction rate decreased with increasing substituent size and secondly the relative regiochemistry was related to the bulk of the substituent. With the methyl substituent, 1,2- and 1,3-disubstituted products resulted (1 : 1.85 ratio), whereas only 1,3-disubstituted products resulted when the substituents were $SiMe_3$ and $SiMe_2Ph$ [156(a)].

Experiments with a complex containing a chiral silicon ligand, $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Si(Me)(Ph)$(1-naphthyl), showed that migration of silicon groups occur with retention of configuration at silicon. This can be explained by a mechanism involving concerted frontside attack on the empty silicon orbital [484].

Reaction between the compounds $FpSiMe_2X$, $X = H$, Cl and Br, and amides followed by MeI addition resulted in initial substitution of X by the amide at silicon and subsequent migration of the new silyl functionality to the ring. The overall reaction is presented as [154]:

$$FpSiMe_2X \xrightarrow[(2)\,MeI]{(1)\,LiNR'_2} (\eta^5\text{-}C_5H_4SiMe_2NR'_2)Fe(CO)_2Me$$

$X = Cl \quad H \quad Br$

$R' = Me \quad Me \quad i\text{-}Pr$

Similar reactions were carried out for $X = Me$, but, in this case, only the migration reaction occurred [154]:

$$FpSiMe_3 \xrightarrow[(2)\,R''X]{(1)\,LiNR'_2} (\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2R''$$

$R' = Me \quad Me \quad i\text{-}Pr$

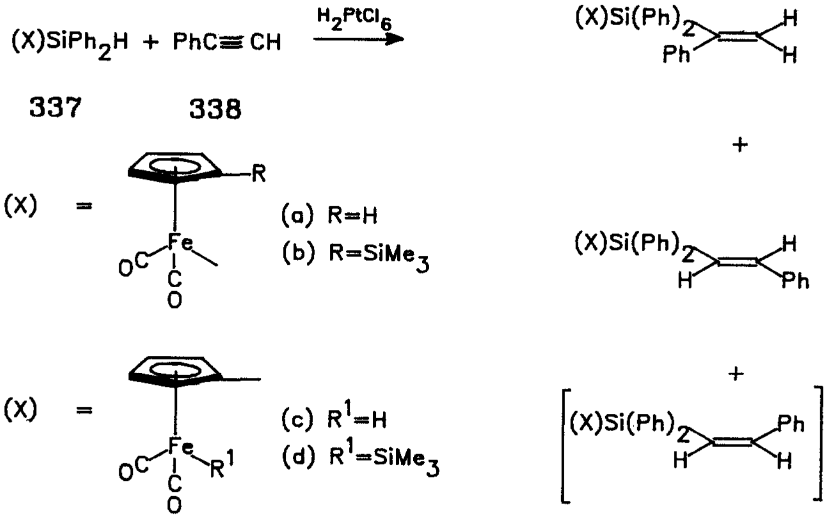
$R''X = MeI \quad MeSiHCl_2 \quad SbMe_2Br$

The analogous ruthenium complexes, $(\eta^5\text{-}C_5H_5)Ru(CO)_2SiMe_3$, also underwent migration reactions when treated with BuLi followed by MeI at −78°C to form $(\eta^5\text{-}C_5H_4SiMe_3)Ru(CO)_2Me$ [485].

The hydrosilyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H$ also underwent migration when reacted with LDA followed by $SiMe_3Cl$ or MeI [486]. Hydrosilylation reactions were performed on phenylacetylene (**338**), using the hydrosilyl complexes $(\eta^5\text{-}C_5H_4R)Fe(CO)_2R'$, $R = H$, $SiMe_3$, $R' = SiPh_2H$ (**337a,b**); $R = SiPh_2H$, $R' = Me$, $SiMe_3$ (**337c,d**), with chloroplatinic acid as catalyst. The products formed were substituted ethenes. The effect of the iron moiety on the regiochemistry of this reaction was compared with that of an "organic" silylating agent such as $SiPh_3H$. Steric factors such as the size of the ring substituents and the size of the metal substituents were found to play a significant role in the reaction [486].

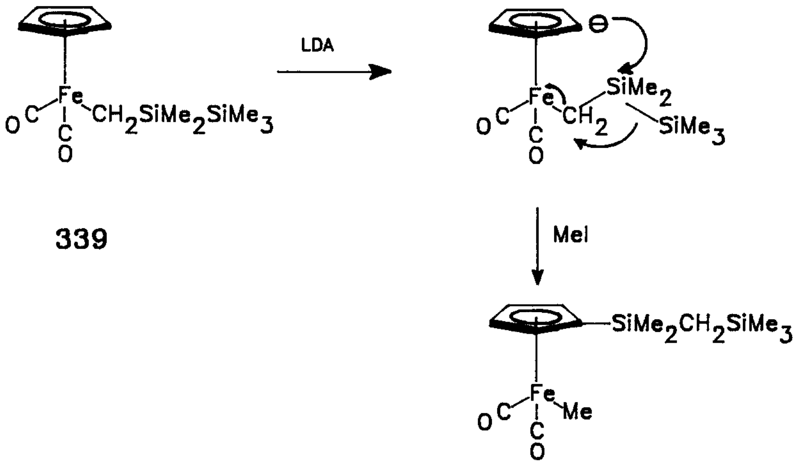
When iron polysilanes were treated with BuLi in THF at −78°C, the entire chain migrated and no polysilane chain cleavage occurred. The migratory aptitude of different groups were compared and the results could be rationalised in terms of steric and electronic effects. Migration removes steric strain at the metal, so that the migratory aptitude increases with the size of the groups: $FpSiMe_3 < FpSi_2Me_5 \leq FpSi_3Me_7 < FpSiMe(SiMe_3)_2$. The migratory aptitude of $FpSiMe_2GePh_3 < FpSiMe_2SiPh_3$ is due to the stronger electron-donating nature of germanium compared with silicon. This results in a shorter and stronger iron–silicon bond in the former complex, making migration less feasible [487].

The methylene polysilane, $FpCH_2SiMe_2SiMe_3$ (**339**), does not undergo silane migration after deprotonation with BuLi at −78°C. Quenching of the reaction mixture with MeI merely leads to methyl substitution at the cyclopentadienyl ring



337 **338**

[487]. However, when the reaction is conducted at room temperature, migration and rearrangement take place and **340** forms. The best yields were obtained for this reaction with the use of LDA at 0°C. This reaction is an example of an intramolecular anion-induced silyl rearrangement [488].



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Fp-polysilanes are thermally stable but depolymerisation occurs photochemically [487]. However, polysilanes bound to the cyclopentadienyl ring do not undergo deoligomerisation [487]. (η^5-C_5H_5)Ru(CO)$_2$-polysilanes are also not photolabile with respect to deoligomerisation [485].

Ring substitution by other Group 14 elements (Ge, Sn, Pb). Migration reactions also occurred in $FpER_3$ complexes ($E = Ge$, Sn, Pb; $R = Me$, Ph) but cleavage of the Fe—E bond was a competitive reaction [301].

Ring substitution by Group 15 elements (P,N). When $(\eta^5\text{-}C_5H_5)Fe(CO)(L)(P(O)\text{-}YZ)$ ($L = CO$; $Y = Z = OEt$; $L = CO$, $Y = OMe$, $Z = NEt_2$; $L = P(OMe)Ph_2$, $Y = Z = Ph$) was treated with LDA at −78°C followed by MeI, the phosphine oxide group migrated to form a cyclopentadienyl phosphine oxide metal complex. In contrast to this, phosphine ligands are stable with respect to migration [489].

Ring metallation of iron and tungsten compounds, followed by reaction with PPh_2Cl, made possible the synthesis of heterobimetallic compounds of the general types **341a,b** with cyclopentadienyl phosphine ligands linking the two metals [286].

(a) **341** **(b)**

The amino-substituent was introduced onto the cyclopentadienyl ring by direct amination of $LiNR_2$ on $(\eta^5\text{-}C_5H_5)FeL'L''X$ derivatives to form, among other products, the mononuclear substituted cyclopentadienyl species $(\eta^5\text{-}C_5H_4NR_2)FeL'L''X$ and $(\eta^5\text{-}C_5H_4NR_2)FeL'L''H$. The nature of the halogen, X and the ligands L′ and L″, as well as the amide NR_2- significantly influenced the outcome of the reactions. The sterically crowded $(\eta^5\text{-}C_5H_5)Fe(CO)LX$ and $(\eta^5\text{-}C_5H_5)FeL'L''X$ complexes favoured formation of the ring-aminated derivatives compared with the $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ complexes. The stronger π-accepting ligands favoured amination. Better yields are obtained for starting materials containing bromide than those containing chloride [163,164]. (See also Sect. C.(ii)(h)).

Boron-substituted cyclopentadienyl complexes. The dimeric iron salt $NEt_4[(\eta^5\text{-}C_5H_4BPh_3)Fe_2(CO)_4(\eta^5\text{-}C_5H_5)]$ was produced when the adduct $NEt_4[(\eta^5\text{-}C_5H_5)Fe(CO)_2BPh_3]$ underwent spontaneous migration of the triphenylboron group from iron to the ring [110(c)].

Carboranyl-substituted cyclopentadienyl complexes were also prepared via migration of the carboranyl group from the metal to the cyclopentadienyl ligand, in this case promoted by bromine in a CCl_4 solution (see Sect. C.(ii)(a)) [109].

"Direct" substitution of the cyclopentadienyl ring. Treatment of the cyclic carbene $(\eta^5\text{-}C_5H_5)Fe(CO)(=C(OMe)OC_6H_{10})$ with trityltetrafluoroborate led to the formation of the tritylsubstituted cyclopentadienylmetal complex [492].

Direct attack of the cyclopentadienyl ring with borohydride or phenyllithium also occurred on the complex $[(\eta^5\text{-}C_5H_5)Fe\{P(OPh)_3\}_3]BF_4$, yielding the substituted *cyclopentadiene* complex $(\eta^4\text{-}C_5H_5R)Fe[P(OPh)_3]_3$ (R = H or Ph). The above complex (R = Ph) forms the substituted *cyclopentadienyl* complexes $[(\eta^5\text{-}C_5H_4Ph)Fe\{P(OPh)_3\}_3]I$ and $(\eta^5\text{-}C_5H_4Ph)Fe\{P(OPh)_3\}_2I$ after treatment with iodine [493].

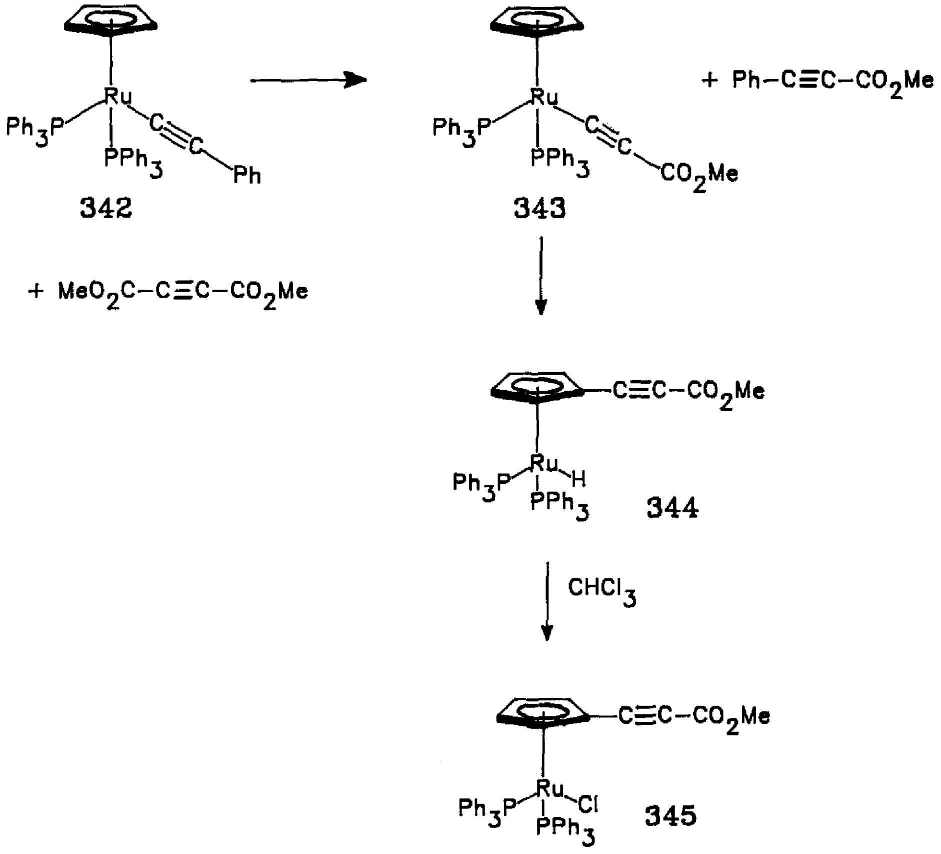
In their investigation of the nucleophilic addition reactions of the complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)P(OPh)_3(\eta^2\text{-alkyne})]BF_4$, Reger et al. found that, depending on the type of nucleophile and the type of alkyne, either alkyne addition or ring-substitution reactions occurred. The reaction proceeds via addition of the nucleophile to the cyclopentadienyl ring, followed by the transfer of a ring hydrogen to the alkyne group. Examples of nucleophiles effecting ring substitution are Et_3BD^- (resulting in a deuterium-substituted cyclopentadienyl ring), MeLi (formation of a methylcyclopentadienyl ring), PhNHLi and Ph_2NLi (nitrogen-substituted cyclopentadienyl ligand formation). Ring substitution also occurs upon reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)P(OPh)_3I$ with Et_2NLi [165,494].

Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Ph$ in alkane solvent at 298 K under 2 atm CO led to the transfer of the benzyl group to the cyclopentadienyl ring to form $(\eta^4\text{-}C_5H_5CH_2Ph)Fe(CO)_3$. Subsequent irradiation resulted in the transfer of a hydrogen from the cyclopentadienyl ring to iron to form $(\eta^5\text{-}C_5H_4CH_2Ph)Fe(CO)_2H$. The transfer of hydrogen rather than benzyl indicated that the benzyl group was in the *exo* position on the cyclopentadienyl ring [495]. Mechanistic studies were conducted on the second step in the addition–substitution sequence of ring modification, the photochemically induced transfer of the *endo*-substituent in complexes $(\eta^4\text{-}C_5H_5R)Fe(CO)_3$ (R = *exo*-H or *exo*-CH_2Ph) and $(\eta^4\text{-}C_5Me_4RR')Fe(CO)_3$ (R = R' = Me; R = *exo*-Me, R' = *endo*-H; R = *exo*-benzyl, R' = *endo*-Me) to form $(\eta^5\text{-cyclopentadienyl})Fe(CO)_2X$ (X = H or R') complexes [496].

Reaction between the cyclopentadienyl ring and phosphine or phosphite ligands coordinated to the metal have also resulted in ring substitution by the ligand. This occurs without cleavage of the metal–phosphorus bond, to form intramolecularly bridging compounds [497–499] (Sect. D.(v)(b)(2)).

Hexafluoroacetone effected substitution of the cyclopentadienyl ring of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(\sigma\text{-}C_2(CO_2Me)_2H)$ to form the complex $(\eta^5\text{-}C_5H_4C(CF_3)_2OH)Ru(PPh_3)(\eta^2\text{-}C_2(CO_2Me)_2H)$ (**349**) [500,501] (Sect. D.(v)(b)(2)).

Reaction between the ruthenium acetylide, $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(CCPh)$ (**342**) and the alkyne $C_2(CO_2Me)_2$ in dichloromethane gave the ring-substituted product $(\eta^5\text{-}C_5H_4CC(CO_2Me))Ru(PPh_3)_2Cl$ (**345**) in low yield. The product was characterised fully by spectroscopic methods, including X-ray crystallography, but the mechanism of the reaction is unknown. It possibly involves replacement of the phenylacetylide by a carbomethoxyacetylide to give (**343**), which forms (**344**) by *acetylide* migration from the metal to the ring, and *hydrogen* migration from the ring to the metal. Chlorination during workup gives the final product (**345**) [502].



(9) Acetylenes as cyclopentadienyl precursors. The bridging complexes, $[(\eta^5,\eta^1\text{-}C_5H_2R_2CHR)Fe_2(CO)_6]$ ($R = H$, Ph) (**304f,h**), have been synthesised from the reaction between triirondodecacarbonyl and acetylene [470] or phenylacetylene [503] under pressure (14–16 atm).

(10) Cyclopentadienones as cyclopentadienyl precursors. The novel oxygen-substituted cyclopentadienyliron complex, $[(\eta^5\text{-}C_5H_4OEt)Fe(CO)_2]_2$, was synthesised from cyclopentadienone diethylacetal and $Fe_2(CO)_9$ [179(c)]. The chemistry of iron could be elaborated further via standard procedures to yield the monomeric complexes $(\eta^5\text{-}C_5H_4OEt)Fe(CO)_2R$ ($R = I$, Me, Ph) [179(c)].

The cyclopentadienone iron carbonyl $(C_5H_4O)Fe(CO)_2$ was used as precursor to the oxygen-substituted complexes, $(\eta^5\text{-}C_5H_4OR)Fe(CO)_2X$ ($X = Cl$, $R = H$, Me, COMe, COPh and $X = Br$, $R = H$). The hydroxy-substituted cyclopentadienyl complexes, $(\eta^5\text{-}C_5H_4OH)Fe(CO)_2X$ ($X = Cl$, Br), were obtained after treatment with the corresponding acids, HCl and HBr. Subsequent treatment of the chloride complex,

$(\eta^5\text{-}C_5H_4OH)Fe(CO)_2Cl$ with dimethyl sulphate, acetylchloride or benzylchloride yielded $(\eta^5\text{-}C_5H_4OR)Fe(CO)_2Cl$ (R = Me, COMe, COPh) [179(b)].

(b) Types of complexes

(1) Complexes with chiral substituents.

Chiral ruthenium complexes. Menthyl and neomenthyl groups attached to the cyclopentadienyl ring have proven to be useful substituents in complexes of the general type $(\eta^5\text{-}C_5H_4R)Ru(CO)LX$ and $[(\eta^5\text{-}C_5H_4R)Ru(CO)(PPh_3)(NCCH_3)]^+$. The two chiral centres, at the ring and at the metal, permit formation of diastereomers that have been easily separated and purified. These compounds were studied by X-ray crystallography, circular dichroism and NMR (^{1}H, ^{13}C and ^{31}P) spectroscopy and the absolute configuration of these compounds have been established. Knowledge of the absolute configuration has permitted the stereochemical course of substitution reactions at the metal to be easily and conveniently followed. The menthyl and neomenthyl substituents were found to have no influence on the stereochemistry of the reactions, but were merely instrumental in the determination of the configurations of the compounds involved [453].

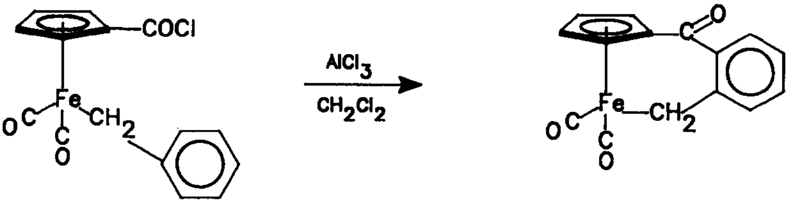
Chiral iron complexes. The chiral substituent –CHPhMe on the cyclopentadienyl ring was used to follow the stereochemistry of reactions at the iron centre. It has the advantage that it does not influence the stereochemistry of reactions at iron. ^{1}H NMR spectroscopy was used to analyse the diasteromeric reaction mixtures and hence to monitor reactions occurring at iron [444].

(2) Intramolecularly bridged monometallic compounds. A number of intramolecularly bridged compounds have been synthesised, in which the substituent on the η^5-cyclopentadienyl ligand is also attached to the metal.

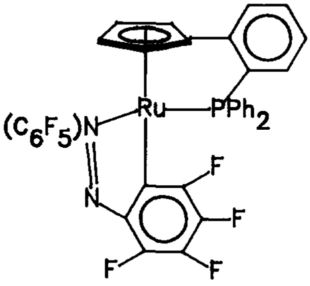
For example, the cyclic complex $(\eta^5\text{-}C_5H_4COC_6H_4\overline{CH_2)F}e(CO)_2$ (**347**) was obtained from the intramolecular Friedel–Crafts acylation of $(\eta^5\text{-}C_5H_4COCl)Fe(CO)_2CH_2Ph$ (**346**) in the presence of $AlCl_3$. The crystal structure of **347** was determined. Two isomeric cyclic complexes analogous to **347** were obtained when the *m*-methyl-substituted phenyl analogue of **346** was reacted under the same conditions [506].

A large number of these metallocyclic complexes are synthesised when the η^5-cyclopentadienyl ligand and a phosphine or a phosphite ligand attached to the metal link up, e.g.

(a) Complex **348** is formed from the reaction between decafluoroazobenzene and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Me$ by substitution of the cyclopentadienyl ring by one of the phenyl rings of the phosphine ligand. The phenyl ring is ortho-substituted in the final product, **348**, which was also the case in **347** [497,498]. The crystal structure of **348** was determined, and confirmed the presence of the cyclopentadienyl ring substituent which had been detected in the ^{1}H NMR spectrum.



346 **347**



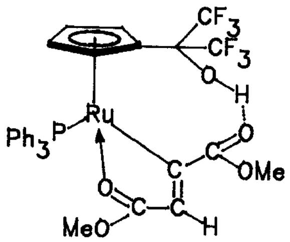
348

(b) Reaction between the dimer $[(\eta^5\text{-}C_5H_5)Fe\{P(OPh)_3\}_2]_2$ and iodine gave two non-interconvertible products which, at first, appeared to be isomers. However, the crystal structures of these compounds showed that the first compound was the expected complex $(\eta^5\text{-}C_5H_5)Fe\{P(OPh)_3\}_2I$, while the second compound, $(\eta^5\text{-}C_5H_4C_6H_4OP(OPh)_2)FeP(OPh)_3I$, had one of the phenyl rings from one of the phosphite ligands linked to the cyclopentadienyl ring. Note that, once again, ortho-substitution of the phenyl group has taken place in the formation of $(\eta^5\text{-}C_5H_4C_6H_4OP(OPh)_2)FeP(OPh)_3I$ [499].

$(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)Ru(PPh_3)Cl$ was synthesised by refluxing $Ru(PPh_3)_3Cl_2$ and $C_5H_5CH_2CH_2PPh_2$ in 1,2-dichloroethane. This compound was studied by NMR methods and X-ray crystallography and substitution reactions were carried out on the metal [507].

Another novel cyclic complex is $[(\eta^5\text{-}C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2]BPh_4$, whose structure was confirmed by X-ray crystallography. In this complex, the thiophene group is attached to the metal, not via the usual η^5-arrangement, but via the sulphur atom [455]. Various reactions were carried out on the above complex, such as protonation, hydrogenation and reaction with hydrogen sulphide. These reactions resulted in the replacement of the thiophene group on the metal and formation of a complex with a free thienylmethyl as the cyclopentadienyl ring substituent. From these results, the strength of the Ru–S bond could be assessed and compared with those in complexes containing other types of sulphur ligand [508].

A cyclic system has also been shown to be generated via intramolecular hydrogen bonding between the hydroxy group of the cyclopentadienyl substituent $-C(CF_3)_2OH$ and a carbonyl group of a diester coordinated to the metal. This compound, **349**, was synthesised from the reaction between hexafluoroacetone and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2\{\sigma\text{-}C_2(CO_2Me)_2H\}$, and its structure was confirmed by X-ray crystallography [500,501].

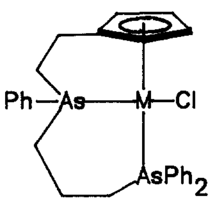


349

The cyclometallated products $(\eta^5\text{-}C_5R_4CH_2\overline{C_6H_4)Fe}(CO)_2$ (R = H, Me) have been prepared via an interesting route, involving a cyclopentadienyl to metal ligand "transfer". Near-UV irradiation of $(\eta^5\text{-}C_5R_4CH_2C_6H_5)Fe(CO)_2Me$ caused the loss of CO and a Me radical, and the vacant site created on the metal was taken up by the phenyl ring. Initially this occurred via formation of an η^2-π-bond, but after loss of hydrogen from the phenyl ring, and re-uptake of CO, a σ-bond was formed. The phenyl ring was ortho-substituted, forming part of an effective five-membered metallocycle [509].

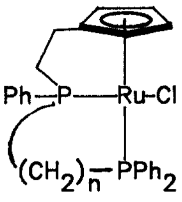
Iron and ruthenium complexes containing macrocyclic cyclopentadienyl ligands, e.g. **350**, **351**, have been found to be of catalytic interest. For example, the catalytic hydrogenation ability of the ruthenium complex **351b**, which contains the tridentate ligand $Ph_2P(CH_2)_4PPh(CH_2)_2C_5H_4$, was found to be superior to other Ru(II) phosphine complexes [510].

Reaction between fulvenes and metal carbonyls (see Sect. D.(v)(a)(6)) have also



M=Fe,Ru

350



351 a n = 3
b n = 4

led to the formation of compounds with intramolecular links between the metal and cyclopentadienyl ring, e.g. **313**, **317**. All these complexes were synthesised from two fulvene molecules and one or two metal units.

Spirocyclopentadienes, when treated with metal carbonyls, can also lead to metallocycles which incorporate the cyclopentadienyl ring (see Sect. D.(v)(a)(7)).

(3) Bimetallic or cluster complexes with cyclopentadienyl bridging ligands. Synthesis of bimetallic and, in some cases, trimetallic or cluster complexes with various types of bridging cyclopentadienyl ligands have been reported.

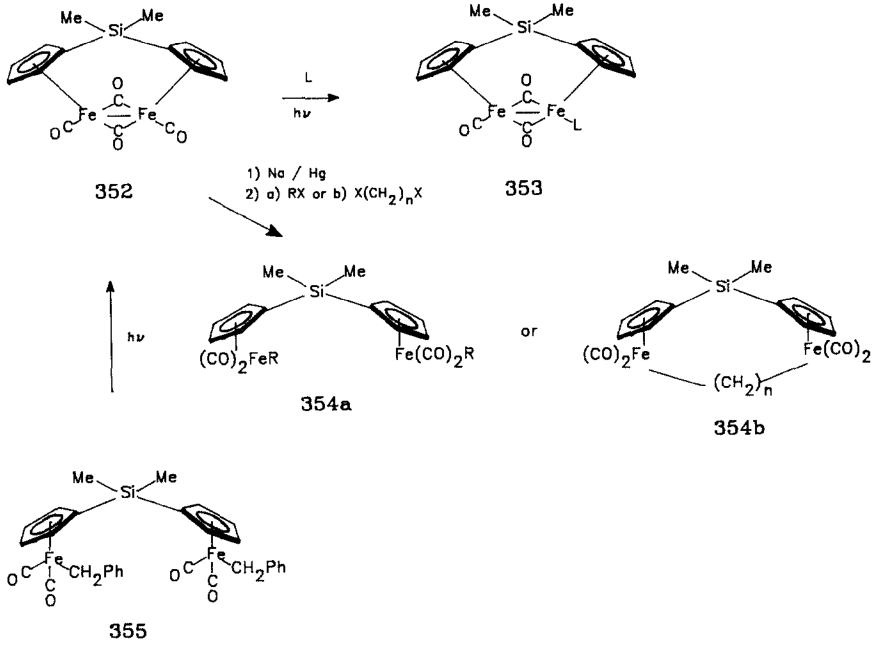
The (C_5H_4–X–C_5H_4) unit as bridge between metals. The linked cyclopentadienyl system has been recognised as a very useful analogue of metal dimer complexes. For example, compounds such as $X[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$, $X=(CMe_2)_2$, $[CH(NMe_2)]_2$, containing bridging cyclopentadienyl units which enforce rigid *cis* conformatiions, were investigated in *cis–trans* isomerisation and carbonyl scrambling studies [460,461] (Sect. D.(v)(a)(6)).

Apart from restricting rotation about the metal–metal bond, the cyclopentadienyl bridge also keeps the two specific metals close together. This prevents the formation of separate monomers, even when the metal–metal bond is cleaved. The close proximity of the two metals also leads to different reaction possibilities, especially since the linking of the cyclopentadienyl rings might result in additional strain being placed on the metal–metal bond. Systems containing more than one metal site per molecule are also suggested to be useful analogues for heterogeneous catalysts. They lend themselves to the study of the effect of one metal site on another. Thermal decomposition studies have been carried out on various dimeric and tetrameric iron alkyl complexes containing the $C_5H_4SiMe_2C_5H_4$ bridge [511].

$Me_2Si[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ (**352**) is a complex that has been studied extensively, especially with regard to comparisons with the unbridged analogue, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. $SiMe_2$ is regarded as an "inert" unit, holding the rings (and metals) together. Reactions have been carried out at the metal centres, e.g. substitution reactions **352**→**353** [445,449], and metal–metal bond cleavage reactions to form two ML_n centres linked only via their bridging ligands **352**→**354** [391(a),450]. Reactions at the metal centres of these latter non-metal bridged complexes, include substitution [447,448], photofragmentation and disproportionation, which can lead to the reformation of the M–M bond **355**→**352** [446,447].

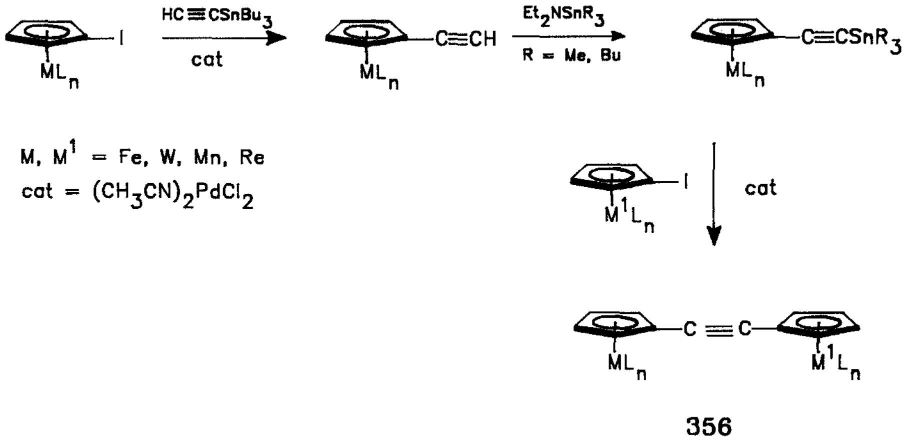
Other groups, X, linking the cyclopentadienyl rings in compounds $X[(C_5H_4)Fe(CO)_2]_2$, that have been synthesised, include: $SiMe_2(2,4\text{-}B_5H_5C_2)SiMe_2$ [391(a)], $Me_2Si(CH_2)_2SiMe_2$ [512], $(SiRR'O)_nSiRR'$, $R=R'=Me$, $n=1,2$; $R=Me$, $R'=Ph$, $n=1$ [452]. Reactions at the metal centres similar to the ones enumerated above were also carried out on these compounds.

The complexes $X[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ were generally synthesised by heating the dicyclopentadiene ligand, $X(C_5H_5)_2$, with $Fe(CO)_5$, under reflux. Bis(cyclopenta-



dienylthallium)methane, $CH_2(C_5H_4Tl)_2$, was also used as an entry to linked cyclopentadienyliron and -ruthenium bimetallic complexes, by reaction with iron or ruthenium carbonyl halides [451].

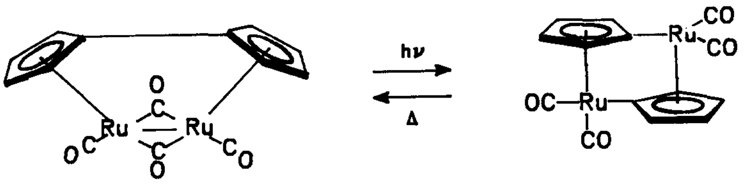
The novel bis(cyclopentadienyl) acetylene heterodinuclear complexes, $L_nM(\eta^5\text{-}C_5H_4)CC(\eta^5\text{-}C_5H_4)M'L_m$, M,M' = Fe, W, Mo, Mn, Re (**356**), were prepared from η^5-iodocyclopentadienyl complexes [394].



Fulvalene complexes. The fulvalene ligand has been incorporated into a number of dimeric, homo- and heterobimetallic ruthenium complexes, with or without metal–metal bonds [79,380,387,403,513]. These compounds were generally synthesised from dihydrofulvalene and metal carbonyls.

Various reactions, including photolysis, ligand exchange and additions, have been carried out at the metal centres to probe the reactivity resulting from the close proximity of the two metals (see, for example, refs. 513 and 514). The reactivity of mixed metal dimers has potential catalytic implications and studies have been conducted on the mutual effects of the two metal centres on one another (see, for example, ref. 380).

The fulvalene diruthenium tetracarbonyl complex, $[(\eta^5,\eta^5\text{-}C_{10}H_8)Ru_2(CO)_4]$ (**357**) was found to have an altered reactivity compared with the dicyclopentadienyldirutheniumtetracarbonyl complex, $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ [513]. The fulvalene complex (**357**), undergoes a very interesting reaction in which the diruthenium moiety adds to the bond between the two cyclopentadienyl rings in the fulvalene ligand. X-Ray crystallography showed that the resulting complex (**358**) contains two η^1,η^5-cyclopentadienyl rings. The reaction is thermally reversible [513].

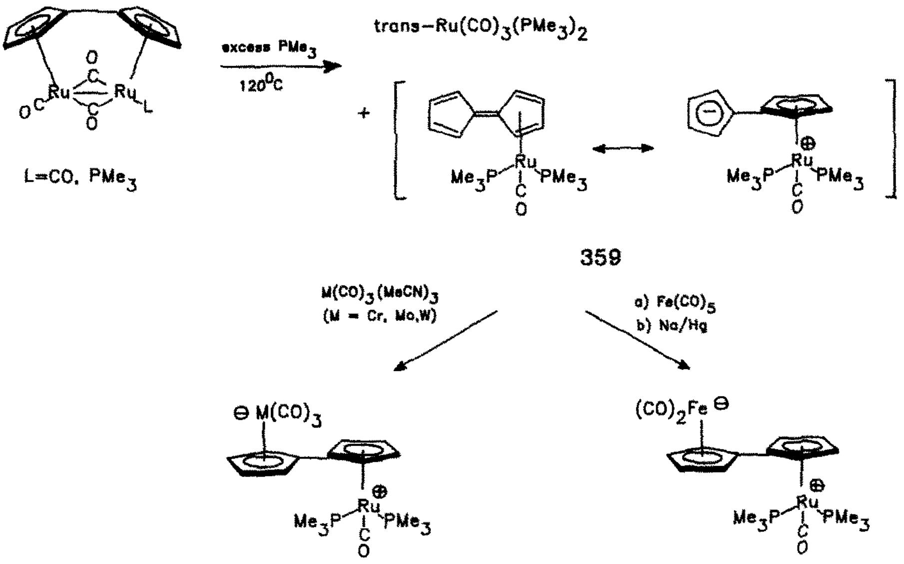


357 **358**

Reaction between $(\eta^5,\eta^5\text{-}C_{10}H_8)Ru_2(CO)_3L$ (L = CO, PMe_3) and a large excess of PMe_3 at 120°C led to two products: *trans*-$Ru(CO)_3(PMe_3)_2$ and the ring-slippage product $(C_{10}H_8)Ru(CO)(PMe_3)_2$ (**359**), a fulvene/ylide-type complex [514]. This complex (**359**) has been used to form heterobimetallic zwitterionic products via reactions with other metal carbonyls. For example, **360** forms from the reaction between **359** and $M(CO)_3(MeCN)_3$, M = Cr, Mo, W. The product from the reaction between **359** and $Fe(CO)_5$, followed by treatment with a Na/Hg amalgam, is **361** [387].

Synthesis of non-sandwich iron fulvalenes was reported only recently [515]. Photolysis of the sandwich fulvalene, $[(\eta^5,\eta^5\text{-}C_{10}H_8)Fe_2(\eta^6\text{-}C_6H_6)_2](PF_6)_2$ (**362**) in the presence of dppe or dppm in MeCN led to the formation of $[(\eta^5,\eta^5\text{-}C_{10}H_8)Fe_2L_2\text{-}(MeCN)_2](PF_6)_2$ (L = dppe, dppm) (**363**). The MeCN is readily displaced by PMe_3 or CO.

Initial attempts to synthesise $[(\eta^5,\eta^5\text{-}C_{10}H_8)Fe_2(CO)_4]$ from $Fe(CO)_5$ and dihydropentafulvalene were unsuccessful [79]. However, synthesis of the analogous *t*-Bu-substituted fulvalene iron complex, $[(\eta^5,\eta^5\text{-}C_{10}H_4(t\text{-}Bu)_4)Fe_2(CO)_4]$ from $Fe(CO)_5$ and 1,1′,3,3′-tetra-*tert*-butyl 5,5′-dihydropentafulvalene has been carried out successfully [516].



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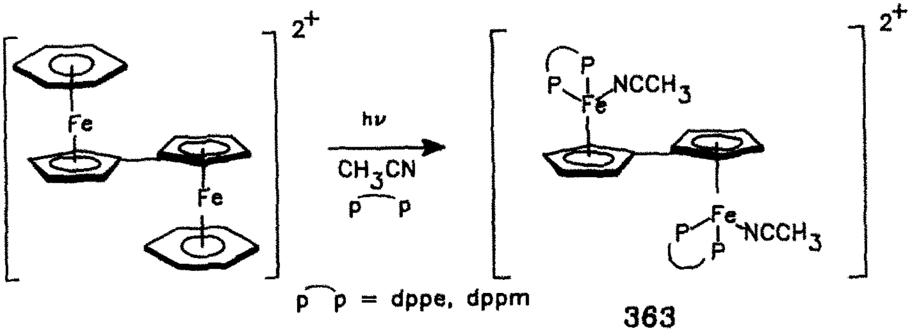
360 **361**



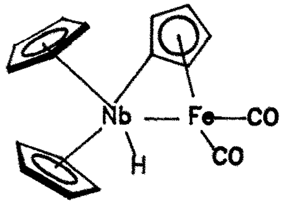
362 **363**

Complexes with η^1,η^5-cyclopentadienyl ligands. These include dimers and trimers, and homo- and heterometallic complexes, e.g. (**334–336**, **358**, **364–366**) [476,477,517,518].

Complex **365** is quite reactive and carbonyl exchange with ^{13}CO occurs instantaneously at 0°C. Ligand exchange at ruthenium occurs in the presence of PMe$_3$ to form **366**. In the presence of ethylene, an insertion reaction between the zirconium atom and the σ-bound cyclopentadienyl occurs to form **367** [518].

The cyclopenta*diene* ligand can bond to three metals, e.g. (**368**) [519].

One of the products formed from the reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and a series of 2-arylazirines was the cyclopentadienone dimer $(C_5H_4O)_2$. The iron hydride dimer containing two η^1,η^5-cyclopentadienyl bridging ligands, $[(\eta^1,\eta^5\text{-}$



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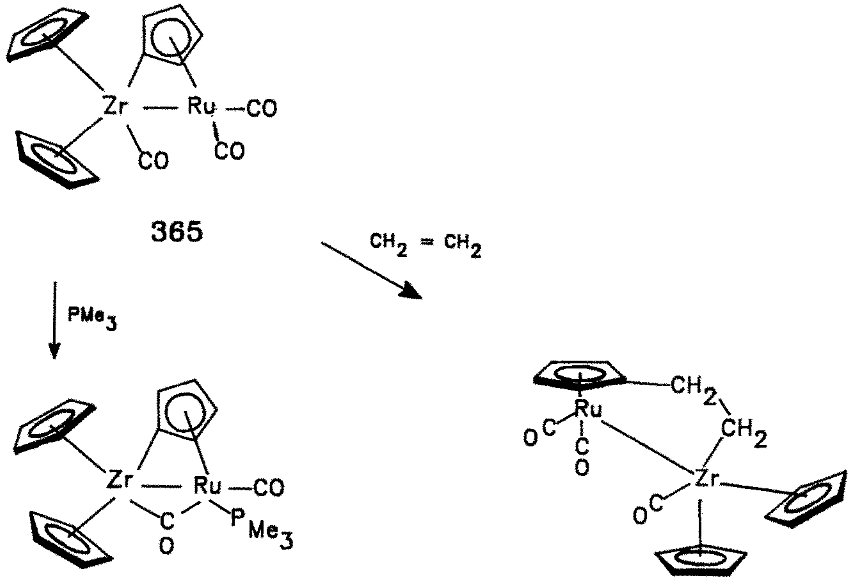

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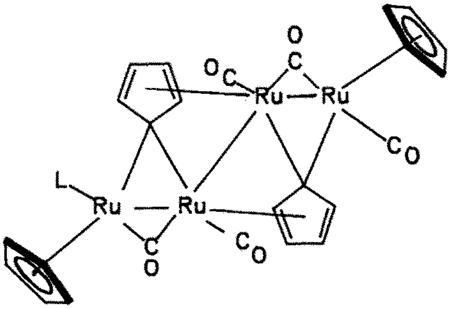
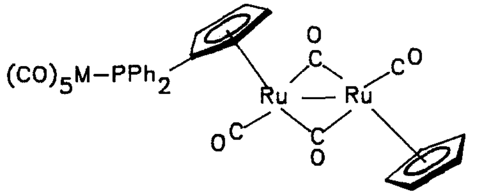


368

$C_5H_4)Fe(CO)H]_2$ was suggested as a possible intermediate in the formation of this product [520].

Bridging phosphino cyclopentadienyl ligands. $(CO)_5\overline{M(\eta^5\text{-}C_5H_4P}Ph_2)(\eta^5\text{-}C_5H_5)\text{-}Ru_2(CO)_4$ (**369**) was formed from the reaction between $[M(CO)_5PPh_2]^-$, M = Mo, W and $(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl$. When M = Cr, no nucleophilic attack on the cyclopentadienyl ring of the ruthenium complex took place and the product that formed was $(CO)_5Cr(\mu\text{-}PPh_2)Ru(CO)_2(\eta^5\text{-}C_5H_5)$ [521].

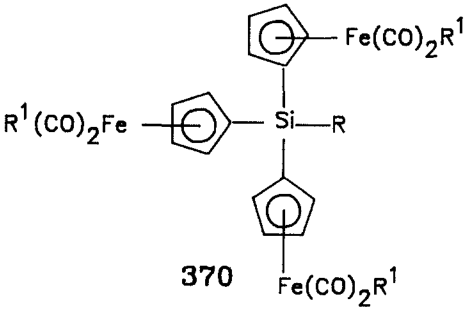


M = Mo, W

369

$(\eta^5\text{-}C_5H_4PPh_2)Fe(CO)_2Me$ reacted with other metal complexes, e.g. $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ to form cyclopentadienylphosphine-bridged heterobimetallic complexes (**341**) (see also Sect. D.(v)(a)(8)) [286].

Trinuclear complexes. The iron trinuclear complexes, $RSi[(\eta^5\text{-}C_5H_4)Fe(CO)_2R']_3$ (R = Me, $(CH_2)_3Cl$, $(CH_2)_2C_6H_4CH_2Cl$; R′ = Me, Et, CH_2Ph) (**370**) were obtained by metallation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R'$, using BuLi, followed by reaction with $RSiCl_3$ [404].



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(4) Substituted cyclopentadienyliron complexes as catalysts. The dimers $[(\eta^5\text{-}C_5R_4R^1)Fe(CO)_2]_2$, R = H, R^1 = H, Me, CO_2Me, OMe, $O(CH_2)_4OH$; R = R^1 = Me, as well as a wide range of other transition metal complexes, were investigated for their ability to catalyse carbonyl substitution reactions in metal carbonyl complexes [522].

The reactions investigated were:

(a) $Fe(CO)_5 + L \rightarrow Fe(CO)_4L + CO$

where L = Group 15 donor ligands.

Of the $[(\eta^5\text{-}C_5R_4R^1)Fe(CO)_2]_2$ ($R = H$, $R^1 = H$, Me, CO_2Me; $R = R^1 = Me$) complexes investigated, all except the CO_2Me-containing complex catalysed the reaction. Factors influencing the catalytic abilities were (i) the nature of the cyclopentadienyl ring substituents, where electron-donating methyl groups increased the reaction rates as opposed to the electron-withdrawing CO_2Me group which decreased the reaction rates, (ii) the steric size of L, which affected the reaction rates for $R = H$, $R^1 = H$, but not for $R = R^1 = Me$ [522(a)].

(b) $Mn_2(CO)_{10} + 2PPh_3 \rightarrow Mn_2(CO)_8(PPh_3)_2 + 2CO$

This reaction was catalysed by the dimers containing $R = H$, $R^1 = H$, Me; $R = R^1 = Me$ [522(a)].

(c) $(\eta^5\text{-}C_5H_4R^2)Fe(CO)_2X + R^3NC \rightarrow (\eta^5\text{-}C_5H_4R^2)Fe(CO)_{2-n}(CNR^3)_nX$

$n = 1, 2$; $R^2 = H$, Me; $X = I$, Br; $R^3 = t$-Bu, 2,6-$Me_2C_6H_3$, $PhCH_2$.

The dimers that catalysed this reaction were $[(\eta^5\text{-}C_5R_4R^1)Fe(CO)_2]_2$, $R = H$, $R^1 = H$, Me [522(c)].

(d) $[Fe(CO)_4(CNBu\text{-}t)] + t\text{-}BuNC \rightarrow [Fe(CO)_3(CNBu\text{-}t)_2] + CO$

This reaction was catalysed by the complexes $[(\eta^5\text{-}C_5R_4R^1)Fe(CO)_2]_2$, $R = H$, $R^1 = H$, Me, CO_2Me, OMe, $O(CH_2)_4OH$. In this case, in contrast to the reactions discussed above, the catalytic ability appeared to increase with the electron-withdrawing substituents: $H < Me < CO_2Me < OMe \approx O(CH_2)_4OH$. The dimer containing the strongly electron-donating pentamethylcyclopentadienyl ligands had no catalytic effect [522(d)].

$[(\eta^5\text{-}C_5H_4R)Fe(R'NC)_2]_2$ complexes, $R = H$, Me, CO_2Me; $R' = 2,6\text{-}Me_2C_6H_3$, C_6H_5; were synthesised from the direct reaction between $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ and aryl isonitriles, R'NC. The substitution rates increased with the electron-withdrawing ability of the cyclopentadienyl ring substituents, R, and the nucleophilicity of the incoming isonitrile [522(b)].

(5) Polymer-supported complexes. The preparation of a number of potentially useful hydrogenation catalysts, including $PS\text{-}CH_2C_5H_4M(CO)_{2-n}L_n$ (PS = a cross-linked polystyrene support; M = Fe, Ru; L = phosphines, phosphites, NO, $SnCl_3$, allyl, halo, H), have been reported. In the absence of air and light, the hydride complex $PS\text{-}CH_2C_5H_4Fe(CO)_2H$ was found to be very stable at room temperature. This is to be compared with the thermally unstable $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$, which reverts to the dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ at room temperature [523].

(c) Studies conducted on substituted cyclopentadienyliron compounds

A number of spectroscopic studies (see refs. 7, 443, 524–526) have been conducted on substituted cyclopentadienyl complexes to determine the electronic and/or steric effects of the ring substituents. These studies will be discussed in Sect. E.

Chemical reactivity studies. (a) Electrochemical studies on the dinuclear complexes $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ ($R = SiMe_2OEt$, $-(CH_2)_3Si(OMe)_3$ [441]: Substitution of the ring is expected to affect the kinetic stability of these complexes. The alkoxysilylcyclopentadienyl ligands are more electron-donating than the unsubstituted cyclopentadienyl ligand and improved the kinetic stability of the oxidation products, which were also found to be dependent on the reaction solvent.

(b) The thermal stability with respect to β-hydride elimination was determined for the complexes Cp^*FeL_2Et ($Cp^* = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4Me$, $\eta^5\text{-}C_5Me_5$; $L = PPh_nMe_{3-n}$, $n = 0\text{–}3$). The stability increased with the basicity of the phosphines and decreased with increasing methyl substitution [527].

(c) The insertion rate of SO_2 into the Fe–R bond of $Cp^*Fe(CO)_2R$ complexes increased with increasing methyl-substitution of the ring for $R = CH_2Ph$, but no regular trend was observed for $R = Ph$ [528].

TABLE 22

Group 8 metal compounds of the general formula (η^5-C_5H_4R)M(A)(B)(C)

M	R	A	B	C	Comments[a]	Ref.
Fe	D	CO	CO	CH_2CO_2Me, $CHDCO_2Me$	IR, NMR (^1H, ^{13}C), MS	103
Fe	D	CO	CO	Ph, CH_2Ph	IR, NMR, MS	153
Fe	D	CO	PPh_3, $P(OPh)_3$	$C(CO_2Me)CHMe$	NMR (^1H, ^2H, ^{13}C)	494
Fe	D	CO	$P(OPh)_3$	CMeCHPh	NMR (^1H, ^2H, ^{13}C)	494
Fe	D	CO	PPh_2Me	I	IR, MS, NMR	443(a)
Fe	Me	CO	CO	Me	Electrochemical studies	464
Fe	Me	CO	CO	$SiMe_3$	IR, NMR	156(a)
Fe	Me	CO	CO	$CH_2Si_2Me_5$, CH_2SiMe_3	IR, NMR (^{29}Si, ^{13}C)	487,488
Fe	Me	*t*-BuNC	I	CO, *t*-BuNC	IR, NMR	522c
Fe	Me	CO	$P(OPh)_3$	CRCHR′[b]	NMR (^1H, ^{13}C), IR	165
Fe	Me	CO	CO	$SP(S)(OR)_2$[c]	IR, NMR (^1H, ^{13}C)	526
Fe	Me	CO	PPh_2Et	COMe	X-ray	490(a)
Fe	Me	PMe_3	η^3-$CH_2CHCHCH_3$		NMR (^1H, ^{31}P)	527
Fe	Me	CO	L[d]	I	IR, NMR, MS, X-ray	7,443(f)
Fe	Me	PMe_3	PMe_3	Et, Cl, Me, Bu, $CHCH_2$, H	NMR (^1H, ^{31}P)	527
Fe	Me	CO	CO	I	IR, NMR	7
Fe	Me	$PPhMe_2$	$PPhMe_2$	H, Me, Et	NMR (^1H, ^{31}P)	527
Fe	Me	*t*-BuNC	*t*-BuNC	Br	IR, NMR	7
Fe	Me	PPh_2Me	PPh_2Me	H, Et, Cl	NMR (^1H, ^{31}P)	527
Fe	Me	CO	I	L[e]	IR	491
Fe	Me	CO	Cl	L[f]	IR	491
Fe	Me	CO	Br	L[g]	IR	491
Fe	Me	CO	PPh_3	I	IR, NMR, MS	529(d)
Fe	Me	CO	CO	R′[h]	IR, NMR	528
Fe	Me	CO	CO	(η^1-CH_2CMeCH_2)	NMR	530
Fe	Me	CO	$P(OCH_2)_3CCH_3$	(η^1-$CH_2CHCHEt$)	NMR, MS	530

TABLE 22 (*continued*).

M	R	A	B	C	Comments[a]	Ref.
Fe	Me	CO	L^i	$SnMe_3$	IR, NMR (^1H, ^{31}P, ^{119}Sn)	443(e)
Fe	Me	CO	L^j	I	NMR (^{13}C)	443(c)
Fe	Me	CO	$(\eta^3\text{-L})^k$		IR, NMR (^1H, ^{13}C)	531
Fe	Me	CO	COMe	PPh_3	X-ray	490(b)
Fe	Me, Et	CO	CO	Me, Et	IR, NMR, MS, UV	471(a), (c), 472
Ru	Me	PPh_3	PPh_3	Cl	NMR	529(c)
Ru	Me	PPh_3	PPh_3	L^l	IR, NMR	454(a)
Ru	Me	PPh_3	$(\eta^2\text{-L})^m$		IR, NMR	454(a)
Ru	Me	L^n		Cl	NMR (^1H, ^{13}C), VIS	532
Ru	Me	CO	I	L^o	IR, NMR, MS	443(b)
Ru	Me	$P(CH_2CH_2CN)_3$	$P(CH_2CH_2CN)_3$	Cl	IR, NMR (^1H, ^{31}P)	454(b)
Ru	Me	$Ph_2P(CH_2)_2PPh_2$		Cl, S_2COR (R = Me, Et)	IR, NMR (^1H, ^{31}P)	454(b)
Fe	$CHMe_2$	CO	I	CO, PPh_3	IR, NMR	443(d)
Fe	*t*-Bu	CO	I	L^p	IR, MS, NMR (^1H, ^{13}C), X-ray	443(a)
Fe	$CHPh_2$	CO	I	PPh_3	IR, NMR, X-ray	443(d)
Fe	$CHPh_2$	CO	Cl	PPh_3	IR, MS	533
Fe	$CHPh_2$	CO	CO	CO_2Me	IR, NMR (^1H, ^{13}C)	458
Fe	$CHPh_2$	CO	$CONH_2$	CO, PPh_3	IR, MS	533
Fe	$CHPh_2$	CO	CO	NCO	IR, MS	533
Fe	CHPhMe	CO	CO	I, Br, Cl, Me	IR, MS, NMR (^1H, ^{13}C)	444
Fe	CHPhMe	CO	PPh_3	I, Br, H, Me, COMe	IR, MS, NMR (^1H, ^{13}C, ^{31}P)	444
Fe	CHPhMe	CO	$P(Tol)_3$	H, I	IR, MS, NMR (^1H, ^{13}C, ^{31}P)	444
Fe	CHPhMe	CO	H	L^q	IR, MS, NMR (^1H, ^{31}P)	444
Fe	CPh_3	CO	$=C(OMe)OC_6H_{10}-$		IR, NMR	492
Fe	Benzyl	CO	CO	Me	IR, UV-VIS, NMR (^1H, ^{13}C)	509

Fe	Benzyl	CO	CO	H, Cl	IR, UV-VIS, NMR	495,496
Fe	Benzyl	CO	PPh_3	Me	IR, UV-VIS	509
Ru	Ph, Bz	CO	CO	Cl	IR, NMR	81
Fe	$-(CH_2)_2CHCH_2$	CO	CO	H	IR	472
Fe	C≡CH	CO	CO	Me	IR, NMR (^1H, ^{13}C), MS	394
Fe	$C\equiv CSnR_3$ R = Me, *n*-Bu	CO	CO	Me	IR, NMR (^1H, ^{13}C), MS	394
Ru	$C_5H_4{}^r$	CO	PMe_3	PMe_3	X-ray	514
Ru	$CH_2C_4H_3S$	PPh_3	PPh_3	SH, H	NMR (^1H, ^{31}P)	508
Ru	$C(CF_3)_2OH$	PPh_3	$C_2H(CO_2Me)_2$		X-ray, MS, IR, NMR (^1H, ^{19}F)	500,501
Ru	C_2CO_2Me	PPh_3	PPh_3	Cl	IR, NMR, MS, X-ray	502
Ru	Menthyl	CO	PPh_3	I	IR, NMR (^1H, ^{13}C, ^{31}P), CD	453(b), (d)
Ru	Menthyl	CO	CO	Cl, Br	IR, MS, CD	453(c)
Ru	Menthyl	CO	PPh_2Me	Cl	IR, MS, CD, NMR (^1H, ^{13}C, ^{31}P)	453(c)
Ru	Menthyl	CO	$PPh_2(CH_2OMe)$	Cl	IR, MS, CD	453(c)
Ru	Menthyl	CO	$P(OPh)_3$	Br	IR, MS, CD	453(c)
Ru	Menthyl	CO	$P(n\text{-}Bu)_3$	Br	IR, MS, CD	453(c)
Ru	Menthyl	CO	PPh_3	Cl	IR, MS, X-ray, CD	453(a)
Ru	Neomenthyl	CO	PPh_3	Me, Br, SO_2Me	IR, NMR (^1H, ^{13}C, ^{31}P), MS, X-ray	453(e)
Ru	Neomenthyl	CO	CO	Cl, Br, I	IR, MS, CD, NMR (^1H, ^{13}C)	453(c)
Ru	Neomenthyl	CO	PPh_3	Cl, Br	IR, MS, CD, NMR (^1H, ^{13}C, ^{31}P)	453(c), (d)
Ru	Neomenthyl	CO	PPh_3	I	IR, MS, X-ray, CD, NMR (^1H, ^{13}C, ^{31}P)	453(c)
Fe	COOH	CO	CO	Ph, CH_2Ph, $C_5H_4Mn(CO)_3$	IR, NMR	145
Fe	CO_2R R = Me, i-Pr, *t*-Bu	CO	PPh_3	H, Me		132

TABLE 22 (*continued*).

M	R	A	B	C	Comments[a]	Ref.
Fe	CO_2R R = 1-menthyl	CO	PPh_3	Me	–	132
Fe	CHO	CO	CO	CH_2Ph	IR, NMR	475
Fe	COCl	CO	CO	CH_2Ph	IR, NMR, MS	475
Fe	COMe	CO	CO	Me	IR, MS	437
Fe	COMe	CO	Me	$P(OMe)_3$	IR, NMR (^1H, ^{13}C), MS	482
Fe	COMe	CO	CO	I	–	480
Fe	COMe	CO	CO	(η^1-C_5H_5)	IR, NMR	480
Ru	COMe	PPh_3	PPh_3	Cl	IR, NMR	454(a)
Ru	COMe	PPh_3	(η^2-L)[g]		IR, NMR	454(a)
Ru	COMe	$P(CH_2CH_2CN)_3$	$P(CH_2CH_2CN)_3$	Cl	IR, NMR	454(b)
Ru	COMe	$Ph_2P(CH_2)_2PPh_2$		Cl	IR, NMR	454(b)
Fe	COPh	CO	Me	PPh_3	–	132
Fe	$COCH_2R$ R = Me, Pr	CO	PPh_3	H, Me	–	132
Fe	$COCH_2CH(Me)Bu$	CO	Me	PPh_3	–	132
Fe	$COCHMe_2$	CO	Me	PPh_3	–	132
Fe	$COCHR^1R^2$ $R^1 = R^2 = H$ $R^1 = H, R^2 = Me$ $R^1 = R^2 = Me$	CO	CO	Me	IR, NMR	479
Fe	$C(OH)RR^1$ $R = R^1 = Ph$ $R = H, R^1 = Ph$	CO	CO	CH_2Ph	IR, NMR	475
Ru	COBu	CO	Me	PPh_3	–	132
Fe	*o*- and *m*-Carboran-9-yl	CO	CO	Br	NMR (^1H, ^{11}B)	109(a)
Fe	*o*-Carboran-3-yl	CO	CO	Br, Cl	NMR, IR	109(b)
Fe	*o*-Carboranyl	CO	CO	Br	NQR	534

Fe	$SiMe_3$	CO	CO	Me, $SbMe_2$ SiMe(H)Cl	IR, NMR	154
Fe	$SiMe_3$	CO	CO	Me, Et, *n*-Bu, CH_2Ph, $CH_2CH{=}CH_2$, $CH_2CMe{=}CH_2$, $SiMe_3$, $SiMe_2Ph$	IR, NMR, MS	156(a)
Fe	$SiMe_3$	CO	CO	Me, Et, *n*-Bu	IR, NMR, MS	483
Fe	$SiMe_3$	CO	PPh_3	COMe, $COCH_2Me$	IR, NMR	483
Fe	$SiMe_3$	CO	CO	$SiPh_2H$, $SiPh_2CPh{=}CH_2$, $SiPh_2$-*trans*-CH=CHPh	IR, NMR (^1H, ^{13}C, ^{29}Si)	486
Ru	$SiMe_3$	CO	CO	Me	IR, NMR (^1H, ^{13}C, ^{29}Si)	485
Fe	$SiMe_3$, $SnMe_3$, Me, Et	CO	CO	Ph	IR, NMR, MS	153
Fe	$SiMe_2Ph$	CO	CO	Me, Et, $SiMe_3$	IR, NMR	156(a)
Fe	$SiMe_2$*n*-Pr	CO	CO	Me, Et	IR, NMR	156(a)
Fe	$SiPh_2H$	CO	CO	Me, $SiMe_3$	IR, NMR (^1H, ^{13}C, ^{29}Si)	486
Fe	$SiPh_2CPh{=}CH_2$	CO	CO	Me, $SiMe_3$	IR, NMR (^1H, ^{13}C, ^{29}Si)	486
Fe	$SiPh_2$-*trans*-CH=CHPh	CO	CO	Me, $SiMe_3$	IR, NMR (^1H, ^{13}C, ^{28}Si)	486
Fe	Si(Me)(Ph)(1-Np)^t	CO	CO	Me	IR, NMR, MS	484
Fe	Various SiX^u	CO	CO	Me	IR, NMR (^{13}C, ^{29}Si)	487
Fe	$SiMe_2CH_2SiMe_3$	CO	CO	Me	IR, NMR (^{13}C, ^{29}Si)	488
Fe	$SiMe_2NMe_2$, $SiMe_2Ni$-Pr_2	CO	CO	Me	IR, NMR	154
Fe	GeR_3 R = Me, Ph	CO	CO	Me	IR, NMR (^1H, ^{13}C)	301
Fe	SnR_3 R = Me, Ph	CO	CO	Me	IR, NMR (^1H, ^{13}C)	301
Fe	NMe_2	CO	Br	$PhP(OEt)_2$	IR, NMR (^1H, ^{31}P)	163
Fe	NEt_2	CO	Br	Various^v	IR, NMR (^1H, ^{31}P), X-ray^v	163,164
Fe	NEt_2	CO	Cl	$PhP(OEt)_2$	IR, NMR (^1H, ^{31}P)	163

TABLE 22 (*continued*).

M	R	A	B	C	Comments[a]	Ref.
Fe	NEt_2	CO	H	Various[w]	IR, NMR (^1H, ^{31}P)	163
Fe	NEt_2	H	$PhP(OEt)_2$	$PhP(OEt)_2$	IR, NMR (^1H, ^{31}P)	163
Fe	NEt_2	CO	$P(OPh)_3$	I	NMR (^1H, ^{13}C), IR	165
Fe	NHPh	CO	$P(OPh)_3$	CR=CHR[x]	NMR (^1H, ^{13}C), IR	165
Fe	NPh_2	CO	$P(OPh)_3$	CMe=CHPh	NMR (^1H, ^{13}C), IR	165
Fe	PPh_2	CO	CO	Me	IR, NMR (^1H, ^{31}P)	286
Fe	$P(O)(OEt)_2$	CO	CO	Me	IR, NMR (^1H, ^{31}P)	489
Fe	$P(O)Ph_2$	CO	Me	$P(OMe)Ph_2$	IR, NMR (^1H, ^{31}P)	489
Fe	$P(O)(OMe)(NEt_2)$	CO	CO	Me	IR, NMR (^1H, ^{31}P)	489
Fe	I	CO	CO	C_3F_7	IR, NMR (^1H, ^{13}C), MS	182(a),456(b)
Fe	I	CO	CO	I	IR, NMR (^1H, ^{13}C), MS	182(a)
Fe	I	CO	CO	Me	IR, NMR, MS	182(a),394
Fe	I	CO	PPh_3	I	IR, NMR, X-ray	443(d)
Fe	Br	CO	CO	Br	IR, NMR, MS	182(a)
Ru	Cl	CO	CO	Cl	IR, NMR	456(a)
Fe	OH	CO	CO	Cl, Br	IR	179(b)
Fe	OEt	CO	CO	Me, Ph	IR, NMR	179(c)
Fe	OMe	CO	CO	Cl	IR	179(b)
Fe	OCOMe	CO	CO	Cl	IR	179(b)
Fe	OCOPh	CO	CO	Cl	IR	179(b)

[a] For abbreviations, see p. 3.

[b] $R = R' = Me$; $R = Me$, $R' = Ph$; $R = CO_2Me$, $R' = Me$.

[c] R = Et, i-Pr.

[d] L = *t*-BuNC, 2,6-$Me_2C_6H_3NC$, PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, $P(OMe)_3$, $P(Oi\text{-}Pr)_3$, $P(OMe)_2Ph$, $P(C_6H_{13})_3$, $P(CH_2C_6H_5)_3$.

[e] L = $P(n\text{-}Bu)_3$, PPh_3, $P(OMe)_3$, $P(Oi\text{-}Pr)_3$, $P(OCH_2)_3CCH_3$, $P(OPh)_3$, $AsPh_3$.

[f] L = $P(OMe)_3$, $P(OPh)_3$.

[g] L = $P(OPh)_3$.

[h] R′ = CH_2Ph, Ph, *p*-Me-Ph, SO_2CH_2Ph, SO_2-*p*-Me-Ph.

[i] L = $P(OMe)_3$, $PMePh_2$, PPh_3, $P(CH_2Ph)_3$, CO.

[j] L = CO, t-BuNC, $P(OMe)_3$, PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, $P(C_6H_{11})_3$.
[k] L = N_3(4-Me-Ph)(4-Cl-Ph).
[l] L = Cl, S_2CCN, S_2COMe.
[m] L = S_2CX, X = OCH_3, OC_2H_5, OC_6H_{11}, $N(C_2H_5)_2$, $N(CH_2)_4$.
[n] L = Phen, 2,9 Me_2-phen, 4,7 Me_2-phen, 5,6 Me_2-phen, 3,4,7,8-Me_4-phen, 4,7 Ph_2-phen, S-NO_2-phen, bipy, 4,4′-Me_2-bipy, phen = 1,10-phenanthroline, bipy = 2,2′-bipyridine.
[o] L = CO, $P(OMe)_3$, $P(OEt)_3$, $P(Oi\text{-}Pr)_3$, PPh_3, PMe_2Ph t-BuNC, 2,6-$Me_2C_6H_3NC$.
[p] L = CO, $P(OMe)_3$, $P(Oi\text{-}Pr)_3$, $P(OCH_2)_3CCH_3$, $P(O\text{-}o\text{-}CH_3C_6H_4)_3$, PPh_3, $P[OCH_2C(CH_3)_3]_3$. The crystal structure was determined for the compound with L = PPh_3.
[q] L = $P(Cy)_3$, $P(OPh)_3$, $P(OEt)_3$, ETPB.
[r] A fulvene–ylide-type ligand.
[s] L = S_2CX, X = OCH_3, OC_2H_5, $N(CH_2)_4$.
[t] 1-Np = 1-naphthyl. The (R)-(−)-stereoisomer of the iron compound was obtained.
[u] SiX = $SiMe_3$, $SiMe_2SiMe_3$, $SiMe_2SiMe_2SiMe_3$, $SiMeSiMe_3$, $SiMe_2SiPh_3$, $SiMe_2GePh_3$.
[v] C = CO, PPh_3, $P(OPh)_3$, $PhP(OEt)_2$ (its crystal structure was determined), $PhP(OMe)_2$, $P(OEt)_3$.
[w] C = CO, $P(OPh)_3$, $PhP(OMe)_2$, $P(OEt)_3$.
[x] R = Me, R′ = Ph; R = CO_2Me, R′ = Me.

TABLE 23

Group 8 metal compounds of the general formula $(\eta^5\text{-}C_5H_4R)M(CO)_2^- M'^+$

M	R	M′	Comments[a]	Ref.
Fe	$SiMe_3$	Li, Na	IR	156(a),483
Fe	$SiMe_2Ph$	Li, Na	IR	156(a)
Fe	$SiMe_2OEt$	K	IR	441
Fe	$-(CH_2)_3Si(OMe)_3$	K	IR	441

[a] For abbreviations, see p. 3.

TABLE 24

Group 8 metal compounds of the general formula $(\eta^5\text{-}C_5H_4R)M(A)(B)(C)(D)^+ M'^-$

M	R	A	B	C	D	M′	Comments[a]	Ref.
Fe	Me	CO	CO	L[b]	–	I	IR, NMR	7
Fe	Me	CO	$P(OCH_2)_3CCH_3$	L[c]	–	BF_4	IR, NMR	530
Fe	Me	CO	CO	CO	–	A[d]	IR, NMR	535
Fe	Me	CO	$SiCl_3$	$SiCl_3$	H	–	IR, NMR	535
Fe	Me, Et	L	L	L[e]	–	PF_6	NMR	439
Fe	$CHPh_2$	CO	CO	CO	–	PF_6	IR, MS	533
Fe	$CHPh_2$	CO	CO	PPh_3	–	Cl, BPh_4	IR, MS	533
Fe	$(CH_2)_3Si(OMe)_3$	CO	CO	PPh_3	–	PF_6	IR, NMR	441
Ru	$CH_2C_4H_3S$	PPh_3	PPh_3	–	–	OTf	NMR	508
Ru	$CH_2C_4H_3S$	PPh_3	PPh_3	H	H	OTf	NMR	508
Ru	$CH_2C_4H_3S$	PPh_3	PPh_3	SH_2	–	BF_4	NMR	508
Fe	Ph	$P(OPh)_3$	$P(OPh)_3$	$P(OPh)_3$	–	I	NMR	493
Ru	Menthyl	CO	PPh_3	NCMe	–	BF_4	IR, NMR (^1H, ^{13}C, ^{31}P), CD	453(b),(d)
Ru	Neomenthyl	CO	PPh_3	NCMe	–	BF_4	IR, NMR (^1H, ^{31}P), CD	453(d)
Ru	Neomenthyl	CO	PPh_3	NCMe	–	PF_6	X-ray	453(d)
Fe	COMe, COPh	$P(OMe)_3$	$P(OMe)_3$	$P(OMe)_3$	–	PF_6	IR, NMR (^1H, ^{13}C)	438
Fe	COMe	$P(OMe)_3$	$P(OMe)_3$	NCMe	–	PF_6	IR, NMR (^1H, ^{13}C, ^{31}P)	438

TABLE 24 (*continued*).

M	R	A	B	C	D	M′	Comments[a]	Ref.
Fe	COPh	$P(OMe)_3$	$P(OMe)_3$	NCMe	–	PF_6	IR, NMR	438
Fe	COMe	$Ph_2P(CH_2)_2PPh_2$		NCMe	–	PF_6	IR, NMR (^1H, ^{13}C), X-ray	438,504
Fe	COPh	$Ph_2P(CH_2)_2PPh_2$		NCMe	–	PF_6	IR, NMR (^1H, ^{13}C)	438
Fe	COMe, COPh	CO	$P(OMe)_3$	$P(OMe)_3$	–	PF_6	IR, NMR	438
Fe	COMe	$Ph_2P(CH_2)_2PPh_2$		CO	–	PF_6	IR, NMR	438
Fe	COMe	L	L	L[e]	–	PF_6	NMR	439
Fe	CO_2R[e]	L	L	L[e]	–	PF_6	NMR	439
Fe	Cl	L	L	L[e]	–	PF_6	NMR	439
Fe	OEt	CO	CO	–	–	BF_4	IR, NMR	179(c)
Fe	$SiMe_3$	CO	CO	η^2-L[f]	–	PF_6	IR, NMR	156(a)
Fe	$SiMe_3$	CO	CO	η^2-CH_2=CH_2	–	BF_4	IR, NMR	483
Fe	$SiMe_2Ph$, $SiMe_2$*n*-Pr	CO	CO	η^2-CH_2=CH_2	–	BF_4	IR, NMR	156(a)
Fe	$SiMe_2OEt$	CO	CO	PPh_3	–	PF_6	IR, NMR	441

[a] For abbreviations, see p. 3.

[b] $L = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3, $P(C_6H_{11})_3$.

[c] $L = \eta^2\text{-}CH_2 = CMe_2$; *cis*-$\eta^2$-$CH_3CH$=$CHCH_2CH_3$.

[d] An $A\text{–}C^+$ complex where $A = (\eta^5\text{-}C_5H_4Me)Fe(CO)(SiCl_3)_2$ and $C = (\eta^5\text{-}C_5H_4Me)Fe(CO)_3$.

[e] $L = P(OR)_3$, R = Me, Et, Ph.

[f] $L = CH_2 = C(Me)R$; R = H, Me.

TABLE 25

Group 8 metal compounds of the general formula $(\eta^{5:1}\text{-}C_5H_4R)M(CO)_2$

M	R	Comments[a]	Ref.
Ru	$-CMe_2\overline{CHCH\underset{|}{C}HCHC}(CMe_2)$	X-ray, IR, NMR	462
Fe	$-CEt_2\overline{C(CH)_3C}CEt_2-$	IR, NMR	459
Fe	$\{(CR_2C_5H_4CR_2)Fe(CO)_3\}$		
	$R = Me$	X-ray, IR, NMR	459, 467
	$R = H$	X-ray, IR, NMR	398
Fe	$-CR'R^2CH_2CO-$	–	97
	$R' = R^2 = H$		
	$R' = H$; $R^2 = Me$		
	$R' = R^2 = Me$		
Fe	$-(CH_2)_4-$	IR, UV, NMR	122a,472
Fe	$-(CH_2)_2CO-$	IR, UV, NMR	122(a)
Fe	$-CMe_2CH_2-$	NMR, MS	122(c)
Fe	$-CH_2CMe_2CO-$	NMR, IR, MS	122(c)
Fe	$-CMe_2CH_2CO-$	NMR, IR, MS	122(c)
Fe	$-(CMe_2)_2-$	NMR, IR, MS	122(c)
Fe	$-(CMe_2)_2CO-$	NMR, IR, MS	122(c)
Fe	$-(CHMe)_2-$ (E- and Z-)	NMR, IR, MS	122(c)
Fe	$-(CHMe)_2CO-$ (E- and Z-)	NMR, IR, MS	122(c)
Fe	$\{(\eta^4\text{-}\underset{|}{C}_6H_6\underset{|}{C}O)Fe(CO)_3\}$	IR, NMR, X-ray	123(a)
Fe	$-C_6H_4CO-$	IR, NMR	123(a)
Fe	$\{(\eta^4\text{-}\underset{|}{C}_6H_4Me_2\underset{|}{C}O)Fe(CO)_3\}$	IR, NMR, MS	123(a)
Fe	$-CH(CH_3)CH_2CO-$	IR, NMR, UV, MS	471(d)
Fe	$-CH_2CH(CH_3)CO-$	IR, NMR, UV, MS	471(d)
Fe	$-CH(CH_3)CH_2-$	IR, NMR, UV, MS	471(d)
Fe	$-CH_2CH(CH_3)-$	IR, NMR, UV, MS	471(d)
Fe	$-CH_2C(=CHCH_3)CO-$	IR, NMR, UV, MS	471(d)
Fe	$-COC_6H_4CH_2-$	X-ray, NMR, IR, MS	506
Fe	$-CO(C_6H_3Me)CH_2-$[b]	NMR, IR, MS	506
Fe	$-CH_2C_6H_4-$	IR, UV-VIS, NMR (^1H, ^{13}C), X-ray	509
Fe	$-CEt_2-\underset{|}{C}_5H_4-CEtCHMe$	X-ray, IR, NMR	398

[a] For abbreviations, see p. 3.

[b] Two isomers of this compound were obtained; the difference lay in the substitution pattern of the phenyl ring.

TABLE 26

A Group 8 metal compounds of the general formula $(\eta^{5:1}\text{-}C_5H_4R)ML^1L^2$

M	R	L^1	L^2	Comments[a]	Ref.
Ru	$-C_6H_4PPh_2-$	$-N(C_6F_5)N(C_6F_4)-$		X-ray, NMR (^{1}H, ^{19}F)	497,498
Ru	$-(CH_2)_2PPh_2-$	PPh_3	Cl	NMR (^{1}H, ^{13}C, ^{31}P, VT), X-ray, MS	507
Ru	$-(CH_2)_2PPh_2-$	$P(OMe)_3$	Cl	NMR (^{1}H, ^{13}C, ^{31}P), MS	507
Fe	$-C_6H_4OP(OPh)_2-$	$P(OPh)_3$	I	X-ray, NMR	499
Fe	$-CH_2C_6H_4-$	CO	PPh_3	IR	509

B Group 8 metal complexes containing cyclopentadienyl chelate ligands

Complex	Comments[a]	Ref.
$(\eta^{5:1:1}\text{-}C_5H_4(CH_2)_2PPh(CH_2)_nPPh_2)RuCl$ $n = 3, 4$	NMR	510(b)
$(\eta^{5:1:1}\text{-}C_5H_4(CH_2)_2AsPh(CH_2)_3AsPh_2)MCl$ M = Fe, Ru	–	510(a)
$(\eta^{5:1:1}\text{-}C_5H_4(CH_2)_2AsPh(CH_2)_3SPh)RuCl$	–	510(a)

TABLE 27

Group 8 metal compounds of the general formula $[(\eta^{5:1}\text{-}C_5H_4R)ML^1L^2]^+M^{1-}$

M	R	L^1	L^2	M^1	Comments[a]	Ref.
Ru	$-CH_2C_4H_3S-$	PPh_3	PPh_3	BPh_4, BF_4, OTf	X-ray, NMR (^1H, ^{31}P, ^{13}C)	455,508
Ru	$-(CH_2)_2PPh_2$	PPh_3	$(+)\text{-}NH_2CHMePh$[b]	BF_4	NMR (^1H, ^{13}C, ^{31}P), MS	507

[a] For abbreviations, see p. 3.

[b] Diastereomeric mixture of this compound was obtained.

TABLE 28

Group 8 metal dimers of the general formula $(\eta^5\text{-}C_5H_4R)M_2(CO)_4(\eta^5\text{-}C_5H_4R')$

M	R	R′	Comments[a]	Ref.
Fe	D	H	IR, NMR, MS	153
Fe	CH_2D	R	NMR	103
Fe	Me	R	IR, NMR (^1H, ^{13}C)	104,465,522,525
Ru	Me	R	IR, NMR (^1H, ^{13}C)	525
Fe	Et	R	IR	123(b),469
Fe	$CHMe_2$	R	IR, NMR	443(d),460(a)
Fe	CHMeEt	R	IR	469
Fe	CHMePh	R	IR, NMR (^1H, ^{13}C), MS	444,469
Fe	$CHPh_2$	R	IR, NMR	443(d),457,460
Fe	*t*-Bu	R	IR, MS, NMR	443(a)
Fe	Cyclohexyl	R	IR	457
Fe	$(CH_2)_3Si(OMe)_3$	R	IR, NMR (^1H, ^{13}C)	441
Fe	Ph	R	NMR, IR	81,123(a)
Fe	CH_2Ph	R	IR, NMR, UV-VIS	81,495,496,509
Fe	C(Et)(CHMe)	R	IR, NMR	459
Ru	$-\overline{C=CH(CH_2)_3C}H_2$	R	IR, NMR	462
Ru	Menthyl, neomenthyl	R	IR, MS, CD, NMR (^1H, ^{13}C)	453(c)
Fe	COMe	H	IR, NMR	480,524
Fe	COMe	R	IR, NMR, MS	437,524
Fe	CO_2Me	R	Catalytic use	522
Fe	$SiMe_3$	H	IR, NMR, MS	154,156(a)
Fe	$SiMe_3$	R	NMR, MS	156(a),440
Fe	$SiMe_2Ph$	R	NMR	156(a)
Fe	$SiMe_2NMe_2$	R	IR, NMR	154
Fe	$SiMe_2OEt$	R	IR, NMR (^1H, ^{13}C)	441
Fe	$Si(Me)(CH_2)_3$	R	–	442
Fe	I	R	IR, NMR (^1H, ^{13}C), MS	182(a)
Fe	NEt_2	H	IR, NMR	163
Fe	$BPh_3^-NBu_4^+$	H	IR, NMR, X-ray	110(c)
Fe	OMe	R	Catalytic use	522(d)
Fe	$O(CH_2)_4OH$	R	Catalytic use	522(d)
Fe	OEt	R	IR, NMR	504

[a] For abbreviations, see p. 3.

TABLE 29

Various Group 8 metal dimers

Formula	Comments[a]	Ref.
$[(\eta^5\text{-}C_5H_4R)Fe(R'NC)_2]_2$[b]	IR, NMR	522(b)
$[(\eta^5\text{-}C_5H_4Me)FeS_2]_2CO$	MS, IR, NMR (^1H, ^{13}C), X-ray	505
$[(\eta^5\text{-}C_5H_4R)Fe(CO)_2CHR'CO]_2O$[c]	IR, NMR (^1H, ^{13}C)	103
$[(\eta^5\text{-}C_5H_4BPh_3)Fe_2(CO)_4(\eta^5\text{-}C_5H_5)]^-NEt_4^+$	IR, NMR, X-ray	110(c)

[a] For abbreviations, see p. 3.

[b] $R = Me$, CO_2Me, $R' = 2,6\text{-}Me_2C_6H_3$, $R = Me$, $R' = C_6H_5$.

[c] $R, R' = H, D$.

TABLE 30

Group 8 linked cyclopentadienyl metal dimers of the general formula $\{(\eta^5\text{-}C_5H_4CRR')_2M_2(CO)_4\}$

M	R	R′	Comments[a]	Ref.
Fe	H	NMe_2	X-ray, IR, NMR	57(a),460
Ru	H	$-CH{=}CHCH_3$	IR, NMR, MS	469
Fe[b]	Me	Me	IR, NMR	461
Fe	Me	Me	IR	457

[a] For abbrevations, see p. 3.

[b] A derivative where one of the CO ligands was replaced by $P(OPh)_3$ was also prepared.

TABLE 31

Group 8 metal dimers of the general formula $(\eta^{5:3}\text{-}C_5H_4R)M_2(CO)_5$

M	R	Comments[a]	Ref.
Fe	$-CPh_2$	X-ray	459,467
Ru	$-CPh_2$	X-ray, IR, NMR	457,462
Ru	$-C(Et)(CHCH_2)$	NMR, IR	462(b)
Fe	$-CHCHCHMe$	IR, NMR (^1H, ^{13}C), MS	469
Ru	$-CHCHCHMe$	IR, NMR, MS	469
Fe	$-\mathrm{CH}\overline{\mathrm{CC(CHNMe_2)CHCHC}}\mathrm{H}$	X-ray, IR, NMR	459,468

[a] For abbreviations, see p. 3.

TABLE 32

Group 8 metal dimers of the general formula $[(\eta^{5:1}\text{-}C_5H_4R\text{-})M_2(CO)_6]$

M	R	Comments[a]	Ref.
Fe	$-CHEtCH_2-$	NMR, IR, MS	122(c)
Fe	$-(CH_2)_2-$	NMR, IR, MS, UV	471(b),(d)
Fe	$-CH_2C(=CHCH_3)-$	NMR, IR, MS, UV	471(d)

[a] For abbreviations, see p. 3.

TABLE 33

Group 8 metal dimers of the general formula $[(\eta^{5:1}\text{-}C_5H_4CRR')M_2(CO)_5L]$

M	R	R′	L	Comments[a]	Ref.
Fe	H	H	CO	IR, X-ray	104,466,470
Fe	D	H, D	CO	IR, NMR, MS	103
Fe	H	Me	CO	IR, NMR, MS, UV	471(d)
Fe	H	Et	CO	IR, NMR, MS, UV	471(d)
Fe	H	Pr^n	CO	IR, NMR, MS, UV	469,471(b),(c)
Fe	H	OMe	CO	IR, NMR, MS	58
Fe	Me	Me	CO	IR, NMR, MS, UV	457,471(d)
Fe	Me	Et	CO	IR, NMR, MS	122(c)
Fe	$RR' = -CH_2(CH_2)_3CH_2-$		CO	IR	457
Fe	$CRR' = C{=}CH_2$		CO	NMR, MS, IR	465
Ru	Ph	Ph	Various[b]	IR, NMR (^1H, ^{13}C, ^{31}P), X-ray	463

[a] For abbreviations, see p. 3.

[b] $L = CO$, PMe_3, PPh_3, $P(c\text{-}C_6H_{11})_3$, $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, $SbPh_3$, $P(OEt)_3$. The crystal structure was determined for the complex containing $L = SbPh_3$.

TABLE 34

Group 8 bridging cyclopentadienyl bimetallic complexes of the general formula $L_mM(\eta^{5:1}C_5H_4R\text{-})M'L_n$

ML_m	R	$M'L_n$	Comments[a]	Ref.
$Fe(CO)_2Me$	PPh_2	$(\eta^5\text{-}C_5H_5)W(CO)_2X$ $X = H, CO, Me, Cl, COMe$	IR, NMR (^1H, ^{31}P), X-ray	286
$Ru_2(CO)_4C(\eta^5\text{-}C_5H_5)$	PPh_2	$M(CO)_5$ $M = Mo, W$	IR, NMR (^1H, ^{31}P), MS, X-ray	521
$Ru(CO)_2$	$(CH_2)_2$	$(\eta^5\text{-}C_5H_5)_2Zr$	NMR	518
$Ru(CO)_2H$	$(CH_2)_2$	$(\eta^5\text{-}C_5H_5)_2ZrOC(CH_3)_3$	NMR	518

[a] For abbreviations see p. 3.

TABLE 35

Group 8 bimetallic complexes of the general formula $M'L_n(\eta^1,\eta^5\text{-}C_5H_4)ML_m$

ML_m	$M'L_n$	Comments[a]	Ref.
$Fe(CO)_2R$ $R = Me, CH_2Ph$	$(\eta^5\text{-}C_5H_5)Fe(CO)_2$	–	477
$Fe(CO)_2I$	$(\eta^5\text{-}C_5H_5)Fe(CO)_2$	X-ray	477
$Fe(CO)_2(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_3$	$(\eta^5\text{-}C_5H_5)Fe(CO)_2$	X-ray	477
$Fe(CO)_2R$ $R = Me, CH_2Ph$	$(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2$	–	477
$Fe(CO)_2$	$(\eta^5\text{-}C_5H_5)_2NbH$	X-ray	517
$Fe(CO)_2Me$	$(\eta^5\text{-}C_5H_5)Fe(CO)_2$	X-ray	476
$Ru(CO)(PMe_3)$	$(\eta^5\text{-}C_5H_5)_2Zr(CO)$	X-ray	518
$Ru(CO)_2$	$(\eta^5\text{-}C_5H_5)_2Zr(CO)$	X-ray	518
$[(\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$		X-ray	513

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[a] For abbreviations see p. 3.

TABLE 36

Group 8 linked cyclopentadienyl metal complexes of the general formula $[\{(\eta^5\text{-}C_5H_4)_2X\}M^1M^2L_m]C$

X	$M^1M^2L_m$	C	Comments[a]	Ref.
$SiMe_2$	$[Fe(CO)_2]_2$	–	IR, NMR, MS, X-ray	391(a)
	$[Fe(CO)_2Me]_2$	–	IR, NMR	391(a)
	$[Fe(CO)_2]_2(CH_2)_5$	–	IR, NMR	391(a)
$-(SiMe_2(2,4B_5H_5C_2)SiMe_2)-$				
	$[Fe(CO)_2]_2$	–	IR, NMR, MS	391(a)
	$[Fe(CO)_2Me]_2$	–	IR, NMR	391(a)
$SiMe_2$	$[Fe(CO)_2R]_2$			
	$R=CH_2Ph$		IR, NMR (^1H, ^{13}C)	446
	$R=CD_2C_6D_5$		IR, NMR (^1H, ^{13}C)	446
	$R=COCHPh_2$		IR, NMR (^1H, ^{13}C)	446
	$R=CO(m\text{-}OMeC_6H_4)$		IR, NMR (^1H, ^{13}C)	446
$SiMe_2$	$Fe_2(CO)_2(PPh_2)_2R$			
	$R=CH_2, (CH_2)_2$		IR, NMR (^1H, ^{13}C), X-ray ($R=CH_2$)	445,449
	$R=(CH_2)_3$		IR, NMR (^1H, ^{13}C)	449
$SiMe_2$	[b]		IR, NMR (^1H, ^{13}C)	445,449
$SiMe_2$	$[Fe(CO)(L)I]_2$		IR, NMR (^1H, ^{13}C, ^{31}P)	448
	$L=PPh_3, P(OPh)_3$			
$SiMe_2$	$[Fe(CO)_2(n\text{-}C_5H_{11})]_2$		IR, NMR (^1H, ^{13}C)	511
CH_2	$[Fe(CO)_2]_2$, $[Ru(CO)_2]_2$		IR, NMR	451
	$[Fe(CO)_2Br]_2$, $[Fe(CO)_2^-]_2$, $[Fe(CO)_2Me]_2$		IR, NMR	451
	$[Ru(CO)_2Cl]_2$, $[Ru(CO)_2^-]_2$, $[Ru(CO)_2Me]_2$		IR, NMR	451

TABLE 36 (*continued*).

X	$M^1M^2L_m$	C	Comments[a]	Ref.
$(SiRR'O)_nSiRR'$[c]	$[Fe(CO)_2]_2$	–	IR, NMR (^1H, ^{13}C)	452
	$[Fe(CO)_2PPh_3]_2$	$[PF_6]_2$	IR, NMR (^1H, ^{13}C)	452
	$[Fe(CO)_2]_2$	K_2	IR, NMR (^1H, ^{13}C)	452
$-SiMe_2(CH_2)_2SiMe_2-$	$[Fe(CO)_2]_2$	–	IR, NMR (^1H, ^{13}C)	512
	$[Fe(CO)_2I]_2$	–	IR, NMR (^1H, ^{13}C)	512
	$[Fe(CO)_2Me]_2$	–	IR, NMR (^1H, ^{13}C)	512
	$[Fe(CO)(PPh_3)I]_2$	–	IR, NMR (^1H, ^{13}C, ^{31}P)	512
$SiMe_2$	$[Fe(CO)_2(\eta^1\text{-}CH_2CR=CH_2)]_2$ $R=H$, Me	–	IR, NMR	450
	$[Fe(CO)_2(\eta^2\text{-}CH_2CR=CH_2)]_2$ $R=H$, Me	$(BF_4)_2$	IR, NMR (^1H, ^{13}C)	450
	$[Fe(CO)_2I]_2$	–	IR, NMR (^1H, ^{13}C)	450
	$[Fe(CO)_2IFe(CO)_2]$	BF_4	IR, NMR (^1H, ^{13}C)	450
$SiMe_2$	$[Fe(CO)LI]_2$ $L=PPh_3$, $P(OPh)_3$	–	IR, NMR	447
	$[Fe(CO)P(OPh)_3]_2$		IR, NMR	447
	$[Fe(CO)P(OPh)_3(\eta^1\text{-}C_4H_9)]_2$		IR, NMR	447
	$[Fe(CO)(PPh_3)(\eta^1\text{-}C_4H_9)]_2$		IR, NMR	447
	$[Fe(CO)_2Fe(CO)(PPh_3)]$		IR, NMR	447
	$[Fe(CO)(PPh_3)IFe(CO)(PPh_3)(\eta^1\text{-}C_4H_9)]$		IR, NMR	447
$C\equiv C$	$Fe(CO)_2MeM(CO)_3Me$ $M=Mo$, W	–	IR, NMR (^1H, ^{13}C)	394
$C\equiv C$	$Fe(CO)_2MeM(CO)_3$ $M=Mn$, Re	–	IR, NMR (^1H, ^{13}C), X-ray	394

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[a] For abbreviations see p. 3.

[b] The complex is $[\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}Fe_2(CO)_3]_2(PPh_2(CH_2)_nPPh_2)$ $n=2$, 3.

[c] $R=R'=Me$, $n=1$, 2; $R=Me$, $R'=Ph$, $n=1$.

TABLE 37

Group 8 metal fulvalene complexes of the general formula $[(\eta^5{:}\eta^5\text{-}C_{10}H_8)MM'L_n]C$

$MM'L_n$	C	Comments[a]	Ref.
$Ru_2(CO)_4$	–	UV-VIS, NMR, IR, MS, X-ray	513
$Ru_2(CO)_3L$	–	–	514
L = PMe_3, PEt_3			
$MoRu(CO)_5$	–	UV-VIS, NMR, IR, MS	513
$Fe_2(P{-}P)_2(L)_2]^{2+}$	$(PF_6^-)_2$	IR, NMR (^1H, ^{31}P)	515
P–P = dppe, L = $NCCH_3$, CO			
P–P = dppm, L = $NCCH_3$			
$[Fe_2(dppm)_2(CO)_2]^{2+}$	$(PF_6^-)_2$	IR, NMR (^1H, ^{31}P), X-ray	515
$[Fe_2(dppe)_2(PMe_3)_2]^{2+}$	$(PF_6^-)_2$	NMR (^1H, ^{13}C)	515
$[Fe_2(dppe)_2(PMe_3)_2]^{3+}$	$(PF_6^-)_2(SbCl_6^-)$	Mössbauer	515
$Ru_2(CO)_2(\mu\text{-}\eta^2\text{-}C_2H_2)$	–	X-ray, IR, NMR, MS	380
$Ru(CO)_2Mo(O)(\eta^2\text{-}C_2Ph_2)$	–	X-ray, IR, NMR, MS	380
$M(CO)_3Ru(CO)(PMe_3)_2$	–	–	387
M = Cr, Mo, W			
$Fe(CO)_2{}^-Ru(CO)(PMe_3)_2^+$	–	–	387
$Mo(CO)_2L{-}M(CO)_2$	–	–	387
M = Fe, Ru; L = CO, PMe_3			
$Ru_2(CO)_4$	–	Electrochemistry	403
$MoRu(CO)_5$	–	Electrochemistry	403

[a] For abbreviations, see p. 3.

TABLE 38

Group 8 metal cluster complexes

Complex	Comments[a]	Ref.
$[Rh\{(\eta^5\text{-}C_5H_4Me)Fe(PPh_2)(CO)_2\}_2]^+PF_6^-$	X-ray	529(a), (b)
$[Fe_4(\eta^5\text{-}C_5H_4Me)_4(\mu^3\text{-}S)_4][Fe_4(NO)_4(\mu^3\text{-}S)_4]$	–	337(a)
$[Fe_4(\eta^5\text{-}C_5H_4Me)_4(\mu^3\text{-}S)_4][TCNQ]$	–	337(a)
$\{SiMe_2[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2(CH_2)_5\}_2$	–	511
$RSi[(\eta^5\text{-}C_5H_4)Fe(CO)_2R']_3$	IR, NMR (^1H, ^{13}C), X-ray	404
R = Me, R′ = Me, Et, CH_2Ph		
R = $(CH_2)_3Cl$, R′ = Me		
R = $(CH_2)_2C_6H_4CH_2Cl$, R′ = Me		

[a] For abbreviations see p. 3.

TABLE 39

Group 8 metal polystyrene-bound complexes

Complex	Comments[a,b]	Ref.
PS–CH_2–$C_5H_4Fe(CO)_2H$	IR	523(a),(b)
PS–$CH_2(C_5H_4M(CO)_xL_y)_z$ M = Fe, Ru, $x = 1$, 3, L = phosphine, phosphite, NO, $SnCl_3$, allyl, halo, H; $y = 0$–2, $z = 1$–4	–	523(b)

[a] For abbreviations see p. 3.
[b] PS = polystyrene divinylbenzene.

(vi) Cobalt, rhodium, and iridium [536–612] (Tables 40–46, pp. 192–204)

Synthetic routes to complexes of the type (η^5-C_5H_4R)$M(CO)_2$ and (η^5-C_5H_4R)M(diene) (M = Co, Rh) have been well developed and consequently many complexes of this type have been prepared In particular, the Rausch and Bonnemann groups have carried out extensive studies on the synthesis of the Co and Rh complexes and have investigated their use in both the synthesis of metallo-polymers and the catalytic synthesis of substituted pyridines, respectively. Wakatsuki, Yamazaki and their co-workers have also carried out extensive studies on the reaction of Co complexes with acetylenes to produce Co metallocycles. Correlation between the ring substituents and the chemical properties of the complexes have also been investigated by the above authors, as well as by Arthurs and co-workers, on the related (η^5-C_5H_4R)Rh(diene) complexes. The above studies, plus many others, described below, have thus provided much valuable information on the influence of the η^5-C_5H_4R ring on the chemistry and catalytic properties of these transition metal complexes. Because the metal atom is relatively sterically unencumbered in (η^5-C_5H_4R)ML_2 complexes, electronic rather than steric effects associated with the ligand can be expected to dominate in studies using these complexes.

(a) (η^5-C_5H_4R)M(I) complexes (Tables 40–43)

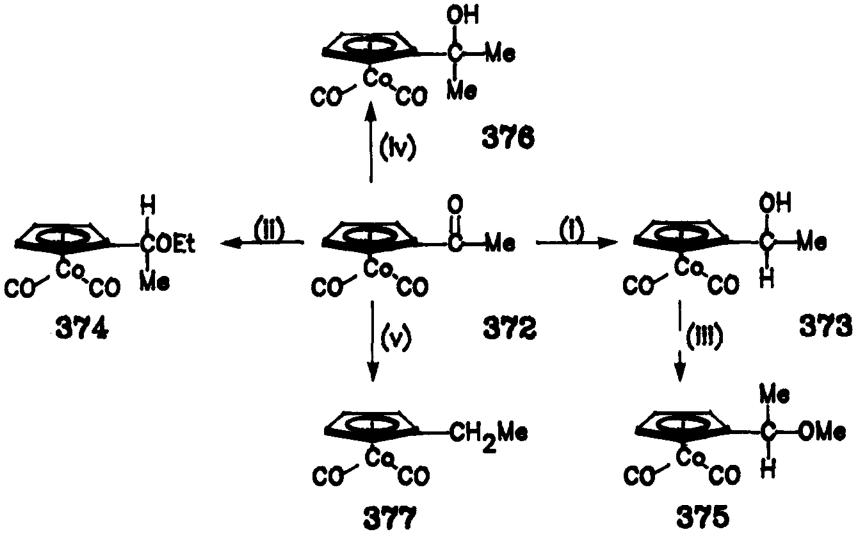
Facile synthetic routes to (η^5-C_5H_4R)ML_2 complexes are available; in particular with L = CO, PR_3, olefin or L_2 = diene. Routes to the η^5-C_5H_4R ligand include starting from $C_5H_4R^-$ salts or fulvenes [16].

Rausch and co-workers (and others) have developed efficient syntheses of a series of $C_5H_4R^-$ salts, where R = CHO [134(a),536(a)], COMe [134(a),536(a)], COOMe [134(a),536(b)], COOEt [287,536(b)], BMe_2·py [108], CR′=CH_2 (R′ = H, Me) [53,69], Ph [81], CH_2Ph [81], X [80], NO_2 [157(b)], etc. In many instances, stable Tl salts have been prepared and have been characterised. Reaction of the above salts with $Co_2(CO)_8$, $[Rh(CO)_2Cl]_2$ or $Ir(CO)_3Cl$ readily gives the complexes (η^5-C_5H_4R)$M(CO)_2$ (**371**).

371

An alternative, and preferable, methodology for synthesising the Co complexes, is to add I_2 to the $Co_2(CO)_8$ substrate to give "$Co(CO)_4I$". This reagent readily reacts with $C_5H_4R^-$ salts to give the "(η^5-C_5H_4R)Co"-containing complex [536(b)].

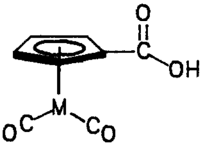
Modification of the ring substituent on the Co complexes by standard procedures has given rise to a range of new (η^5-C_5H_4R)$Co(CO)_2$ complexes [289,536]. For example, reactions of **372** to give **373**–**377** are shown.



Reactions of (η^5-C_5H_4COMe)$Co(CO)_2$ (i) $NaBH_4/MeOH$
(ii) $NaBH_4/EtOH/HCl$
(iii) p-$CH_3C_6H_4SO_3H$
(iv) MeMgBr
(v) $LiAlH_4/AlCl_3$

The synthesis of (η^5-C_5H_4X)ML_2 (X = Cl, Br, I) has been achieved by two routes. The first involves reaction of diazocyclopentadiene with $[RhCl(COD)]_2$ to give (η^5-C_5H_4Cl)Rh(COD) [181]. A more facile procedure involves the reaction of $Tl[C_5H_4X]$ with the requisite metal carbonyl complex, and this procedure gives (η^5-C_5H_4X)$Co(CO)_2$ (X = Cl, Br, I) and (η^5-C_5H_4Cl)$Rh(CO)_2$ in good yield [564(b)]. Not unexpectedly, addition of (η^5-C_5H_4Br)$Co(CO)_2$ to *n*-BuLi (− 78°C) gave (η^5-C_5H_4Li)-

$Co(CO)_2$. Reaction of the Li salt with CO_2 gave the acid (**378**, M = Co), while reaction with acetone gave the alcohol (**379**) [80].



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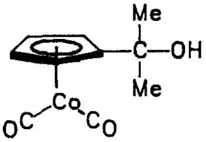
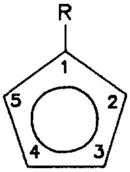


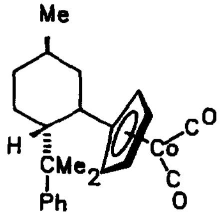
379

Reaction of dienes with $[RhCl(C_2H_4)]_2$ followed by reaction of the new dimers with $Tl[C_5H_4R]$ salts yields the (η^5-C_5H_4R)Rh(diene) complexes. A comprehensive NMR (^{13}C, ^1H) study of these (η^5-C_5H_4R)Rh(diene) complexes has been undertaken, mainly by Arthurs et al. [136,537]. The study, which has been supported by theoretical calculations and X-ray crystallography, has provided information on an unsymmetrical binding of the ring to the Rh atom. The degree of asymmetry is governed by both the ring substituent and the diene. Although ^{13}C NMR spectroscopy has been used to assess ring slippage in related indenyl complexes [538] (in particular the downfield shift of the ring junction C atoms correlate with σ/π ligand properties [539]), a related correlation with η^5-C_5H_4R ligands has not been detected. On lowering the temperature, resonances in the NMR spectrum assigned to C(1), C(2) and C(5) (numbering system shown in **380** move slightly upfield while resonances associated with C(3) and C(4) move rapidly downfield, a result said to be consistent with increased bond localisation. It has been suggested that the small ring slippage predicted for the Rh complexes may be detected by $^1J(^{13}C-^1H)$ coupling constants. The small changes observed for the coupling constants [537(c)] are in keeping with a diolefin rotamer being present in solution. Chiral cyclopentadienyl ligands have been synthesised but only one example of a (η^5-C_5H_4R)ML_2 (R = chiral group) is presently known (**381**) [117]. The use of **381** as a diastereoselective catalyst in alkene cyclisation reactions was reported, but only modest stereoselective effects were observed.



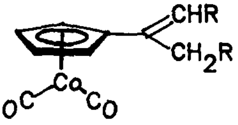
380

Fulvenes have also been reacted with Co, Rh and Ir complexes, to give (η^5-C_5H_4R)ML_2, as well as other related products. These products are dependent on M, L and the fulvene [69,126,540]. Reaction of $Co_2(CO)_8$ with 6,6-dimethylfulvene gave two expected, but non-separable compounds (**382**,**383**) (R = H) [126] resulting



381

from hydride abstraction. (A better route to the separate complexes has since been developed [69].)



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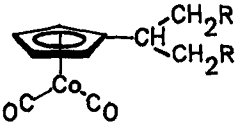

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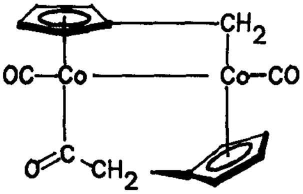
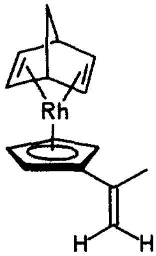


384

Reaction of $Co_2(CO)_8$ with the parent fulvene gave the unexpected dimer (**384**) [540(e)], which was characterised by NMR spectroscopy and X-ray crystallography.

The reaction between dialkylfulvenes and $[Rh(CO)_2Cl]_2$ did not give the cyclopentadienyl complex, but rather a fulvene polymer [126]. However, it was later reported that reaction between MeLi and the dimethylfulvene with $[Rh(NBD)Cl]_2$ or $Rh(COD)Cl(PMe_3)$ gave the complexes, containing a substituted cyclopentadienyl ring, **385–387** [540(a)].

Changing the fulvene substituents also had a major impact on the reaction products. Initially, reaction of 6,6-diarylfulvenes with $[Rh(CO)_2Cl]_2$ was suggested to give **388**, i.e. with Rh coordinated to the exocyclic double bond [126]. However, later NMR studies (^{13}C and J(Rh–C) coupling constant values) supported an alternative structure **389** [540(b)]. Reaction with $Rh[P(OPh)_3]_2^+$ (prepared in situ from $RhCl[P(OPh)_3]_2$) or $[Rh(COD)Cl]_2$ gave **390** [540(b)]. An unsual complex (**391**) related to **390**, has been reported in the patent literature [541].



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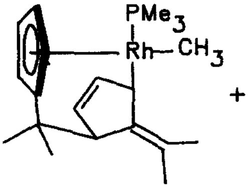

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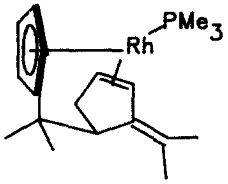

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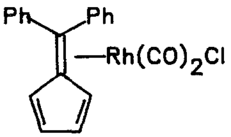

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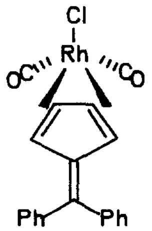

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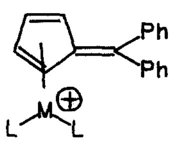
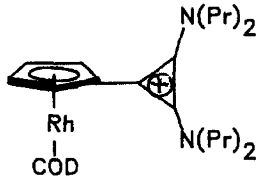


Ph = $C_6H_5, C_6H_4Cl\text{-}p$
L = $P(OPh)_3$, 1/2COD
M = Rh, Ir

390

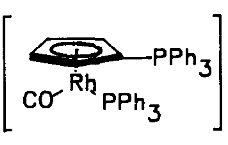


391

Behrens and co-workers have since reacted $CoCl_2$ and i-PrMgBr with the diphenylfulvene and this yielded a cobaltocene complex [540(e)].

There has also been a report of the reaction of $[Ir(COD)Cl]_2$ with i-PrMgBr or MeLi and dimethy or diethylfulvene in which a series of expected $(\eta^5\text{-}C_5H_4R)$-Ir(COD) complexes were formed [540(d)].

Triphenylphosphonium cyclopentadienide has been reacted with both Rh and Co complexes to give $(\eta^5\text{-}C_5H_4PPh_3)ML_2^+$ [176,177,542,543]. X-Ray structures of $(\eta^5\text{-}C_5H_4PPh_3)M(COD)^+$ (M = Rh, Co) have been presented [176,542,543] and, although the metals show coordination to all C ring atoms, the C–C bond lengths are all similar to those reported in the uncomplexed ylide [544]. Reaction of $(\eta^5\text{-}C_5H_4PPh_3)Rh(CO)_2^+$ with a series of Group 15 donor ligands has yielded the substituted products (**392,393**) [177]. The use of the $\eta^5\text{-}C_5H_4PPh_3$ ligand in Co and Rh complexes has also been mentioned in other studies (Table 40).



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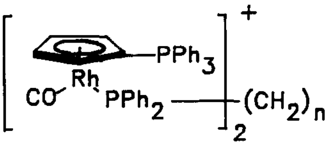
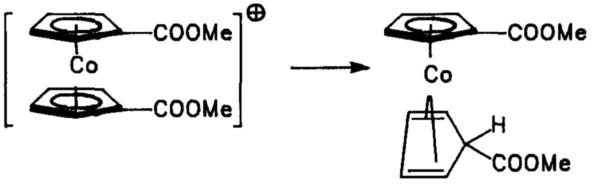


393 (n = 1,4)

The chemistry of $(\eta^5\text{-}C_5H_5)_2Co^+$ and $(\eta^5\text{-}C_5H_5)$Co(cyclobutadiene) has been well documented and classical substitution reactions of the cyclopentadienyl ring on both complexes have been reported [545]. Much of this chemistry lies outside the scope of this review. However, nucleophilic addition (e.g. H^-) to the cyclopentadienyl ring of $(\eta^5\text{-}C_5H_4COOMe)_2Co^+$ permits the synthesis of $(\eta^5\text{-}C_5H_4R)$Co(diene)-complexes [546,547], e.g.

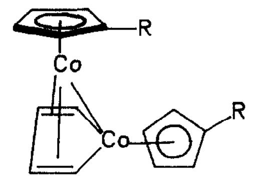


394

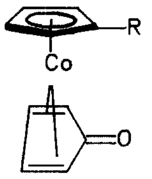
Alternative procedures, such as electrochemical techniques, to convert a cyclopentadienyl ligand to a diene, should also generate related complexes [547(b)]. Electrochemical reduction of $(\eta^5\text{-}C_5H_4R)M(\eta^6\text{-}C_6H_5R)$ provides yet another route to diene complexes, and this procedure has been shown to occur for $(\eta^5\text{-}C_5Me_5)Rh\text{-}(\eta^6\text{-}C_6Me_6)$ [548]. The reaction involves an $\eta^6\text{–}\eta^4$ ring slip of the arene ring, similar to the $\eta^5\text{–}\eta^3$ ring slip of the related cyclopentadienyl ring [2].

$(\eta^5\text{-}C_5H_4R)Co(\eta^4\text{-}C_4H_4)$ (R = COOMe) can be synthesised by reaction of $(\eta^5\text{-}C_5H_4R)Co(CO)_2$ and photo-α-pyrone [549(b)]. This reaction also generates an unusual mixed metal–metal bonded Co(I)/Co(III) dimer (**395**) which was characterised by IR, UV/vis and NMR spectroscopy. Reaction of $(\eta^5\text{-}C_5H_4R)Co(CO)_2$ (R = $SiMe_3$, Ph) with acetylenes to give $(\eta^5\text{-}C_5H_4R)$Co(cyclobutadiene) also produces **396** in low yield [549(b)].

There are more facile and logical routes to $(\eta^5\text{-}C_5H_4R)$M(diene) complexes, starting from readily available $[RhCl(diene)]_2$ [550] or by substitution of the CO ligand in $(\eta^5\text{-}C_5H_4R)Co(CO)_2$ by dienes. The influence of the properties of the cyclopentadienyl ring on the diene (and vice versa) have been comprehensively studied. One of the earliest studies of the influence of the ring substituent on the



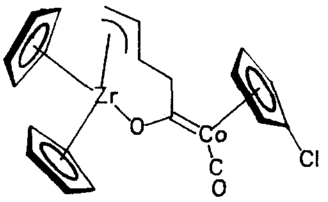
395 a R = COOMe
b R = COMe



396 R = $SiMe_3$,Ph

properties of L in (η^5-C_5H_4R)ML_2 was reported by Cramer and Mrowca [551]. In these studies on (η^5-C_5H_4R)RhL_2 (L = C_2H_4, 1,5 butadiene), it was observed that the barrier to ring rotation of the olefin was influenced by the R group; electron-donating groups increased the Rh–olefin bond strength and, hence, the barrier to olefin rotation. Not unexpectedly, kinetic data [552] on the replacement of C_2H_4 by L (L = Group 15 donor ligand) was also influenced by R. The data indicate an influence of the ring on the transition state in the replacement reaction and the associative kinetics were interpreted in terms of an η^5–η^3 slip in the transition state. Later kinetic studies by Basolo and his group [553], on the substitution of CO by PPh_3 on (η^5-C_5H_4R)Rh$(CO)_2$, confirmed the influence of the R group on the replacement reaction. Thus, a plot of Hammett σ_p against log k_{co} for the substitution reaction was found to be remarkably linear and the data were consistent with a mechanism in which delocalisation of electron density from the metal to the ring must take place.

A novel method for transforming M–CO to M–carbene bonds using metal carbonyl complexes has been achieved. The method circumvents possible anion stabilisation and involves a C–C coupling process without nucleophilic reaction requirements. Thus, coupling of (η^5-C_5H_5)$_2$Zr(butadiene) with (η^5-C_5H_4Cl)Co$(CO)_2$ gives the carbene (**397**) [554], a reaction that is enhanced by the electron-withdrawing Cl group.



397

(1) Fulvalene and related complexes. Two metals in proximal environments (Tables 42 and 43). The study of bimetallic complexes in which two metals are held together in close proximity to each other is of current interest and could provide information on surface-supported materials [555(b)]. The synthesis of the above types of complex

can be achieved by the use of suitable bridging ligands and bridging cyclopentadienyl ligands provide one possibility in this regard. The cyclopentadienyl rings can be directly linked together, e.g. fulvalene, or linked via a bridging group, e.g. CH_2, $SiMe_2$. Another possibility is to use suitably substituted cyclopentadienyl ligands in which the substituent can act as a bridging ligand, e.g. PMe_2. The above approaches have been used successfully to produce complexes in which the metals are in close proximity or bonded to each other, and, potentially, can produce chemistry different from the analogous separated (unlinked) mono-cyclopentadienyl complexes.

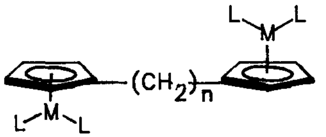
Fulvalene and related complexes of Co, Rh and Ir have been known for some time. They can be prepared as follows:

(a) by addition of ML_x to fulvalene or the fulvalene dianion [79,381,382,556,557];

(b) by coupling of $(\eta^5\text{-}C_5H_5)ML_x$ radicals [557(a)]; and

(c) via an Ullmann coupling reaction of $(\eta^5\text{-}C_5H_4I)ML_x$ complexes [556(b)].

The synthesis of the fulvalene dianion [382] and the isolation of the thallium fulvalene dianion [79] have permitted the synthesis of a range of bimetallic complexes (**398**, $n = 0$).

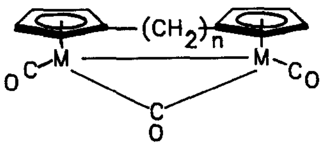


M = Co,Rh,Ir
L = CO.C_2H_4.COT,1.5COD

398

The Co complex has also been synthesised in higher yield directly from the (purified) dihydrofulvalene [381].

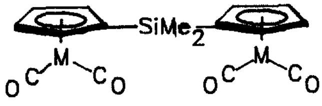
Use of $Li_2[(C_5H_4)_2CH_2]$ [555(a),558] also provides a range of related Rh complexes (Table 42). The μ-CO bridged complex (**399**, $n = 1$) is obtained thermally from **398** ($M = Rh$, Co; $L = CO$, $n = 1$) and the structure has been confirmed by X-ray



399

crystallography. Protonation and methylation of **399** results in formation of Rh(III) complexes (see below).

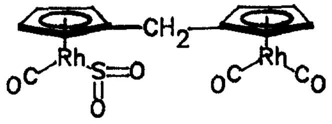
By judicious choice of the ring substituents in bis-substituted cyclopentadienes, it has been possible to synthesise an Si-bridged cyclopentadienylcobalt complex. Reaction of $SiMe_3C_5H_5$ with NMe_3SnMe_3 gave $(SiMe_3)(SnMe_3)C_5H_4$ and reaction with ML_x resulted in preferential displacement of $SnMe_3$ to give $(\eta^5\text{-}C_5H_4SiMe_3)ML_2$ [150]. Extension of this concept to a bridged complex gave **400**.



400

The close proximity of the two metals in the bridged cyclopentadienyl complexes can lead to metal–metal bond formation, which can be achieved by ligand displacement reactions. For instance, addition of Me_3NO to **398** ($n = 0$) gave **399** ($n = 0$) in 43% yield [79]. This reaction can also be achieved thermally [555(a),556]. The ease with which the reaction occurs suggests that other bridging groups could link the two metal centres. Reaction of **398** ($n = 1$) with SO_2 [558(a)] gives products **401** and **402**.

Reaction of SO_2 with the ethylene complex **403** gave **404** [558(a)].



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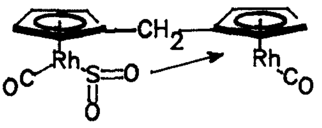

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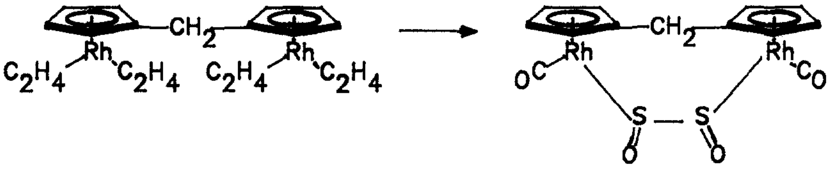
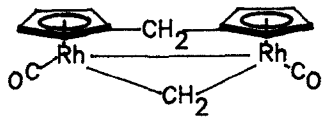


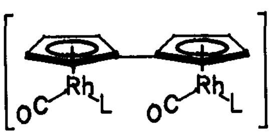
403 **404**

Conversion of the μ-CO to a μ-CH_2 group [558(b)] can be achieved by conventional procedures [559] using *N*-methyl-*N*-nitroso-urea. The structure **405** has been confirmed by X-ray crystallography.



405

A second route to the synthesis of metal-containing bridged cyclopentadienyl complexes is via the coupling of $(\eta^5\text{-}C_5H_5)ML_x$ radicals. Thus, one-electron electrochemical (or ferrocenium) oxidation of $(\eta^5\text{-}C_5H_5)Rh(CO)L$ ($L = P(OPh_3$, PMe_3, PPh_3) [557(b),(c)] gives the bridged Rh(II) complex **406**. The reaction involves H_2



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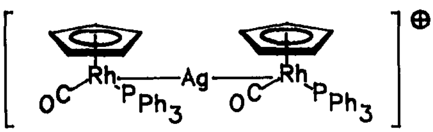
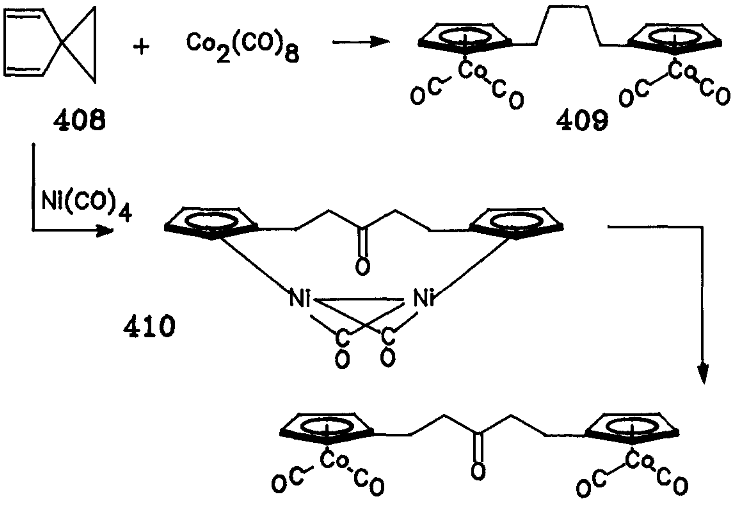


407

displacement from the coupled rings. The dication can be converted to **398** ($n=0$) by two-electron reduction; the overall process involving a *cis–trans* rearrangement with respect to the fulvalene rings bond [557(b),(c)]. Oxidation of (η^5-C_5H_5)Rh(CO)PPh_3 with Ag gives **407**, which contains a linear Rh–Ag–Rh bond [557(c)]. Oxidation of the corresponding Co complexes, (η^5-C_5H_5)CoL_x gives a thermally stable Co(II) complex, (η^5-C_5H_5)CoL_x^+, with no dimer formation. It appears that, when L is bulky, dimerisation and disproportionation reactions are prevented [560].

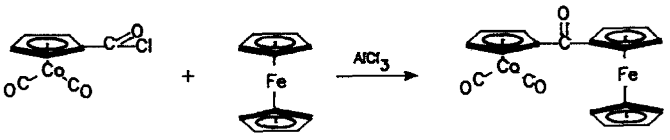
Extension of the chain between the two cyclopentadienyl rings eventually will result in the metals attached to the rings acting independently of each other. Although this aspect has not been explored in detail, examples of long bridging groups are known. Reaction of $Co_2(CO)_8$ with **408**, for instance, gives **409** [561]. Reaction of the same spiro ring with $Ni(CO)_4$ gives **410**, which undergoes ligand exchange with $Co_2(CO)_8$ to give **411**.



411

Other examples of bridged cyclopentadienyl complexes are **412**, and **415** which was synthesised by coupling of two metal–ring systems **413** and **414** [536].

Another approach to constructing bimetallic complexes is via the use of η^5-$C_5H_4PR_2$ ligands. Both the ring and the PR_2 group can coordinate to metals and reaction of Li[$C_5H_4PR_2$] with Co, Rh or Ir carbonyls yields **416** [169,562]. The



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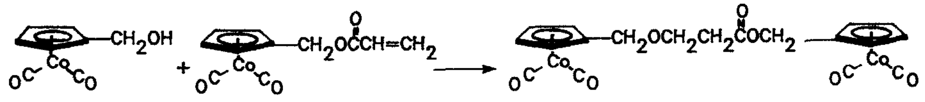
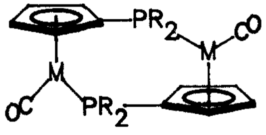


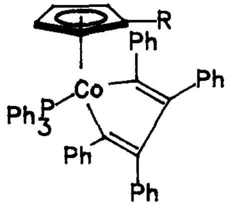
413 414 415

reaction occurs via initial formation of $(\eta^5\text{-}C_5H_4PR_2)M(CO)_2$ and one CO group is readily displaced by a "PR_2" group. The reverse reaction does not occur in the presence of CO, even under forcing conditions.



416

(2) Catalysis. In 1973, Yamazaki and Wakatsuki [563] reported that a cobalt metallocycle (**417**) catalysed the reaction between alkynes and nitriles to give substituted pyridines. This report was soon followed by a publication from the Bönnemann group [564(a)] in which Co(I) complexes were used to induce the same reaction.



417

The reaction produces a variety of pyridine isomers as well as substituted benzene derivatives. Comprehensive mechanistic investigations have been undertaken on the reaction [564–566], and a catalytic cycle as shown in Fig. 3 is believed to be operating. Fine tuning of the catalyst by variation of the ring substituent is possible, and this has led to maximisation of reactant activity and product distributions.

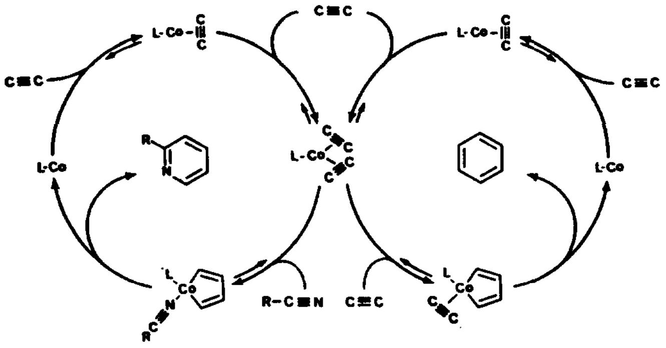


Fig. 3. Catalytic cycle for the reaction of ethyne and alkylnitriles to produce substituted pyridines and benzene [564(d)].

Synthetic routes to the required (η^5-C_5H_4R)Co complexes have been elaborated [564(b),(c)] and include:

(a) Reaction of substituted cyclopentadienes with $Co_2(CO)_8/I_2$ to give (η^5-C_5H_4R)$Co(CO)_2$ followed by reaction with COD (or other dienes) to yield (η^5-C_5H_4R)Co(COD).

(b) Reaction of $XCo(PR'_3)_3$ (X = Cl, Br; R' = O-i-Pr, Ph) with Li[C_5H_4R] (R = H, PPh_2, CF_3) followed by reaction with COD to give (η^5-C_5H_4R)Co(COD).

(c) Reduction of CoX_2 (X = Cl, Br, I, acac) to "Co" followed by reaction with (η^5-C_5H_4R) and L (L = diene) in a one pot process. Magnesium was found to be the best reducing agent, although other reducing agents such as $AlEt_3$, Na, K, etc. have been used.

(d) The use of (η^5-C_5H_4R)$_2$Co. In these reactions either the cyclopentadienyl ring could be displaced, to give **418**, or it could be transformed into a diene (**419**).

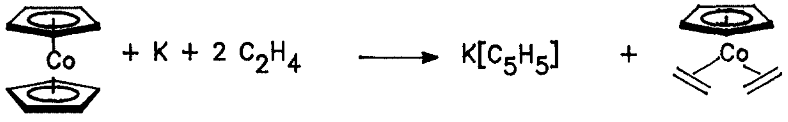
The complexes (as well as annelated and boron-containing cyclopentadienyl derivatives) produced by the routes described above, readily lose the diene under the conditions required to produce pyridines. Thus, correlation of reactivity and activity relate directly to the influence of the ring substituent, if appropriate reaction conditions are chosen. The influence of R on the properties of (η^5-C_5H_4R)Co(COD) (and hence catalytic activity) has been probed by ^{59}Co NMR spectroscopy [564,565]. Relative to (η^5-C_5H_5)Co(COD), it is observed that electron-donating substituents cause deshielding at the metal centre while electron-withdrawing substituents cause shielding. The catalytic activity of the complexes correlates directly with the electronic property of the R group:

(a) electron-withdrawing groups increase catalytic activity,

(b) mesomeric effects are more important than inductive effects, and

(c) the influence of substituents is additive.

A relationship has also been found between regioselectivity and the electronic



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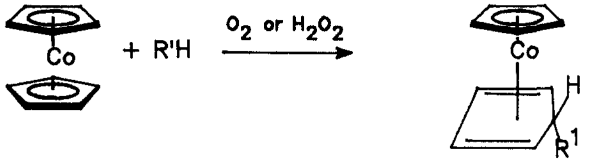


419

effect of the R group as reflected by the ^{59}Co NMR data. For instance, the more electron-donating the R group, the greater the amount of the symmetrical isomer produced in the catalysed reaction between EtCN and MeC≡CH (Fig. 4).

A series of crystal structure determinations of some of the Co catalyst precursors, (η^5-C_5H_4R)Co(COD), have been carried out [564(b)]. The double bonds of the COD can lie perpendicular (**420a**) or parallel (**420b**) to the ring substituent. The analysis of the data revealed that, when R is a strong electron-donating substituent, then the double bonds lie perpendicular to the substituent. Sterically demanding substituents could override this electronic preference. The average C–C bond lengths in the ring and COD ligands, as well as the average Co–ring distances, do not show any significant variation as the R group is varied.

Wakatsuki et al. have reported similar studies on the correlation of activity with the physical properties of (η^5-C_5H_4R)CoL_2 (L = CO, L_2 = COD; R = electron-

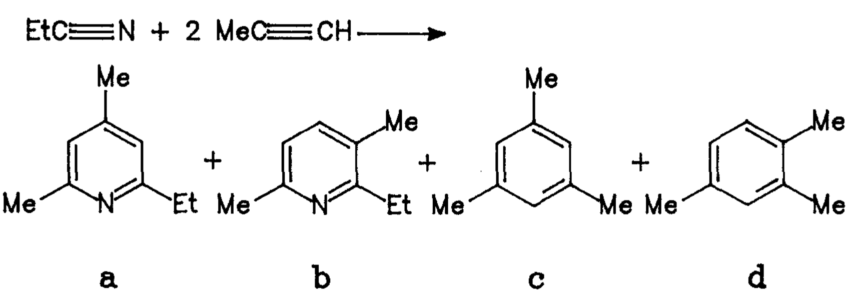
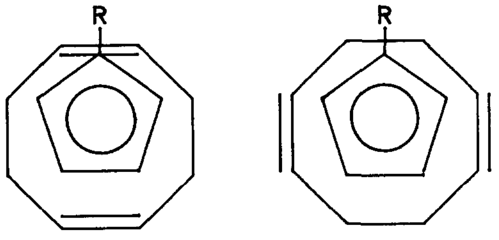


Fig. 4. Products from the Co-catalysed reaction between propyne and acetonitrile.



a b

420

withdrawing group) [566–569]. They have observed a correlation between ^{13}C NMR shifts and σ_F (field parameter [570]) but not with σ_x (electronegativity parameter [571]) and suggest that the transmission of the electronic effect is mainly a through-space phenomenon. PES of a series of complexes (η^5-C_5H_4R)Co(COD) (R = H, CO_2Me, $COCF_3$) have revealed that the HOMO, which involves backbonding from Co to the olefin, is stabilised by ca. 0.5 eV as R becomes a better electron-donating group. Kinetic studies were also performed on these complexes and revealed that:

(a) displacement of the COD occurred by stepwise replacement of the double bonds,

(b) displacement of the second double bond occurred by an S_N2 pathway, and

(c) the electron-withdrawing group had a significant effect on the above step.

In other studies, the influence of O_2 on the catalytic reaction was investigated [567(b)].

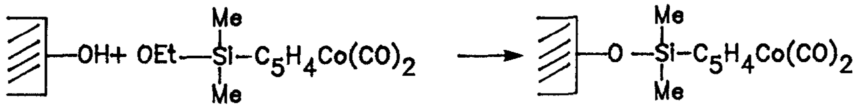
In recent reports [572(a),(b)], the reaction of (η^5-C_5R_5)Co(C_2H_4)$_2$ (R = Me, H) with *n*-BuC≡CH and various nitriles, R′CN, has led to the high regiospecific synthesis of pyridines, while reaction of acetylenes with heterocumulenes (carbodiimides, isocyanates, CO_2) led to the synthesis of novel heterocyclic compounds. Rhodium analogues of the above complexes, as well as polymer-supported Rh complexes, have also been used to synthesise substituted pyridines [572(c)].

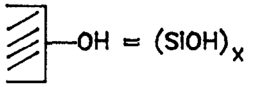
Mechanistic information on the catalysed reaction has also been obtained from the reaction of (η^5-C_5H_4R)Co complexes with acetylenes (see, for example, ref. 573), and this will be discussed below.

(3) Supported (η^5-C_5H_4R)M complexes (Table 41). Polymers containing cyclopentadienyl ligands can be used to support transition metals, and these types of complex have been explored for catalytic activity. Two approaches have been used in this regard; to attach the metal to a preformed polymer or to generate a metal complex containing a moiety which can be polymerised (see, for example, ref. 574).

Two types of support have been used to attach Group 9 metals to polymers. Attachment to silica has been achieved by the reaction of $C_5H_5(CH_2)_3Si(OMe)_3$ or

$C_5H_5Si(OEt)_{3-x}Me_x$ with $(SiOH)_x$. Reaction to give **421** can occur prior to, or after, reaction of Co or Rh carbonyl complexes with the η^5-C_5H_4R ring [241(b),575,576].

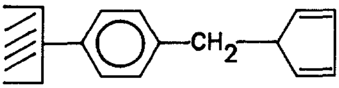


where 

421

The catalysts have been successfully used in the cyclotrimerisation of acetylene (e.g. MeOOCC≡CCOOMe) and the hydroformylation of olefins [241(b),575,576].

Metal complexes have also been attached to polystyrene supports (**422–424**) [85,523(a),572(d),577–579]. An early report by Perkins and Vollhardt [577] using a



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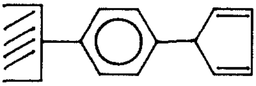
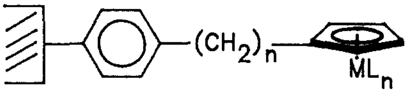


423

 = polystyrene cross linked with 1%,3% and 20% DVB

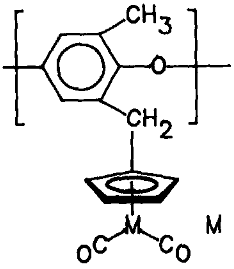


M = Co,Rh

424

Co derivative of **423** (3% crosslinked with DVB) suggested that the supported Co complex **424** (M = Co, $n = 0$) was a Fischer–Tropsch catalyst. This was a unique result as the homogeneous counterpart showed no Fischer–Tropsch activity. Later work by Sekiya and Stille [85], using an alternative synthetic strategy to the synthesis of the polymer-supported cyclopentadiene **423**, gave a Co complex with no Fischer–Tropsch polymerisation activity. It was also shown that the synthetic route used by Vollhardt, via the cyclopentenone (see Sect. C.(ii)(e)), gave low yields of the required phenyl-substituted cyclopentadienyl ring. Co(0), possibly formed in the reaction, is a known Fischer–Tropsch catalyst (see, for example, ref. 580), and could account for the odd result.

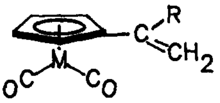
Polymer-supported Rh(III) has also been found to be an active catalyst for hydrogenation and isomerisation reactions [579]. Finally, it has to be noted that poly(phenylene oxide)-supported cyclopentadienyl Co and Rh complexes [581] (**425**) have been prepared and are active hydroformylation catalysts.



425

M = Co,Rh

The alternative approach of polymerizing suitable substituted cyclopentadienylmetal complexes has been extensively developed by Rausch, Pittman and co-workers [16,17,290,582]. The entry to these polymers is via vinyl-substituted cyclopentadienyl rings [69]. Reaction of 6,6-dimethylfulvene or 6-methylfulvene with lithium diisopropylamide gave $[C_5H_4CR{=}CH_2]^-$ (R = H, Me) in 85–95% yield. Reaction of the vinyl ligand with $Co_2(CO)_8$, $[Rh(CO)_2Cl]_2$ or $Ir(CO)_3Cl$ gave the required complexes (**426**). Full details of the synthesis have been published [17,553,582] and polymerisation studies reveal that best results are obtained for the Ir analogue [17].

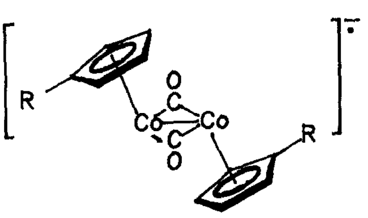


426

M = Co,Rh,Ir R = H(a),Me(b)

(b) (η^5-C_5H_4R)M(II) complexes (Table 44)

Stable complexes of this type contain M–M bonds and they can be synthesised from either M(I) or M(III) complexes. Reduction of (η^5-C_5H_4R)$Co(CO)_2$ with Na/Hg yields dimer anions (**427**), which were characterised by ESR spectroscopy. The ratio of **427** to ring-loss products was dependent on R [583]. Addition of MeI to these anions (R = H) gives the Co(II) dimers (**428**) [584]. Similar studies, using the bridging ligand (η^5-C_5H_5)$_2CH_2$, gave similar bridged Co(II) dimers, which can be cleaved at room temperature, in the presence of PPh_3, to give the Co(I)/Co(III) dimer (**429**) [584]. The reaction, which involves transfer of a methyl group to give the mixed Co(I)/Co(III) complex, could occur by either an intermolecular or intramolecular mechanism. Evidence for the former process comes from exchange studies between (η^5-C_5H_4Me)$Co(PPh_3)_2$ and (η^5-C_5H_5)$Co(PMe_3)(Me)_2$ [585].



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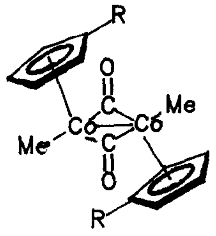

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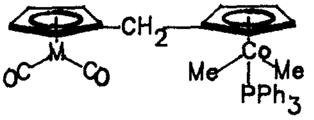
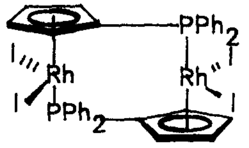


429

(c) (η^5-C_5H_4R)M(III) complexes (Tables 42–46)

Co(III) complexes can be synthesised either by an oxidative addition reaction of, or electrophilic addition to, Co(I) complexes. Conversion of one Co(III) complex into another, by ligand substitution has also been studied.

The oxidative addition reaction typically involves addition of a suitable reagent (e.g. I_2) to a metal substrate which results in a metal oxidation state change (e.g. conversion of **416** to **430** [169]).



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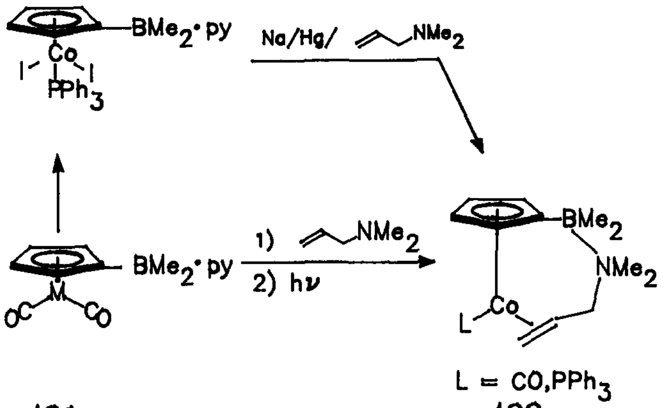
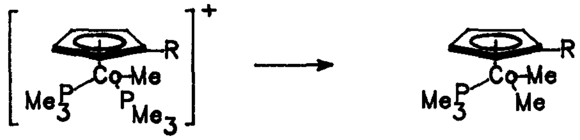
A combination of an oxidative–addition reaction followed by a reductive elimination reaction is useful for inducing mild ligand replacement of Co(I) (e.g. conversion of **431** to **432** [108]).

Reagents other than I_2 have also been used in the oxidative–addition reaction. For instance, $(XCN)_2$ (X = Se, S) reacts with (η^5-C_5H_4R)Co$(CO)_2$ (R = H, $SiMe_3$) to give (η^5-C_5H_4R)Co(Y)(Z)(CO) (Y, Z = NCS, NCSe, CN) [586].

Werner and Hofmann [587,588] have exploited the electrophilic addition route by using the "super" nucleophilic properties of (η^5-C_5H_4R)Co$(PMe_3)_2$. Thus, reaction of (η^5-C_5H_4R)Co$(PMe_3)_2$ (R = *t*-Bu, i-Pr) with MeLi, initially gives [(η^5-C_5H_4R)Co$(PMe_3)_2$Me]$^+$ (**433**), and treatment of this salt with more MeLi gives neutral (η^5-C_5H_4R)Co(PMe_3)(Me)$_2$ (**434**). (An X-ray structure determination of the related (η^5-C_5H_4COMe)Co(PPh_3)(Me)$_2$ complex has been reported [589]). Addition of CF_3COOH to **433** yields (η^5-C_5H_4R)Co$(PMe_3)(OOCCF_3)_2$, which reacts with $P(OMe)_3$ to give (η^5-C_5H_4R)Co$(PMe_3)[P(OMe)_3]_2^{2+}$. This dication did not react with NaH to give a metal-to-ring ligand shift (see below), but rather gave a Michaelis–

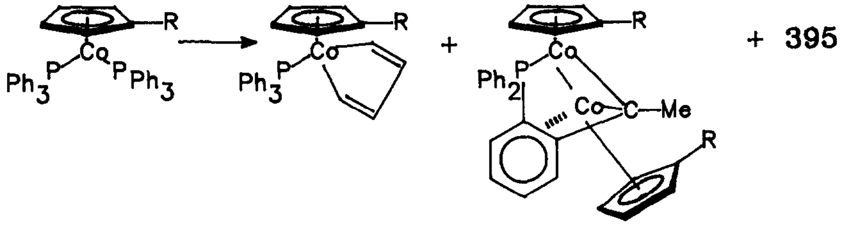


431 **432**



433 **434**

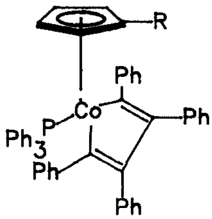
Arbuzov reaction in which Me groups were removed from the ligand. Reaction of **435** (R = H, COOMe, COMe) with acetylene gives three products (**395**, **436**, **437**) in modest yield [590]. The structures of **436** and **437** were established by X-ray crystallography.



435 **436** **437**

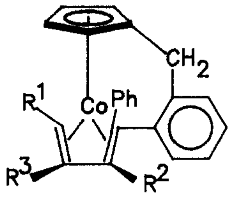
Modification of R (R = Me, CH_2Ph) in **434** and reaction with diphenylacetylene gave **438** [591]. Thermal reaction provided the expected cyclobutadiene complex as well as **439a**. In **439a**, the ring substituent is coordinated to the Co (see ref. 108 for another example of this phenomenon). Reaction of **438** with methyl phenylpropiolate gave similar products involving substituent coordination to Co, but a wider range of isomeric products (**439b,c**) were produced [591].

A novel method of synthesising cyclopentadienyl rings, is from cyclopentane, a reaction discovered by Crabtree and co-workers [592–594]. The reaction exploits the use of $[Ir(H)_2(acetone)L_2]$, a complex which has been shown to induce homogen-



(R = H,Me,CH_2Ph)

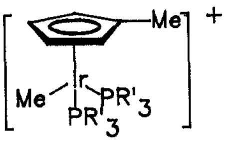
438



439

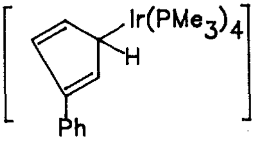
(a) R^1,R^2,R^3 = Ph
(b) R^1 = Ph; R^2,R^3 = CO_2Me
(c) R^1,R^3 = CO_2Me; R^2 = Ph

eous C–H bond activation (bond cleavage) [593]. By judicious choice of reagents, including the use of t-$BuCH{=}CH_2$ as H acceptor [593,595], it has been possible to generate η^5-C_5H_4R or η^6-C_6H_6 complexed rings, e.g. reaction with 1,1-dimethylcyclopentane yields **440**. This product was independently synthesised from [Ir(cyclooctene)Cl]$_2$ and $C_5H_4R^-$ [592(b)].



440

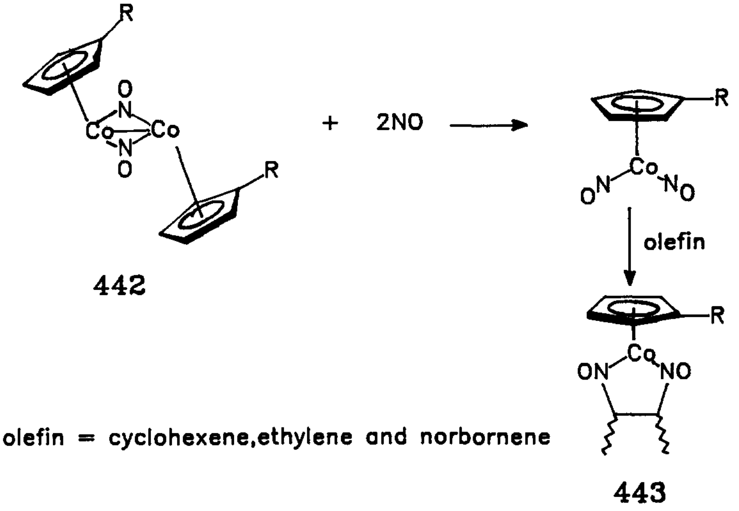
$[(\eta^5$-$C_5H_4Ph)IrL_2H]^+$, which was prepared as above, reacts with PMe_3 to give **441** with the specific cyclopentadiene geometry shown [594]. This is an example of a ring-slip reaction in which the η^1 "intermediate" has been trapped. In this specific reaction, the ring-slip reaction is suggested to be enhanced by a "phenyl cyclopentadienyl effect".



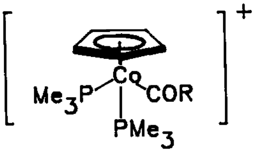
441

Addition of NO gas to $(\eta^5$-$C_5H_4R)Co(CO)_2$ gives the dimer $[(\eta^5$-$C_5H_4R)Co(NO)]_2$ (**442**), which reacts with olefins to give monometallic nitrosoalkane complexes (**443**) [596] by the pathway proposed below. Modification of the cyclopentadienyl ring (ring = η^5-C_5H_5, η^5-C_5H_4COOMe, η^5-C_5Me_5) did not influence the rate of the reaction between **442** and olefins, although the more electron-withdrawing group (R = COOMe) did enhance the stability of the reaction intermediates.

(1) Electrophilic substitution of the complexed cyclopentadienyl ring. This reaction, which results in the formation of substituted cyclopentadienyl rings, involves either



direct attack at the ring by an external electrophile, or metal-to-ring ligand shift and is achieved with relative ease by Co(III) complexes. In an early study, Werner and Hofmann observed the aryl substitution of the cyclopentadienyl ring in **444** [588b].



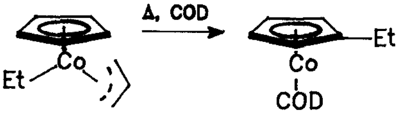
444

Reaction of **444** (prepared from $(\eta^5\text{-}C_5H_5)Co(PMe_3)_2$ and CH_3COCl), with PhLi gave CH_4 and $(\eta^5\text{-}C_5H_4Ph)Co(CO)(PMe_3)$ via a novel decarbonylation reaction. Reaction of $(\eta^5\text{-}C_5H_5)Co(PMe_3)_2(COR)^+$ (R = aryl) with NaH also gave the related $(\eta^5\text{-}C_5H_4R)Co(PMe_3)(CO)$ complexes. Studies to elaborate on the migration reaction have shown that a range of alkyl groups can also migrate from Co to the ring. To undergo the migration, the R group must contain two ethyl or methyl groups on the α-C atom of the reagent, e.g. R = i-Pr, *t*-Bu, CMe_2Et, etc. Steric effects rather than electronic effects are thought to be decisive for the migration reaction [588].

A variety of reactions in which electrophilic substitution of the coordinated cyclopentadienyl ring has been observed, are to be found in the literature:

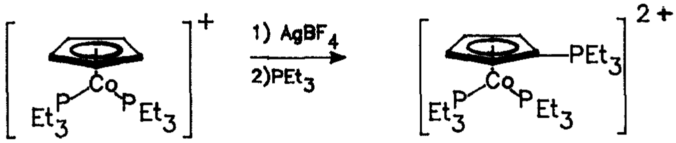
(a) Thermal reaction (30–80°C) between **445** and an excess of COD results in ethyl group migration to give **446** [597].

(b) One of the earliest reports in this area involved a Rh complex. Both $(\eta^5\text{-}C_5H_5)Rh(PPh_3)I_2$ and $(\eta^5\text{-}C_5H_4R)Rh(PPh_3)I_2$ were obtained on heating RI (R = i-Pr, Me) with $[(\eta^5\text{-}C_5H_5)Rh(PPh_3)_2Me]I$ [598].



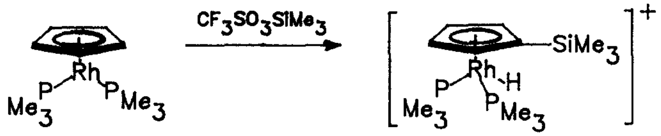
445 **446**

(c) The cyclopentadienyl ring can be substituted by a neutral ligand, viz. conversion of **447** to **448** [560].



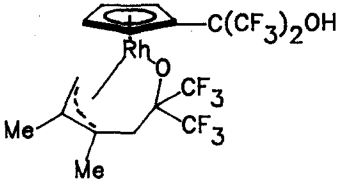
447 **448**

(d) Reaction of (η^5-C_5H_5)Rh(PMe_3)$_2$ with $CF_3SO_3SiMe_3$ results in $SiMe_3$ substitution, viz. conversion of **449** to **450** [599].

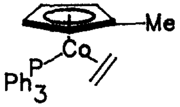


449 **450**

(e) Irradiation of hexafluoroacetone and (η^5-C_5H_5)Rh(2,3-dimethylbuta-1,3-diene) gave **451** [600].



451



452

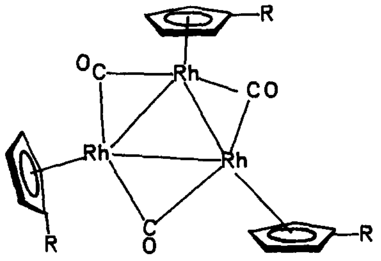
(f) Thermal reaction of (η^5-C_5H_5)Co(PPh_3)(Me)$_2$ in the presence of CH_2=CH_2 gives **452** [601].

(g) Heating an Ir(III) complex, [(η^5-C_5H_5)IrEt(PR_3)$_2$]$^+$, yields [(η^5-C_5H_4Et)IrH(PR_3)$_2$]$^+$ by an ethyl migration reaction [592(b)].

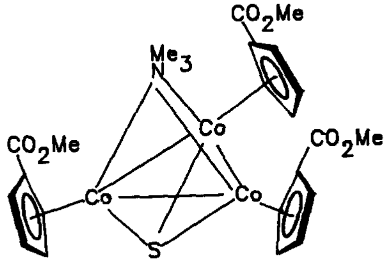
(d) Metal clusters

Very few Group 9 metal complexes are known in which substituted cyclopentadienyl ligands are contained in metal cluster complexes. The simplest member of this type is [(η^5-C_5H_4R)Rh(CO)]$_3$ (R = Ph, CH_2Ph) (**453**), a trimer containing bridging

CO groups [582]. A doubly capped Co trimer has been prepared by the reaction of (η^5-C_5H_4COOMe)Co(COD) with S(*N*-*t*-Bu)$_2$. The product (**454**) is a 50-electron complex which has been characterised by X-ray crystallography and magnetic susceptibility measurements [602]. The complex is related to a series of Co trimers with different capping groups which usually contain 48 electrons.

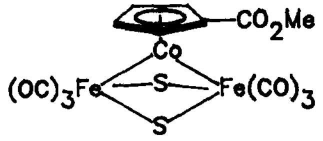


453

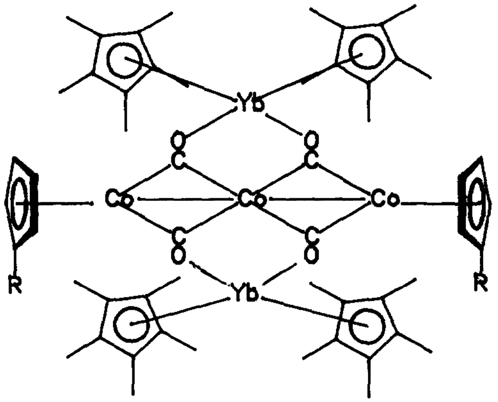


454

Other metal clusters containing substituted cyclopentadienyl fragments are also known and examples include **455** and **456** [603,604].



455



456 (R=Me,SiMe$_3$)

TABLE 40

(η^5-C_5H_4R)M(X)(Y)(I) complexes (M = Co, Rh, Ir)

M	R	X	Y	Comment[a]	Ref.
Co	Me	CO	CO	IR, NMR, MS	553(a),563(a),611
Co	Me	COD		IR, NMR (^{1}H, ^{13}C)MS, Cat	564(b),(c),(d)
Co	Me	C_2H_4	PPh_3, C_2H_4	NMR	601,565
Co	Et	CO	CO	IR, NMR, MS	536(a),561
Co	Et	COD		NMR	597
Co	i-Pr	CO	CO	IR, NMR	126
Co	i-Pr	PMe_3	PMe_3	NMR, MS	588(a),(c)
Co	*t*-Bu	COD		NMR (^{13}C, ^{59}Co)MS, Cat	564(b),(c)
Co	*t*-Bu	PMe_3	PMe_3	NMR, MS	588(a),(c)
Co	CHR'_2[b]	CO	CO	–	126
Co	CHMeEt	CO	CO	–	126
Co	CMe_2Et	PMe_3	PMe_3	MS	588(a),(c)
Co	CH_2Ph	CO	CO	NMR, MS	81
Co	Ch_2SiMe_3	CO	CO	IR, NMR, MS	150(b)
Co	NM[c]	CO	CO	NMR (^{1}H, ^{13}C)MS	117
Co	CF_3	COD			564(b)
Co	CPh_3	CO	CO		564(b)
Co	CPh_3	COD		IR, NMR	564(b), 609
Co	Ph	CO	CO		549(b)
Co	Ph	COD		NMR (^{59}Co), MS, Cat	564(b),(c),(d)
Co	Ph	C_5Ph_4O[d]		NMR	549(b)
Co	Aryl[e]	CO	PMe_3	NMR	588(b)
Co	Cl	CO	CO	IR, NMR, MS	80,554,564(b)
Co	Cl	CO	[f]	IR, NMR (^{1}H, ^{13}C) X-ray	554(a)
Co	Cl	COD		NMR (^{59}Co), Cat	564(b)
Co	Br	CO	CO	IR, NMR, MS	80,564(b)
Co	Br	COD		X-ray, Cat	564(b)
Co	I	CO	CO	IR, NMR, MS	80,564(b)

Co	I	COD		–	564(b)
Co	CH=CH_2	CO	CO	IR, NMR, MS	53,69,126,287,289,290,536(a), 561,573(a)
Co	CMe=CH_2	CO	CO	IR, NMR	69,126,287,290,536(a),564(b)
Co	CMe=CH_2	COD		NMR (^{59}Co), Cat	564(b)
Co	CH=CHEt	CO	CO	IR, NMR, MS	561
Co	CMe=CHMe	CO	CO	–	126
Co	CH_2R'=CHMe^b	CO	CO	–	126
Co	COMe	$C_5H_5R'^g$			607
Co	COMe	CO	CO	IR, NMR	134(a),287,290,536(a),564(b)
Co	COMe	COD		NMR (^{13}C, ^{59}Co)MS, cat, X-ray	564(b),(c),567
Co	COMe	PPh_3	PPh_3	–	590
Co	COEt	CO	CO	–	564(b)
Co	COEt	COD		NMR (^{59}Co), Cat	564(b)
Co	CHO	CO	CO	IR, NMR	134(a),287,290,536(a),564(b)
Co	CHO	COD		NMR (^{59}Co), Cat	564(b),566
Co	COCl	CO	CO	IR, NMR	536(b), 564(b)
Co	CoCl	COD			564(b)
Co	COPh	COD		NMR (^{59}Co), Cat	564(b)
Co	COi-Pr	COD		NMR	566
Co	$COCF_3$	CO	CO	IR, NMR	566
Co	$COCF_3$	COD		NMR	566
Co	CO_2Me	CO	CO	IR, NMR	134(a),287,290,536(b),546, 564(b),583,596
Co	CO_2Me	COD		IR, NMR (^{59}Co, ^{1}H), Cat	564(b),567(b)
Co	CO_2Me	COT		IR, NMR	567(b)
Co	CO_2Me	NBD			569
Co	CO_2Me	$C_5H_5CO_2Me$		IR, NMR	546,547(b)
Co	CO_2Me	PPh_3	PPh_3		590
Co	CO_2Et	CO	CO	IR, NMR	536(b)
Co	COOH	CO	CO	IR, NMR, pKa	536(b),80,564(b)
Co	COOH	COD		NMR (^{59}Co), Cat	564(b)
Co	CH_2OH	CO	CO	IR, NMR	536(a)
Co	C(OH)MeH	CO	CO	IR, NMR	536(a),564(b)
Co	C(OH)MeH	COD		NMR (^{59}Co)	564(b)
Co	CR'(OR'')H^h	CO	CO	IR, NMR	536(a)

TABLE 40 (*continued*).

M	R	X	Y	Comment[a]	Ref.
Co	$CR'(OH)Me^{i}$	CO	CO	IR, NMR	80,536(a)
Co	$CHR'O_2CCH{=}CH_2$	CO	CO	IR, NMR, MS	290,536(a)
Co	CH_2CO_2Me	CO	CO	IR, NMR, MS	583
Co	CONHPh	CO	CO	IR, NMR	536(b),564(b)
Co	CONHPh	COD		NMR (^{59}Co), Cat	564(b)
Co	$CONH_2$	CO	CO	IR, NMR	536(b)
Co	$SiMe_3$	CO, C_2H_4	CO, C_2H_4	IR, NMR, MS	150(a),549(b),583,586,565
Co	$SiMe_3$	COD		IR, NMR (^1H, ^{59}Co), Cat	564(b),(c),565
Co	$SiMe_3$	PMe_3	PMe_3	NMR	588(a)
Co	$SiMe_3$	$C_5PH_4O^{d}$		NMR, MS	549(b)
Co	$SiMe(OEt)_2$	CO	CO	IR	576
Co	$Si(OEt)_3$	CO	CO	IR	576
Co	$SiMePh_2$	CO	CO	IR, NMR	583
Co	$GeMe_3$	COD		Cat	564(b)
Co	PPh_2	CO	CO		564(b)
Co	PPh_2	COD			564(b)
Co	PPh_2S	CO	CO		564(b)
Co^+	PPh_3	CO	CO	IR, Cat, X-ray	176,542
Co	Li	CO	CO	–	80
Co	$BMe_2 \cdot py^{j}$	CO	CO	IR, NMR (^1H, ^{13}C, ^{11}B)	108
Co	$BMe_2NMe_2CH_2CH{=}CH_2$	CO	CO	IR, NMR (^1H, ^{13}C, ^{11}B)	108
Co	$BMe_2NMe_2R'^{k}$	CO	^{k}	IR, NMR (^1H, ^{13}C, ^{11}B)	108
Co	$BMe_2NMe_2R'^{k}$	PPh_3	^{k}	IR, NMR (^1H, ^{13}C, ^{11}B)	108
Co	$BMe_2NMe_2R'^{l}$	$CH_2CH{=}CH{-}CPh{=}CPh(H)$		IR, NMR (^1H, ^{13}C, ^{11}B)	108
Co	$CH_2R'^{m}$		^{m}	NMR	591
Rh	Me	CO	CO	IR, NMR (^1H, ^{13}C) MS	136(c), 553, 611(a)
Rh	Me	Buta-1,3-diene		NMR	136(c)
Rh	Me	C_2H_4	C_2H_4	NMR (^1H, ^{13}C)	136(c)
Rh	Me	CO	PPh_3	IR, kin	553

Rh	Et	Nido-carborane		IR, NMR (^{11}B), MS	105
Rh	t-Bu	C_2H_4	C_2H_4	NMR (^{1}H, ^{13}C)	136(c)
Rh	t-Bu	Buta-1,3-diene		NMR	136(c)
Rh	CH_2Ph	CO	CO	IR, NMR	81
Rh	CF_3	COD		IR, NMR (^{1}H, ^{13}C), MS	89
Rh	CF_3	CO	CO	IR	553(a)
Rh	CF_3	CO	PPh_3	IR, kin	553(a)
Rh	CPh_3	COD		NMR, IR	537(a),609
Rh	Ph	CO	CO	IR, NMR	81
Rh	Ph	C_2H_4	C_2H_4	NMR (^{1}H, ^{13}C)	136(b)
Rh	Ph	2,5 Dimethylhexa-1,5 diene		–	537(c)
Rh	m,p-C_6H_4F	NBD, COD, CHD		^{19}F	606
Rh	Cl	CO	CO	IR, NMR, MS	80,553(a)
Rh	Cl	C_2H_4	C_2H_4	NMR (^{1}H, ^{13}C)	136(b)
Rh	Cl	CO	PPh_3	IR, kin	553(a)
Rh	Cl	COD		IR, NMR	181(a),(b),537(c)
Rh	Cl	Diene^n		isom	136(a),537(c)
Rh	CN	1,4 CHD		NMR	136(c)
Rh	CN	C_2H_4	C_2H_4	NMR (^{1}H, ^{13}C)	136(c), 551
Rh	CN	PR_3^{o}	PR_3^{o}	NMR	552
Rh	$CMeCH_2$	CO	CO	Polym	17
Rh	$CH{=}CH_2$	CO	CO	NMR, Cat	17,53,69,80,289,573(a)
Rh	$(CH_2)_3Si(OMe)_3$	CO	CO	IR, NMR, MS	241(b)
Rh	$(CH_2)_3Si(OMe)_3$	COD		NMR (^{1}H, ^{13}C), MS	241(b), 575
Rh	COMe	CO	CO	IR, NMR	134(a),287,290
Rh	COMe	C_2H_4	C_2H_4	NMR (^{1}H, ^{13}C), MS	136(b)
Rh	COMe	Diene		IR	549(a)
Rh	CHO	CO	CO	IR, NMR (^{1}H, ^{12}C)	134(a),136(c),287,290
Rh	CHO	C_2H_4	C_2H_4	NMR (^{1}H, ^{12}C)	136(c)
Rh	CHO	COT		NMR	537(a)
Rh	CHO	COD		NMR	136(c)
Rh	CHO	Dienes		NMR (^{1}H, ^{12}C), MS, X-ray, iso	136(a),(c),537(a),(c)
Rh	$COCO_2Et$	CO	CO	NMR	136(c)

TABLE 40 (*continued*).

M	R	X	Y	Comment[a]	Ref.
Rh	$COCO_2Et$	C_2H_4	C_2H_4	NMR (^1H, ^{13}C)	136(c)
Rh	$COCO_2Et$	CHD		NMR	136(c)
Rh	CO_2Me	CO	CO	IR, NMR (^1H, ^{13}C)	134(a),136(c),287,290
Rh	CO_2Me	C_2H_4	C_2H_4	NMR (^1H, ^{13}C)	136(c),551
Rh	CO_2Me	COD, COT, NBD		NMR (^1H, ^{13}C), X-ray	136(c),537(a)
Rh	CO_2Me	Dienes[n]		IR, NMR (^1H, ^{13}C), MS, Cat	136(a),(c),537(a),(c),549(a)
Rh	CO_2Me	Pr_3[p]	PR_3[p]	NMR	552
Rh	CO_2Et	C_2H_4	C_2H_4	NMR	136(c)
Rh	CO_2i-Pr	C_2H_4	C_2H_4	NMR	136(c)
Rh	$SiMe_3$	CO	CO	IR, NMR, MS	150(b)
Rh	PPh_2	CO	PPh_3	IR, NMR (^1H, ^{31}P), MS	169
Rh^+	PPh_3	CO	CO	NMR (^1H, ^{13}C), Kin, Cat	177,413,573(b)
Rh^+	PPh_3	COD		NMR (^1H, ^{13}C), X-ray	177,543
Rh^+	PPh_3	NBD		NMR (^1H, ^{13}C)	177
Rh^+	PPh_3	CO	L[q]	NMR (^1H, ^{13}C)	177,553(b)
Rh	$BMe_2 \cdot py$	CO	CO	NMR (^1H, ^{13}C, ^{11}B)	108
Rh	$BMe_2 \cdot py$	CO	PPh_3	NMR (^1H, ^{13}C, ^{11}B)	108
Rh	NMe_2	CO	CO	IR	553
Rh	NMe_2	CO	PPh_3	IR, NMR, kin	553(a)
Rh	NO_2	CO	CO	IR, NMR, MS, X-ray	157(b),553
Rh	NO_2	CO	PPh_3	IR, NMR	553
Rh^+	CPh_2, $C(C_6H_4Cl\text{-}4)_2$	COD		NMR (^1H, ^{13}C), X-ray	540(b),(c)
Rh^+	CPh_2, $C(C_6H_4Cl\text{-}4)_2$	$P(OPh)_3$	$P(OPh)_3$	NMR (^1H, ^{13}C), X-ray	540(b),(c)
Rh^+	$C_3(NPr)_2$[r]	COD		–	541
Rh	$CMe{=}CH_2$[s]	NBD		IR, NMR, MS	540(a)
Rh	[t]	PMe_3		NMR, X-ray, MS	540(a)
Rh	[u]	PMe_3		NMR, MS	540(a)
Rh	CPh_2	CO	CO, Cl	NMR	540(b)
Ir	CF_3	COD		IR, NMR (^1H, ^{13}C)MS 89	
Ir	$CH{=}CH_2$	CO	CO	IR, NMR, polym.	17,53,69

Ir	CMe=CMeH		COD		NMR, MS	540(d)
Ir	CEt=CH_2		COD		NMR, MS	540(d)
Ir	CMe=CH_2		COD		NMR, MS	17,540(d)
Ir	CMe=CH_2	CO		CO	IR, NMR, polym.	69
Ir	CMe(Et)(i-Pr)		COD		NMR, MS	540(d)
Ir	CMe_2(i-Pr)		COD		NMR, MS	540(d)
Ir	PPH_2, PMe_2	CO		PPh_3	IR, NMR (^1H, ^{31}P), MS	169,562
Ir	COMe	C_2H_4		C_2H_4	NMR (^1H, ^{31}P), MS	136(b)

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[a] For abbreviations see p. 3.

[b] R′ = Et, i-Pr.

[c] See **73** and **381**.

[d] See **396**.

[e] aryl = C_6H_5, p-C_6H_4OMe, p-C_6H_4Me, 3,5-$C_6H_3(OMe)_2$.

[f] See **397**.

[g] R′ = Me, t-Bu, CH=$CH_2C_6H_{13}$, C≡$CSiMe_3$.

[h] R′ = H, Me; R″ = Me, Et and R′ = Ph; R″ = H.

[i] R′ = H, Me, Ph.

[j] Also for d^5-pyridine.

[k] R′ = $CH_2CH = CH_2$; see **432**.

[l] R′ forms part of diene ligand.

[m] R′ forms part of diene ligand; see **439**.

[n] Range of tetra, penta and hexadienes.

[o] R = Ph, n-Bu, OEt, Me, F.

[p] R = Me, n-Bu.

[q] L = PPh_3, $\frac{1}{2}$diphos, $\frac{1}{2}$dppb.

[r] See **391**.

[s] See **385**.

[t] See **386**.

[u] See **387**.

TABLE 41

Supported (η^5-C_5H_4R)M(X)(Y) complexes

M	R	X	Y	Comments[a]	Ref.
Co	$OSiMe_2$[b]	CO	CO	IR	576
Co	$OSi(OEt)_2$	CO	CO	IR	576
Co	PS–$C_6H_4CH_2$[c]	CO	CO	IR, Cat	577,578
Co	PS–C_6H_4[d]	CO	CO	IR, Cat	85,577
Co	Polyphenoxide[e]	CO	CO	IR, Cat	581
Rh	–$(CH_2)_3Si(OMe)_3$	COD		Cat	241(b)
Rh	PS–$C_6H_5CH_2$[c]	CO	CO	Cat	578
Rh	PS–C_6H_4[d]	CO	CO	Cat	85
Rh	PS–C_6H_4[d]	Various		XRF, IR, Cat	572(d)
Rh	Polyphenoxide[e]	CO	CO	IR, Cat	581

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[a] For abbreviations, see p. 3.

[b] See **421**.

[c] See **424** ($n=1$).

[d] See **424** ($n=0$).

[e] See **425**.

TABLE 42

Cyclopentadienyl bridged complexes of Co(I) and Rh(I) in which only the cyclopentadienyl ligand acts as a bridge

M	M′	Bridge	Ligands on M	Ligands on M′	Comments[a]	Ref.
Co	Co	–	COD	COD	X-ray	564(b)
Co	Co	–	CO, CO	CO, CO	IR, NMR, MS, UV	79,556(b),564(b)
Co	Co	–	COT	COT	IR, NMR, MS	79
Co	Co	CH_2	CO, CO	CO, CO	IR, NMR	584(a),612
Co	Co	CH_2	PMe_3, PMe_3	PMe_3, PMe_3	IR, NMR (^1H, ^{31}P), MS	612
Co	Co	CH_2	CO, L[c]	CO, L[c]	IR, NMR (^1H, ^{31}P), MS	612
Co	Co	$(CH_2)_4$[b]	CO, CO	CO, CO	IR, NMR, MS	561
Co	Co	$CH_2CH_2OCH_2CH_2$	CO, CO	CO, CO	IR, NMR, MS	561
Co	Co	$CH_2OCH_2CH_2COOCH_2$[d]	CO, CO	CO, CO	IR, NMR	536(a)
Co	Co	$SiMe_2$	CO, CO	CO, CO	IR, NMR	150(b)
Rh	Rh	–	CO, CO	CO, CO	IR, NMR, MS	79
Rh	Rh	–	C_2H_4, C_2H_4	C_2H_4, C_2H_4	NMR, MS	79
Rh	Rh	–	COT	COT	NMR, MS	79
Rh	Rh	–	COD	COD	NMR, MS	79
Rh	Rh	–	CO, PPh_3	CO, PPh_3	IR, NMR, X-ray	557(b),(c)
Rh	Rh	CH_2	PPh_3, PPh_3	PPh_3, PPh_3	IR, NMR, MS	560(b)
Rh	Rh	CH_2[e]	CO, μ-CO	CO, μ-CO	IR, NMR	558(a),555
Rh	Rh	CH_2	CO, CO	CO, CO	IR, NMR, MS	555,556(a)
Rh	Rh	CH_2	C_2H_4, C_2H_4	C_2H_4, C_2H_4	IR, NMR, MS	556(a)
Rh	Rh	CH_2	C_2H_4, PMe_3	C_2H_4, PMe_3	IR, NMR, MS	556(a)
Rh	Rh	CH_2	PMe_3, PMe_3	PMe_3, PMe_3	NMR	556(a)
Rh	Rh	CH_2	PMe_3, CO	PMe_3, CO	IR, NMR	556(a)
Rh	Rh	CH_2[f]	CO, CO	CO, μ-SO_2	IR, NMR, UV	558(a)
Rh	Rh	CH_2[g]	C_2H_4, S_2O_4	C_2H_4, S_2O_4	IR, NMR, UV	558(a)
Rh	Rh	CH_2[h]	CO, μ-SO_2	CO, μ-SO_2	IR, NMR, UV, MS	558(a)
Rh	Rh	$SiMe_2$	CO, PMe_3	CO, PMe_3	NMR	556(a)
Rh	Rh	$SiMe_2$	PMe_3, PMe_3	PMe_3, PMe_3	NMR	556(a)

TABLE 42 (*continued*).

M	M′	Bridge	Ligands on M	Ligands on M′	Comments[a]	Ref.
Rh	Rh	$SiMe_2$	CO, μ-CO	CO, μ-CO	NMR	556(a)
Ir	Ir	–	CO, CO	CO, CO	IR, NMR, MS	79
Ir	Ir	CH_2	CO, CO	CO, CO	IR, NMR, MS	555(a)
Ir	Ir	$PPh_2IrCOCl(PPh_3)_2$	CO, PPh_3	CO, PPh_3	IR, NMR (^1H, ^{31}P)MS	169
Co	Fe	CO	CO, CO	C_5H_5	IR, NMR, MS	536(b),564(b)
Co	Fe	CO	COD	C_5H_5	–	564(b)

[a] For abbreviations see p. 3.
[b] See **409**.
[c] $L = \frac{1}{2}PMe_2PMe_2$ or $\frac{1}{2}PMe_2CH_2CH_2PMe_2$.
[d] See **415**.
[e] See **399** ($n = 1$).
[f] See **401**.
[g] See **404**.
[h] See **402**.

TABLE 43

Bridged cyclopentadienyl metal dimers of Co, Rh, Ir in which the cyclopentadienyl substituent acts as the bridging ligand

M	M′	Bridges	Ligands on M	Ligands on M′	Comments[a]	Ref.
Co	Co	PR_2 ($R = Me$, Ph)	CO, μ-PR_2[b]	CO, μ-PR_2	IR, NMR, MS	562
Co	Co	CH_2,CH_2CO	CO[c]	CO	NMR, X-ray	540(e)
Rh	Rh	PR_2 ($R = Me$, Ph)	CO, μ-PR_2[b]	CO, μ-PR_2	IR, NMR, (^1H, ^{31}P), MS, X-ray	169,562
Ir	Ir	PR_2 ($R = Me$, Ph)	CO, μ-PR_2[b]	CO, μ-PR_2	IR, NMR (^1H, ^{31}P), MS	169,562
Rh(III)	Rh(III)	PPh_2	I, I, μ-PPh_2[d]	I, I, μ-PPh_2	IR	562

[a] For abbreviations see p. 3.
[b] See **416**.
[c] See **384**.
[d] See **430**.

TABLE 44

(η^5-C_5H_4R)M(A)(B)(C) (III) complexes (M = Co, Rh, Ir)

M	R	A	B	C	Comments[a]	Ref.
Co	Me	Me, I	Me, I	PPh_3	NMR	601
Co	i-Pr	Me	Me	PMe_3	NMR, MS	588(e)
Co	i-Pr	$PO(OMe)_2$	$PO(OMe)_2$	PMe_3	NMR	588(d)
Co	i-Pr	CF_3COO	CF_3COO	PMe_3	NMR, MS	588(d),(e)
Co^+	i-Pr	H, Me	PMe_3	PMe_3	NMR, MS	588(a),(c)
Co^+	i-Pr	$PO(OMe)_2$	PMe_3	$P(OMe)_3$	NMR	588(d)
Co^{2+}	i-Pr	PMe_3	PMe_3, $P(OMe)_3$	PMe_3, $P(OMe)_3$	NMR	588(d)
Co	*t*-Bu	CF_3COO	CF_3COO	PMe_3	NMR, MS	588(e)
Co	*t*-Bu	Me	Me	PMe_3	NMR, MS	588(e)
Co	*t*-Bu	$PO(OMe)_2$	$PO(OMe)_2$	PMe_3	NMR	588(d)
Co^+	*t*-Bu	H, Me	PMe_3	PMe_3	NMR, MS	588(a),(c)
Co^{2+}	*t*-Bu	$P(OMe)_3$	$P(OMe)_3$	PMe_3	NMR	588(d)
Co^+	CMe_2Et	H, Me	PMe_3	PMe_3	NMR	588(a),(c)
Co	CH_2Ph	PPh_3	Diene[b]		NMR	591
Co	COMe	C_4H_4		PPh_3	IR, NMR	590
Co	COMe	Me	Me	PPh_3	X-ray	589
Co	CO_2Me	C_4H_4		PPh_3	IR, NMR, X-ray	590
Co	CO_2Me	[c]	[c]		IR	596
Co	$SiMe_3$	NCS	NCS	CO	IR, UV	586
Co	$SiMe_3$	NCSe	NCSe	CO	IR, UV	586
Co	$SiMe_3$	NCS	CN	CO	IR, UV	586
Co	$SiMe_3$	NCSe	CN	CO	IR, UV	586
Co^+	$SiMe_3$	H	PMe_3	PMe_3	NMR	588(a)
Co^{2+}	PEt_3	H	PEt_3	PEt_3	IR, NMR	560(a)
Co	$BMe_2 \cdot py$	I	I	CO, PPh_3	IR, NMR (^1H,^{13}C,^{11}B)	108
Co	$OSiMe_2$[d]	I	I	CO	IR	576
Co	$OSi(OEt)_2$[d]	I	I	CO	IR	576
Co	CO_2Me	I	I	PPh_2py, CO,	IR, NMR	605

TABLE 44 (*continued*).

M	R	A	B	C	Comments[a]	Ref.
Co	CO_2Me	I	I	Diphosphines	IR, NMR (^1H,^{31}P), ES	605
Rh	Me	I	I	PPh_3, CO, *t*-BuNC	IR, NMR	598
Rh	i-Pr	I	I	PPh_3	IR, NMR	598
Rh^+	$CH_2CH{=}CH_2$	(η^2,η^3-C_8H_9)				608
Rh^+	$SiMe_3$	H	PMe_3	PMe_3	NMR, MS	599
Rh^+	PS–$C_6H_4CH_2$[e]	Cl	Cl	—	IR, Cat	579
Rh^+	CPh_3	Allyl[f]		Diene[f]	IR	610
Rh^+	CPh_3	Alleyl[g]		Diene[g]	IR	610
Rh^+	$C(CF_3)_2OH$[g]	[h]	[h]	[h]	NMR	600
Ir^+	Me	Me, H	PR_3[i]	PR_3[i]	NMR (^1H,^{13}C,^{31}P)	592(a),(b),595
Ir^+	Et	Me, H	PR_3[i]	PR_3[i]	NMR	592(a),(b),595
Ir^+	$-(CH_2)_4-$	$-(CH_2)_4-$	P(*p*-$C_6H_4F)_3$	P(*p*-$C_6H_4F)_3$/H	NMR	592(b)
Ir^+	Ph	H	PPh_3	PPh_3	NMR	594

[a] For abbreviations, see p. 3.

[b] Diene = 2,4-diphenyl-3,5-dimethoxycarbonylcobaltocyclopentadiene and 2,5-diphenyl-3,4-dimethoxycarbonylcobaltocyclopentadiene (see **438** for a related complex).

[c] See **443**.

[d] Bonded to SiO_2.

[e] See **424**.

[f] Ligand = 6-hydroxytricyclo[6,2,1,$0^{2,7}$]undeca-4,9-dien-3-yl.

[g] Ligand = 6-oxotricyclo[6,2,1,$0^{2,7}$]undeca-4,9-dien-3-yl.

[h] See **451**.

[i] R = C_6H_5, *p*-C_6H_4F.

TABLE 45

Cyclopentadienyl-bridged complexes of Co(III) and Rh(III)

M	M′	Bridges	Ligands as M	Ligands as M′	Comments[a]	Ref.
Co^+	Co^+	CH_2	X[b], PMe_3, PMe_3	X[b], PMe_3, PMe_3	IR, NMR (^1H, ^{31}P)	612
Co	Co	CH_2	Me, Me, PMe_3	Me, Me, PMe_3	NMR (^1H, ^{31}P)	612
Co	Co	CH_2	I, I, CO	I, I, CO	IR	612
Co^{2+}	Co^{2+}	CH_2	PMe_2H, PMe_2H, PMe_2H	PMe_2H, PMe_2H, PMe_2H		612
Co	Co	CH_2	I, COMe, CO	I, COMe, CO	IR, NMR (^1H, ^{31}P)	612
Rh^+	Rh^+	CH_2	H, PMe_3, L[c]	H, PMe_3, L[c]	NMR	556(a)
Rh^+	Rh^+	CH_2	Me, PMe_3, L[c]	Me, PMe_3, L[c]	NMR	556(a)
Rh^+	Rh^+	$SiMe_2$	Me, CO, PMe_3	Me, CO, PMe_3	IR, NMR	556(a)
Rh	Rh	CH_2	COMe, I, PMe_3	COMe, I, PMe_3	IR, NMR	556(a)

[a] For abbreviations see p. 3.

[b] X = H, Me.

[c] L = CO, C_2H_4, PMe_3.

TABLE 46

Substituted cyclopentadienyl dimers of Co and Rh with ligand bridges and metal–metal bonds

M	M′	R	Ligands on M	Ligands on M′	Comments[a]	Ref.
Co(I)	Co(III)	COMe, CO_2Me	C_4H_4[b]	C_4H_4[b]		546,590
Co(II)	Co(II)	$-CH_2-$	μ-PMe_2	μ-PMe_2	NMR	612
Co(II)	Co(II)	$CH_2/COCH_2$	[c]	[c]		540(c)
$Rh(II)^+$	$Rh(II)^+$	—	CO, L[h]	CO, L[h]	IR, NMR, Electro, X-ray	557(a),(b),(c)
Co(II)	Co(II)	Me	Me, μ-CO	Me, μ-CO[d]	IR, NMR	584(a),(b)
Co(II)	Co(II)	COMe, CO_2Me	[e]	[e]	IR, NMR, X-ray	590
Co	Co	Me	μ-NO[f]	μ-NO[f]	IR, NMR, MS	596
Co(0.5)	Co(0.5)	[g]	μ-CO	μ-CO	IR, ESR	583
Rh(I)	Rh(I)	Ph, CH_2Ph	CO, μ-CO	CO, μ-CO	IR, NMR	81
Rh(I)	Rh(I)	$-(CH_2)-$[i], $SiMe_2$	CO, μ-CO	CO, μ-CO	IR, NMR (^1H, ^{13}C), MS	555(a),556(a),558
Rh(I)	Rh(I)	$-(CH_2)-$[j]	CO, μ-CH_2	CO-μ-CH_2	IR, NMR (^1H, ^{13}C), UV, X-ray	558(b)

[a] For abbreviations see p. 3.

[b] See **395**.

[c] See **384**.

[d] See **428**.

[e] See **437**.

[f] See **442**.

[g] Metal–metal-bonded anionic radical dimer with substituted rings on each Co ($R = SiMe_3$, $SiMePh_2$, CO_2Me, CH_2CO_2Me).

[h] $L = P(OPh)_3$, PMe_3.

[i] See **399**.

[j] See **405**.

(vii) Nickel, palladium, and platinum [613–627]

Owing to the paucity of data in this area of chemistry, the three metals in their various oxidation states will be treated together. Preparative routes to the range of (η^5-C_5H_4R)M (M = Ni, Pd, Pt) containing fragments synthesised to date include:

(a) elimination of a cyclopentadienyl ring from substituted nickelocene, (η^5-$C_5H_4R)_2$Ni, or from the triple-decker sandwich complex, (η^5-$C_5H_4R)_3Ni_2^+$;

(b) addition of a substituted cyclopentadiene salt to a metal salt;

(c) reaction of a cyclopentadienyl precursor with $Ni(CO)_4$; and

(d) conversion of an unsubstituted ring attached to a metal to a (η^5-C_5H_4R)M fragment.

The reactive Ni sandwich complexes which contain substituted cyclopentadienyl rings provide a facile route to (η^5-C_5H_4R)Ni fragments. Thus, reaction of (η^5-$C_5H_4R)_3Ni_2^+$ or (η^5-$C_5H_4R)_2$Ni (in the presence of HBF_4/propionic acid) with L (L_2 = COD, NBD, diphos, L = py, etc.) produced the Ni(II), (η^5-$C_5H_4R)NiL_2^+$ complexes in good yield [613] (Table 47).

The logical route of adding a substituted cyclopentadiene salt to a metal complex has also been used successfully. Remarkably, the first report of the synthesis of a Pd(II) complex by this route was only published in 1985 [614]. Thus, reaction of $[PdCl_2(PR'Et_2)]_2$ (R' = Ph, Et) with Tl[C_5H_4C(i-Pr)=NC_6H_4Me] or Na[C_5H_4COR″] (R″ = Me, OMe), gave (η^5-C_5H_4R)PdCl(PR'Et_2) complexes via cleavage of the bridging Cl groups. Similarly, addition of C_5H_5R (R = $SiMe_3$, Me) to [Pd(C_6H_4-2-NNPh)Cl$]_2$ yielded (η^5-C_5H_4R)Pd(C_6H_4-2-NNPh) [615(a)]. Further reaction of this complex with L (L = phosphine) gave (η^5-C_5H_4R)Pd(C_6H_4-2-NNPh)L (**457**). NMR studies revealed that rotation around the Pd-C(aryl) bond was affected by the size of the ring substituent, R i.e. $H < Me < SiMe_3$. In a more recent study, the authors have further studied the Pd complexes as well as some equivalent Pt complexes [615(b)].

Eilbracht et al. [561,616] have synthesised some (η^5-C_5H_4R)Ni-containing complexes starting from $Ni(CO)_4$ and spiro dienes (see pp. 26 and 27, and **76–86**). The reactions yielded both monomeric and dimeric complexes. For instance, reaction of $Ni(CO)_4$ with **76b** yielded **85** and **86**, while reaction with the methyl-substituted three-membered ring ligand gave **458** and a variety of methyl substituted derivatives of **86**. However, no dimeric products were obtained on reaction of **459** with $Ni(CO)_4$; only **460** and **461** were obtained in variable yield, which was dependent on the reaction conditions.

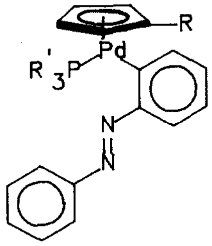
It is possible to prepare the substituted dimer [(η^5-C_5H_4R)Ni(CO)$]_2$ (**462**) by classical procedures [617]. X-Ray structures have been reported for the dimer where R = H, Me [618]. Mixed metal derivatives have also been synthesised and an X-ray structure has been determined for (η^5-C_5H_4Me)NiCo(μ-CO$)_2$(CO$)_2$L (L = PPh_2hexyl) (**463**) [619]. The solution-unstable products were synthesised from (η^5-C_5H_4R)Ni(CO)L^+ and $Co(CO)_4^-$ and the reaction involves an unusual migration of L from Ni to Co [619(b)].

TABLE 47

Substituted cyclopentadienyl complexes (η^5-C_5H_4R)M(A)(B) (M = Ni, Pd, Pt)

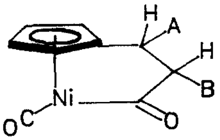
M	R	A	B	Comment[a]	Ref.
Ni^+	Me, *t*-Bu	NBD, COD		IR, NMR	613(a)
Ni^+	Me, *t*-Bu	L[b]	L[b]	IR, NMR	613
Ni	[c]	CO	[c]	IR, NMR, UV, MS	561,616
Ni	[d]	CO	[d]	IR, NMR, UV, MS	616
Ni	[e]	CO	[e]	IR, NMR, UV, MS	616
Ni	[f]	CO	[f]	IR, NMR, UV, MS	616
Ni	CHMePh, NM	$PPhMeCH_2COOEt$	I	NMR (^1H, ^{31}P), MS	626
Ni	CHMePh	$PPhMeCH_2C(OH)Ph_2$	I	NMR (^1H, ^{31}P), MS	626
Ni	CHMePh, NM	PPhR′[g]	I	NMR (^1H, ^{31}P), MS	626
Ni^{2+}	PPh_3	PPh_3	PPh_3	NMR	624(a)
Pd	C(i-Pr)=NC_6H_4Me	$PR'Et_2$[h]	Cl	IR, NMR, UV, MS	614
Pd	COR′ (R′ = Me, OMe)	PEt_2Ph	Cl	IR, NMR, UV, MS	614
Pd	Me, $SiMe_3$	C_6H_4-2-NNPh		NMR (^1H, ^{13}C)	615(a),(b)
Pd	Me, $SiMe_3$	C_6H_4-2-NNPh	PEt_3, PMe_2Ph PEt_2Ph, PCy_3	NMR (^1H, ^{13}C, ^{31}P)	615(a),(b)
Pd	$CH_2CH=CH_2$	CH_2Ph	PMe_3	NMR (^1H, ^{13}C, ^{31}P) IR, MS	113
Pd	p-FC_6H_4	C_3H_5		NMR (^{19}F)	627
Pd	Et, *t*-Bu	Et	CH_2CH_2	NMR (^1H, ^{13}C)	621,622
Pd^{2+}	PPh_3	$C_4(CO_2Me)_4$		X-ray, NMR	624(c)
Pd^{2+}	PPh_3	COD, NBD		NMR, IR	177(b),624
Pt^{2+}	PPh_3	COD, NBD, COT		NMR	177(b)
Pd^{2+}	PR'_3[i]	Allyl[i]		NMR (^1H, ^{19}F)	624(b),626,627
Pd^{2+}	PPh_3	Allyl PR_3^{+}[j]		NMR	624(b),(d)
Pt[k]	$SiMe_3$	CH_3	CH_3	–	625
Pt	$SiMe_3$	C_6H_4-2-NNPh		NMR	615(b)

[a] For abbreviations see p. 3.
[b] $L = PPh_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, $AsPh_3$, Py, ½bipy, ½diphos.
[c] See **85**.
[d] See **458**.
[e] See **460**.
[f] See **461**.
[g] See **467**.
[h] $R' = Ph$, Et.
[i] $R' = Ph$, p-FC_6H_4, m-FC_6H_4, allyl = 2-Me-allyl, 3-Me-allyl, allyl.
[j] Allyl = 1-C_6H_5 allyl, R = Me-allyl, R = Ph, Et.
[k] This is a Pt(IV) complex: $(\eta^5\text{-}C_5H_4SiMe_3)PtCH_3$.



R=Me,SiMe$_3$

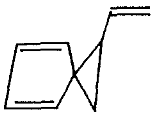
457



A=Me; B=H

A=H; B=Me

458



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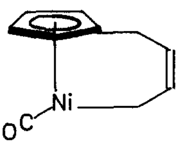

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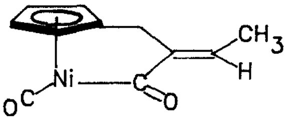

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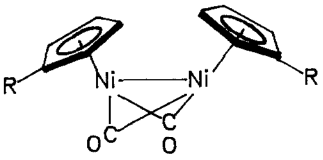

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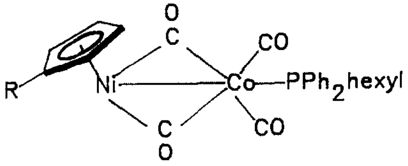
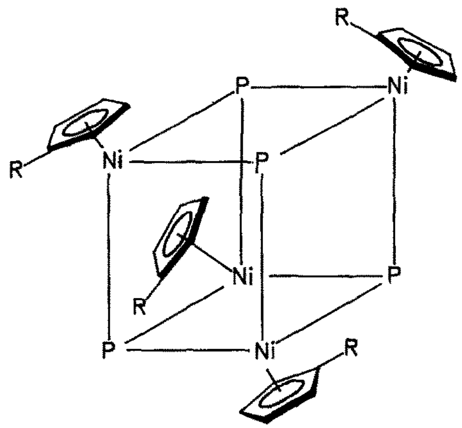


463 (R=Me)

Thermolysis of **462** (R = Me, *t*-Bu) in the presence of P_4 gives the unusual nickelaphosphacubane **464** [620].

Substitution of a C_5H_5 ring attached to a metal has also been reported. Thus, reaction of (η^5-C_5H_5)Pd(η^3-C_3H_6) with PMe_3 and cyclopropabenzene gave **465** [113], a reaction in which a metal-to-ligand shift of an allyl group has taken place.



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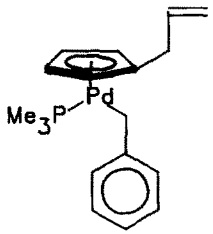
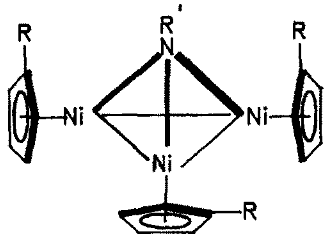
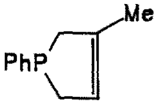


465



R=H,t-Bu,C_6H_5; R'=t-Bu,C_6H_5

466



467

Addition of RMgX (R = *t*-Bu, Et) to $(\eta^5\text{-}C_5H_4R)_2Ni$ in the presence of ethylene yields $(\eta^5\text{-}C_5H_4R)NiEt(CH_2{=}CH_2)$ as the final product [621,622]. Addition of LiR (R = *t*-Bu, Et) to $(\eta^5\text{-}C_5H_5)NiNO$ gives trimer products (**466**) in which the C_5H_5 rings have been substituted, the degree of substitution being dependent on reaction temperature, etc. [623].

It is to be noted that Ni, Pd, and Pt complexes containing the $C_5H_4PPh_3$ ligand have been described [624]. Finally, complexes containing both chiral cyclopentadienyl ligands and chiral phosphine ligands (e.g. **467**) have also been synthesised [626].

E. PROPERTIES OF $(\eta^5\text{-}C_5H_4R)ML_x$ COMPLEXES [628–719]

In this section, an assessment of studies performed on $(\eta^5\text{-}C_5H_4R)ML_x$ complexes will be given. The emphasis will be placed on the properties of the ring with particular emphasis on the influence of the ring substituent on the properties under consideration. This section will include the following topics:

(a) spectroscopic investigations,
(b) crystallographic data analysis,
(c) theoretical studies,
(d) ring rotational barrier studies, and
(e) steric properties.

Although it is not possible to mention all the studies in which the chemical and physical properties of $(\eta^5\text{-}C_5H_4R)ML_x$ complexes have been described, it is believed that this section does include the most pertinent studies.

(i) Spectroscopic studies

(a) IR and Raman spectroscopy

In 1964, Fritz [628] published a review article on the IR and Raman spectra of $(C_nH_n)ML_x$ complexes. Since this review, numerous other studies have been undertaken on related complexes [629–634]. A recent article [632(b)] has tabulated and updated the fundamental frequencies associated with a range of salts and complexes containing the cyclopentadienyl ligand (Table 48). The main points of interest mentioned in this study are:

(a) in the D_{5h} symmetry group (ionic $C_5H_5^-$), four IR and seven Raman active vibrations are permitted;

(b) the band position, $\bar{\nu}$(CH), varies with the polarity of the C_5H_5–M interaction, and can be used to differentiate between ionic and covalent C_5H_5–M bonds; and

(c) the weak intensity of the IR allowed ν(CC) ring breathing mode at 1100 ± 10 cm^{-1}, and the low intensity of the ν(CC) Raman active vibration at 1430 ± 20 cm^{-1}, are useful in establishing the presence of ionic C_5H_5–M bonds.

The above information allows an evaluation of the degree of charge transfer between the cyclopentadienyl ring and the M atom in $(\eta^5\text{-}C_5H_4R)ML_x$ complexes. The influence of ring substituents on the C_5H_4R–M interaction could, in principle, be evaluated by IR and Raman spectroscopy. To date, however, few studies of this type have been undertaken [635]. The main reason for this is that the absorptions of interest occur in the 700–1400 cm^{-1} region of the spectrum, a region in which numerous other absorptions are found, and in which vibrational coupling can occur.

Addition of a substituent to a cyclopentadienyl ring causes a reduction in the overall symmetry of $(\eta^5\text{-}C_5H_4R)ML_x$ complexes and this provides the basis for the "9–10 μ rule" [636], which provides evidence for the replacement of a ring H atom by a substituent.

The ring substituent, R, has its own characteristic IR and Raman absorptions and these can be used to establish ring functionalisation. The position [526,635(d),637] and the intensity [638] of the substituent vibration can be influenced

TABLE 48

Comparison of the C_5H_5-ring fundamental frequencies of various cyclopentadienyl compounds[a]

ν_i	Symmetry C_{5v} model MCp	Symmetry D_{5h} free $C_5H_5^-$	Assignments	C_5H_5K[b]	C_5H_5K	C_5H_5Na	C_5H_5Li	C_5H_5Tl	$(C_5H_5)_2Mg$	$(C_5H_5)_2Fe$
ν_1	A_1	A_1'	ν(CH)	3043	3088	3090	3104	3096	3102	3100
ν_6	E_1	E_1'	ν(CH)	3048	~3061	3067	3082	3070	3076	3080
ν_{11}	E_1	E_2'	ν(CH)	3096	~3061	3060	3080	3065	3064	3090
ν_7	E_1	E_1'	ν(CC)	1445	1440	–	1433	1425	1425	1410
ν_{12}	E_2	E_2'	ν(CC)	1447	1346	1342	1346	1350	1342	1350
ν_2	A_1	A_1'	ν(CC)	983	1119	1114	1114	1120	1113	1110
ν_{13}	E_2	E_2'	β(CH)	1020	1070	1062	1067	1060	1060	1060
ν_8	E_1	E_1'	β(CH)	1008	1008	998	1006	1008	1007	1000
ν_{14}	E_2	E_2'	γ(CH)	565	854	848	854	843	~871	900
ν_9	E_1	E_1''	ρ(CH)	625	719	730	759	754	~750	830
ν_3	A_1	A_2''	ρ(CH)	702	~719	~722	~735	727	~768	800

[a] Data taken from ref. 632(a).

[b] Data from refs. 628 and 629.

by the electronic properties of the ligand set (L_x) and can, in principle, be used to evaluate the electron-accepting/withdrawing capabilities of R.

(b) ESR spectroscopy

ESR spectroscopic studies have been carried out on both cyclopentadienyl radicals and (η^5-C_5H_5R)ML_x complexes. For instance, a series of C_5H_4R radicals have been generated from C_5H_5R by H abstraction with a *t*-butoxy radical [639], or from (η^5-C_5H_4R)$_2$Hg by photolysis [640]. When R = $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, the ESR data indicate that the substituents are electron-accepting as a result of d_π–p_π conjugation. When R = alkyl, an analysis of the ESR spectra provides evidence for the electron-releasing capacity of the R group.

ESR studies performed on (η^5-C_5H_4COPh)$Mn(CO)_2L$ (L = CO, Group 15 donor ligand) and related complexes have been interpreted in terms of extensive electron delocalisation over the *whole* molecule (Mn, Ph, CO) [641].

(c) NQR spectroscopy

This technique can be used to assess the ground-state electron distribution in appropriate (η^5-C_5H_4R)ML_x complexes (e.g. containing the isotopes ^{59}Co [642], $^{187/189}Re$, ^{55}Mn, and ^{127}I).

Extensive studies on (η^5-C_5H_4R)$M(CO)_3$ (M = Mn, Re) have been performed and variation of both R and M permitted the following generalisations:

(a) the influence of R on the asymmetry parameter was ascribed to a direct interaction between M and R (R = COMe, $COCF_3$, COPh) [643–645];

(b) the influence of R on Mn and Re is via a conjugation or resonance, and not inductive, mechanism [645,646];

(c) the electric field gradient at the Re nucleus is five to six times the size of the gradient at the Mn nucleus [647];

(d) the NQR ratios for ^{185}Re and ^{187}Re have been measured for a wide range of R groups [648]; and

(e) the higher NQR frequency for ^{127}I in (η^5-C_5H_4I)$M(CO)_3$ (M = Mn, Re) when M = Re implies that the "(C_5H_4)$Re(CO)_3$" group is a better electron acceptor than the "(C_5H_4)$Mn(CO)_3$" group [645].

(d) NMR spectroscopy

This technique has been widely used in the study of both substituted and unsubstituted cyclopentadienyl rings. In general, three types of study have been undertaken:

(a) characterisation of the (η^5-C_5H_4R)ML_x complex from ^1H and ^{13}C spectra establishing the *presence* of both the ring and the ring substituent, and *correlation* of the specific resonance, with a specific ring atom;

(b) determination of electronic (and steric) parameters associated with the ring substituent by means of ^1H and ^{13}C chemical shift measurements. The influence of these parameters can also be probed by other NMR active nuclei (e.g. ^{31}P, M, etc.); and

(c) determination of ring rotational barriers.

(1) Characterisation of complexes. The unsubstituted cyclopentadienyl ring gives single ^{1}H and ^{13}C resonances, downfield from TMS, at $\delta = \sim 4$ ppm and ~ 80 ppm [649], respectively. The precise value of the chemical shift depends on the metal [650], the other ligands associated with the molecule, the charge on the complex, the solvent, etc. If the molecule is paramagnetic, extreme shifts can be observed (over 230 ppm) [651]. The ^{1}H and ^{13}C resonances occur as multiplets if coupling to the metal or other ligands in the complex takes place.

Replacement of one of the ring protons by a substituent, R, results in magnetic and chemical non-equivalence of the four H atoms and five C atoms. If the complex retains a plane of symmetry, two ^{1}H and three ^{13}C resonances can be observed in the NMR spectrum [443(a),652]. The two ^{1}H resonances are associated with protons H2/H5 (α protons) and protons H3/H4 (β protons), respectively (**380**). Due to the numerous $^{1}H-^{1}H$ couplings that are possible (Fig. 5), the resonances generally occur as multiplets, typically as "triplets". The three ^{13}C resonances are associated with C1 (ipso carbon), C2/C5 (α carbons) and C3/C4 (β carbons), respectively. Since the R group usually provides a poor relaxation pathway for C1 in the NMR experiment, this resonance can readily be identified by its low intensity [136(c),443(a)]. Resonances due to C3/C4 and C2/C5 occur as singlets in the ^{1}H decoupled spectrum provided no coupling to R, M or L takes place.

When the (η^{5}-C_5H_4R)ML_x complex has no plane of symmetry, the molecule becomes chiral, and all four H and all five C atoms are chemically and magnetically

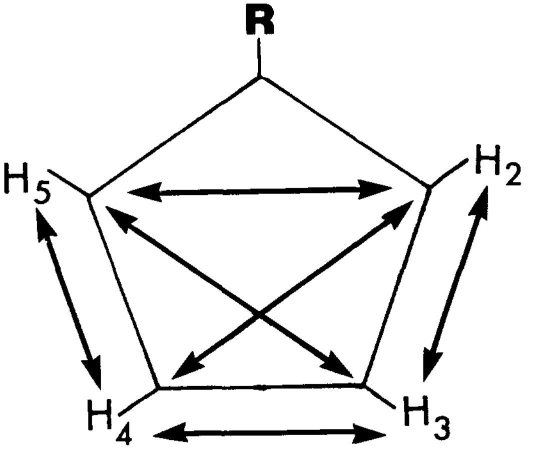


Fig. 5. (C_5H_5)ML_x viewed perpendicular to the ring. The ML_x system is not shown. The possible J(HH) couplings are shown.

non-equivalent. If the four H atoms constitute an ADMX system, four distinct resonances can be observed [443(a),653]. However, more complex spectra associated with an ABCD system have been detected [243].

To assess the influence of steric and/or electronic effects of R on the ring NMR resonances, it is necessary to assign the resonances in the NMR spectrum to specific C and H ring atoms. It is also possible to correlate the steric and electronic effects of R via measurement of other NMR parameters associated with the complex, for instance, chemical shift measurements of M (e.g. Ti, Mo, V) or L (e.g. CO). The procedures to establish the correlations are described below.

(a) Chemical shift measurements. It was initially assumed that R would cause greater shielding (R, electron-donating) or deshielding (R, electron-withdrawing) of the ring atoms (C, H) closest to the R group [654]. Later work has shown that the position of the H resonance is temperature dependent and that the method is unreliable [136(c)].

(b) Deuteration studies. It is possible to deuterate the ring prior to, or after, addition to the metal (see Sect. C.(ii)(a)(4)). Depending on R, and the reagents used, deuteration can be achieved at either H2/H5 or H3/H4. A comparison of the deuterated and non-deuterated NMR spectra thus leads to assignment of the ^{1}H spectrum. This technique was initially used on fulvenes, and later extended by Rausch et al. to ferrocenes [655]. Arthurs et al. have used this technique extensively in a study of (η^5-C_5H_4R)RhL_2 complexes [136(c)].

(c) Lanthanide shift reagents. Addition of a lanthanide shift reagent to suitable (η^5-C_5H_4R)ML_x complexes results in an interaction between the shift reagent and R. This, in turn, results in a shift of the ^{1}H and ^{13}C resonances to lower field. The shift is dependent on the proximity of the H or C ring atoms to R. Generally, a larger downfield shift of ^{13}C and ^{1}H resonances is expected for atoms in positions 2 and 5 than for 3 and 4. The method is most successful when R contains a "hard" atom (e.g. O, N) and has little use when R = Me, *t*-Bu, etc. [136(c)].

(d) Coupling constant measurements. Equal coupling of the ring protons to the ring C atoms, R, other ring protons, or M is not always observed [136(c)]. This has been proposed to arise from variable C—C bond lengths, ring-slip etc. The size of the C—H coupling constant can assist in assigning the ^{13}C NMR spectrum [656], viz. for C3/C4, $^2J(CH) < {}^3J(CH)$ and for C2/C5 $^2J(CH) = {}^3J(CH)$. However, this procedure is not infallible, for instance, the coupling, J(H3–R), is, on occasion, unexpectedly *larger* than J(H2–R) [136(c),656]. Partial proton decoupling of a ^{13}C NMR spectrum establishes a correlation between ring H and C atoms [136(c),656]. This technique does require prior interpretation of the proton spectrum.

(e) 2D NMR spectroscopy. This procedure permits assignment of ^{13}C NMR spectra, again, once the proton spectrum has been elucidated [136(b),443(a)].

(f) NOE measurements. This provides an unambiguous method of correlating ring protons with NMR resonances and is independent of the nature of R [443(a)].

If R contains protons, further correlations are possible. An example of the use of this technique is shown for (η^5-C_5H_4R)Fe(CO)(PPh_3)I below (Fig. 6).

The effect of irradiating the various ring protons, in the NOE experiment, is clearly evident. For example, irradiation of resonance 2 (Fig. 6(f)) indicates that this proton is close to only one other proton (resonance 3). Irradiation of the other resonances provides further information for assigning all protons to the NMR resonances.

(2) Electronic (and steric) effects. NMR spectroscopy provides one method of probing and assessing these parameters in (η^5-C_5H_4R)ML_x complexes.

The electronic effects associated with R are generally determined by correlating an electronic parameter with the position of the ^1H or ^{13}C chemical shift [657,658]. (It is to be noted that attempts to determine *theoretically* the values of the shielding parameters of large molecules containing cyclopentadienyl ligands is continuing [659].) Attempts have been made to correlate Hammett functions [660], substituent electronegativity and field parameters with the electronic properties of R [566,570,571]. Since the influence of R is transmitted to the metal atom and to L in (η^5-C_5H_4R)ML_x complexes, the electronic effect can be determined by measuring properties associated with M or L. These include:

(a) metal NMR spectral parameters (e.g. chemical shift values for ^{59}Co [564(a),565] and ^{49}Ti [661]), or L spectral parameters (^{19}F [148,634,657,663] and ^{17}O [635(c)]). Studies on related (C_nH_n)ML_x complexes have also provided similar results (e.g. ^{59}Mo [662], ^{51}V [260,664], ^{31}P [260]), and

(b) other parameters associated with the molecule, e.g. ν(CO) vibrational data [637(a)].

Data can also be obtained from studies on the cyclopentadienide ion, e.g. pK_a [16,135], ^{19}F NMR data [148] etc.

Although it is often proposed that the steric size of R can influence the chemical and physical properties of (η^5-C_5H_4R)ML_x complexes, no quantitative measure of this effect has been reported to date. (See, however, Sect. E.(v).)

One example, which indicates the importance of the electronic effect of R on chemical reactivity is taken from the work of Bönnemann et al. [564]. The trimerisation of propyne and acetonitrile, to yield substituted pyridines, is catalysed by "(η^5-C_5H_4R)Co". The ^{59}Co chemical shift correlates with the electronic property of the R group. Electron donors (e.g. Me) increase the deshielding of the metal centre, while electron acceptors (e.g. COOMe) cause a decrease in the deshielding of the metal centre. Minimal steric effects are expected. The electronic effect is additive: C_5Me_5 gives a five times higher ^{59}Co shift value than does C_5H_4Me.

Importantly, the electronic effect associated with R correlates directly with the catalyst activity and selectivity in product formation (a and b, Fig. 4). This is shown in Fig. 7 [564(a)].

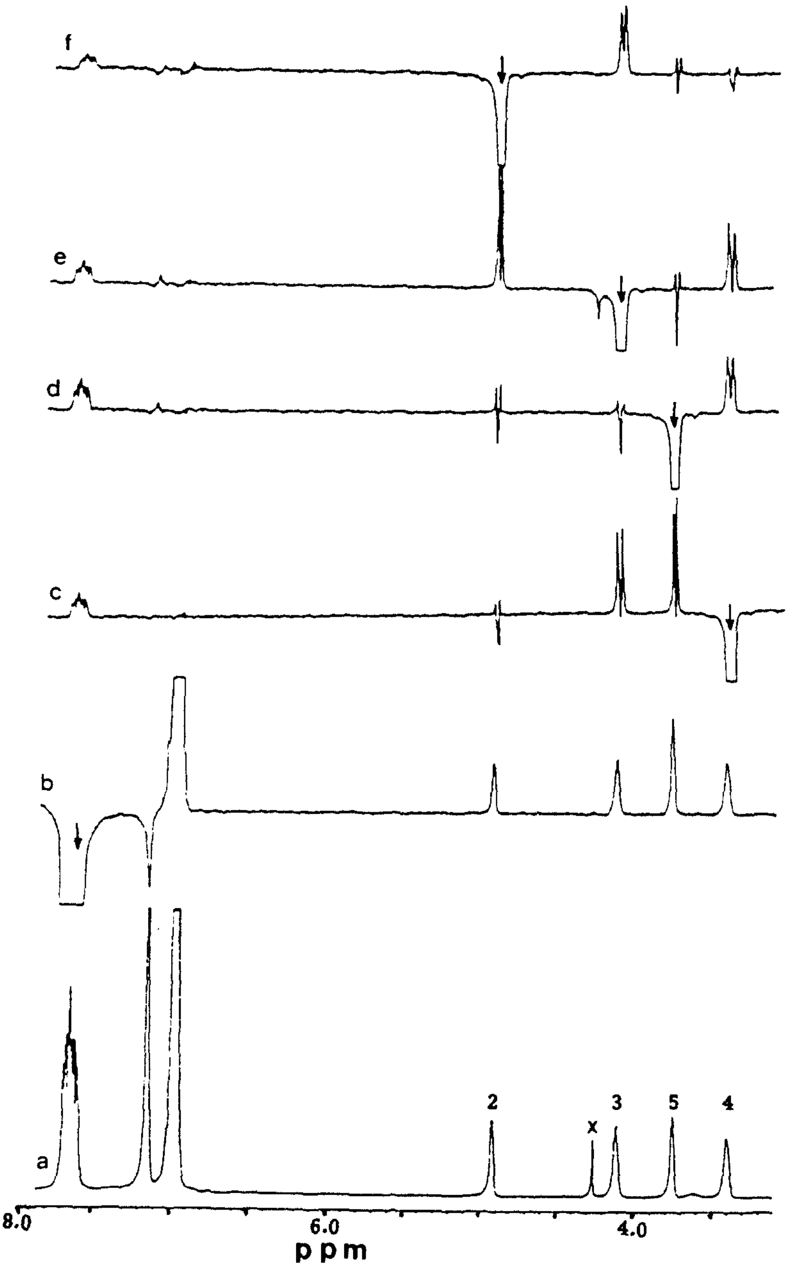


Fig. 6. NOE difference spectra for (η^5-C_5H_4I)Fe(CO)(PPh$_3$)I [715(a)]. The non-irradiated spectrum is shown in (a). Irradiated spectra are shown in (b)–(f). (b) Irradiation of ortho proton of PPh$_3$; (c) irradiation of ring proton 4; (d) irradiation of ring proton 5; (e) irradiation of ring proton 3; and (f) irradiation of ring proton 2. × = impurity peak.

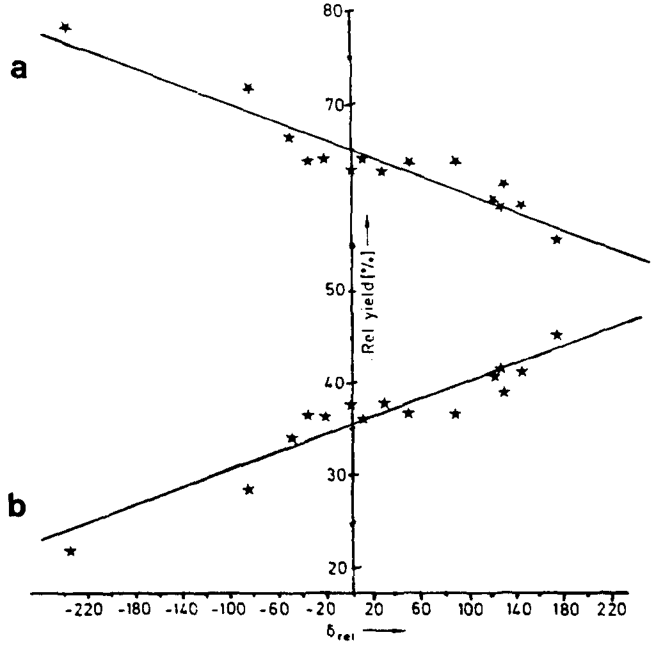


Fig. 7. Reactivity of $(C_5H_5)Co(COD)$ complexes as a function of ^{59}Co NMR spectral shifts. Relative yields of the isomers **a** and **b** from Fig. 4 for the Co-catalysed trimerisation reaction between propyne and acetonitrile [564(a)] are shown.

(3) Ring rotational barriers. To obtain an understanding of the bonding interaction between a C_5H_5 ligand and a metal, it is important to have information about both the static structure and the dynamic behaviour of a $(C_5H_5)ML_x$ complex. Dynamic behaviour can be studied using NMR techniques, which can give information about the rotational behaviour of the ring and other ligands in the complex.

Thus, NMR studies have been performed on a range of $(C_nH_n)ML_x$ complexes where $n=4$ [673], $n=5$ [665–667], $n=6$ [675], and $n=7$ [672]. Because the barrier to ring rotation is low, broad-line NMR measurements of line widths and second moments are possible at low temperatures. Hence, spin-lattice relaxation times for a range of nuclei (^1H [667,672,673], ^2D [670], ^{13}C [668], ^{19}F [672], and ^{103}Rh [665]) have been reported (Table 49). Line-shape analysis of VTNMR solution spectra have also given information about ring rotational barriers (Table 49).

The results in Table 49 clearly indicate the low barrier to ring rotation for the unsubstituted cyclopentadienyl ring. The rotational barrier can be increased by steric (and electronic) factors via modification of the ring or the ligands. For instance, it has recently been reported [666] that the ^{13}C NMR spectrum of $(\eta^5\text{-}C_5H_5)Os(PPh_3)_2(CH_2CHPh)^+$, recorded at −100°C shows five resolved ring C atom resonances. If the temperature is raised to −30°C, a single resonance is observed,

TABLE 49

Ring rotational barriers for some cyclopentadienyl metal complexes

Ring	Complex	Method[a,b]	$E_a{}^c$/kJ mol^{-1}	Ref.
C_5H_5	$(\eta^5\text{-}C_5H_5)Mn(CO)_3$	QENS	16.8	684
C_5H_5	$(\eta^5\text{-}C_5H_5)Mn(CO)_3$	SLR	7.24	667(a)
C_5H_5	$(\eta^5\text{-}C_5H_5)Re(CO)_3$	SLR	7.15	667(a)
C_5H_5	$(\eta^5\text{-}C_5H_5)V(CO)_4$	SLR	7.07	667(a)
C_5H_5	$(\eta^5\text{-}C_5H_5)TiCl_3$	SLR	9.6	667(b)
C_5H_5	$(\eta^5\text{-}C_5H_5)Rh(COD)$	^{13}C SLR	8.1	665
C_5H_5	$(\eta^5\text{-}C_5H_5)Ir(COD)$	^{13}C SLR	7.1	665
C_5H_5	$(\eta^5\text{-}C_5H_5)Os(PPh_3)_2(CH_2CHPh)^+$	^{13}C VTNMR	34.2[d]	666
C_5H_5	$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$	SLR	13.9	667(b)
C_5D_5[e]	$[(\eta^5\text{-}C_5D_5)Fe(CO)_2]_2$	^2D SLR	12.5	670
$C_5H_4n\text{-}Bu$	$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4n\text{-}Bu)Fe$	^{13}C SLR	11.7	668
$C_5H_4CMe_2Et$	$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CMe_2Et)Fe$	^{13}C SLR	15.2	668
$C_5H_3(t\text{-}Bu)_2$	$[\eta^5\text{-}C_5H_3(t\text{-}Bu)_2]_2Fe$	^1H VTNMR	54.7[f]	671
$C_5H_3(i\text{-}Pr)(t\text{-}Bu)$	$[\eta^5\text{-}C_5H_3(i\text{-}Pr)(t\text{-}Bu)]Co(PMe_3)_2$	^1H VTNMR	–	588(c)
$C_5H_3(t\text{-}Bu)_2$	$[\eta^5\text{-}C_5H_3(t\text{-}Bu)_2]Co(PMe_3)_2$[g]	^1H VTNMR	–	588(c)

[a] QENS = quasi-elastic neutron scattering.

[b] SLR = spin lattice relaxation.

[c] Barrier to ring rotation.

[d] $\Delta G_{183}\ddagger$.

[e] 70% C_5D_5 and 30% C_5H_5.

[f] $\Delta G_{300}\ddagger$.

[g] Rotational barrier also established for $[\eta^5\text{-}C_5H_3(t\text{-}Bu)_2]CoMe(PMe_3)_2^+$ salt.

suggestive of free ring rotation. This is the first example of an unsubstituted ring showing restricted rotation, presumably as a result of steric congestion at the metal.

Modification of the complex by the use of bulky ring substituents also leads to restricted ring rotation. This procedure has been applied to both substituted cyclopentadienyl [588(c),669,671] and arene [674–677] metal complexes.

The steric interaction should be reciprocal, and rotation of R or L should thus also be influenced by the cyclopentadienyl (or arene) ligand. Although numerous reports about the rotation of the ligand, L, in cyclopentadienyl-containing complexes have been published [615,679–682], no systematic investigation of the effect of the size of the ring substituent on the L rotational barrier has been established.

(e) Other techniques

(1) Mass spectroscopy. Numerous articles have appeared in which the mass spectra of (η^5-C_5H_4R)ML_x complexes have been reported. Some of these articles have dealt specifically with the influence of R on the detection and intensity of the ions generated in the mass spectrometer. One of the earliest reports of this type was by Cais et al. on (η^5-C_5H_4R)$Mn(CO)_3$ complexes [686]. Since then there have been numerous studies [687–689] on related (η^5-C_5H_4R)$M(CO)_3$ (M = Mn, Re) complexes, mainly by Russian workers [690]. The Re(III) complexes, (η^5-C_5H_4R)$Re(CO)_2XY$, have also been studied [436].

(2) UV/visible spectroscopy. UV spectra have been reported for many (η^5-C_5H_4R)ML_x complexes but, to our knowledge, no systematic studies have been performed.

(3) Redox studies. Comparative studies on the redox properties of cymantrene complexes have been reported [691]. A series of unstable 17-electron species have been generated and proposed as "catalysts" in CO substitution reactions [433].

(4) Miscellaneous. Molar refraction data for a series of (η^5-C_5H_4R)$Mn(CO)_3$ (R = Me, Et, i-Pr) have been reported [692]. Photoelectron spectra are discussed in Sect. E.(iii)(c).

(ii) Crystallographic data analysis (see Table 50)

X-Ray crystallography has been used to elucidate a number of significant structural features of substituted cyclopentadienylmetal complexes [715(d)]. Some examples of these types of feature are outlined below.

When substituted cyclopentadienyl complexes, and complexes with different ligands on the metals, are compared with symmetrical metal cyclopentadienyl complexes, the former cases exhibit far more complex bonding. Thus, the bonding between

TABLE 50

Crystallographic data for the compounds $(\eta^5\text{-}C_5H_4R)M(A)(B)(C)(D)$

M	R ($\alpha^{a,b}$)	A ($\Phi^{b,c}$)	B ($\Phi^{b,c}$)	C ($\Phi^{b,c}$)	D ($\Phi^{b,c}$)	Ref.
V	Me	Cl	Cl	Cl	–	265
	(3, 9)	(−125)	(0)	(118)		
V	COMe	CO	CO	CO	CO	254
	(−0, 7)	(32)	(−58)	(121)	(−149)	
Cr	CHO	CO	CO	NO	–	381(a)
	(1, 5)	(63)	(−50)	(−175)		
Cr^+	CHO	CO	CO	CO	–	146(b)
	(3, 0)	(−65)	(55)	(174)		
Cr	CHO	CO	CO	CO	$AuPPh_3$	324
	(−2, 3)	(49)	(151)	(−58)	(−135)	
Cr	CN	CO	CO	NO	–	381(a)
	(2, 8)	(58)	(−64)	(176)		
Cr	NH_2	CO	CO	NO	–	381(a)
	(7, 2)	(97)	(−21)	(−144)		
Cr	PPh_3^+	CO	CO	CO	–	325
	(9, 8)	(−43)	(79)	(−166)		
	(5, 8)	(−52)	(75)	(−172)		
Cr	SMe_2^+	CO	CO	CO	–	322
	(3, 6)	(171)	(−71)	(53)		
Mo	Me	CO	CO	HgI	$AsPhMe_2$	355
	(6, 3)	(38)	(−135)	(−48)	(129)	
Mo	Me	CO	CO		(THF)	354
	(0, 1)	(156)	(−107)	(51)	(7)	
Mo	Me	CO	CO	$P(OMe)_3$	I	353
	(0, 7)	(38)	(−142)	(127)	(−51)	
Mo^d	Me	CO	CO	CO	HgCl	352
	(2, 9)	(−60)	(36)	(132)	(−144)	

Mo	Me (8, 1)	CO (47)	CO (−47)	I (−5)	I (132)	I (−138)	344
Mo	CHO (2, 2)	CO (145)	CO (−65)	CO (42)		$AuPPh_3$ (−140)	282(a)
Mo	COMe (−1, 2)	CO (−148)	CO (−49)	(η^3-allyl) (85)			302
Mo[e]	NM (2, 4)	NO (−3)	CO (−119)	(η^2-$C_8H_{15}CHO$) (130)		–	309
Mo[f]	NM (10, 3)	NO (23)	Br (126)	(η^3-C_8H_{13}) (−117)			310
Mo[g]	NM (7, 2)	NO (−50)	I (54)	(η^3-C_3H_5) (180)			307,308
W	CH_2OCOMe (7, 7) (6, 8)	CO (−129) (−134)	CO (−37) (−42)	CO (52) (46)		Cl (142) (137)	283
W	C_2X^h (5, 6)	CO (91)	CO (−75)	CO (−170)		Me (10)	394
Mn^-	Me (0)	CO (−178)	CO (−44)	GeH_3 (64)		–	718(a)
Mn	Me (0)	CO (166)	CO (−14)	$GeCl_3$ (−106)		$GeCl_3$ (80)	718(a)
Mn	Me (1, 5)	CO (87)	CO (−30)	PPh_3 (−154)		–	718(b)
Mn	Me (3, 1)	CO (68)	CO (−47)	$S{=}C(Ph)SCH_2C(S)NMe_2$ (−169)		–	718(c)
Mn	Me (2, 3)	CO (−159)	CO (93)	$N_2C_6H_4CF_3$ (−34)		–	718(d)
Mn	Me (6, 0)	CS (−25)	NO (100)	I (−135)		–	718(e)
Mn	Me (3, 9)	CO (−26)	CO (−142)	SMe_2Et (99)		–	718(f)
Mn	COMe (1, 4)	CO (176)	CO (58)	CO (−60)		–	644

TABLE 50 (*continued*).

M	R ($\alpha^{a,b}$)	A ($\Phi^{b,c}$)	B ($\Phi^{b,c}$)	C ($\Phi^{b,c}$)	D ($\Phi^{b,c}$)	Ref.
Mn	CHMe(NHCOMe)[i]	CO	CO	CO	–	653(b)
	(3, 8)	(0)	(−122)	(119)		
Mn	C(S→X)Ph[j]	CO	CO	CO	–	719
	(0, 2)	(−75)	(45)	(165)		
Mn	Ti(η^5-C_5H_5)$_2$X[k]	CO	CO	CO	–	717
	(8, 2)	(12)	(−115)	(134)		
Mn	Fe(η^5-C_5H_5)(CO)L	CO	CO	CO	–	191(a)
L = CO	(7, 1)	(1)	(−118)	(122)		
L = PPh_3	(5, 4)	(−26)	(−143)	(93)		
Mn	C_2X^h	CO	CO	PPh_3	–	394
	(−1, 0)	(−37)	(82)	(−160)		
Re	COMe	CO	CO	CO	–	644
	(1, 6)	(−168)	(65)	(−58)		
Re	$SiMe_3$	CO	CO	CO	–	716
	(3, 5)	(−60)	(60)	(180)		
Fe	Me	CO	I	2,6-$Me_2C_6H_3NC$	–	443(f)
	(4)	(−121)	(22)	(117)		
Fe	Me	CO	I	$P(OMe)_3$	–	443(f)
	(3)	(−47)	(−165)	(74)		
Fe	Me	CO	I	$P(C_6H_{11})_3$	–	443(f)
	(6)	(−154)	(−45)	(80)		
Fe	*t*-Bu	CO	I	PPh_3	–	443(a)
	(8, 8)	(−1)	(−116)	(121)		
Fe	$CHPh_2$	CO	I	PPh_3	–	443(d)
	(3)	(−73)	(44)	(166)		
Fe	I	CO	I	PPh_3	–	443(d)
	(4)	(−48)	(68)	(−167)		
Fe	COMe	NCMe	dppe[l]		–	438,504
	(−2, 0)	(−57)	(68, −174)			

Fe	NEt_2 (6, 8)	CO (−127)	Br (−7)	$PPh(OEt)_2$ (108)	–	163,164
Fe	$SiMeX_2$[m] (−0, 9)	CO (80)	CO (−52)	Et (−163)	–	369
Ru	$C(CF_3)_2OH$ (9, 8)	PPh_3 (156)	$-OC(OMe)CHCCO_2Me$ (−20)	(−101)	–	501(a,b)
Ru	C_2CO_2Me (−2, 8)	PPh_3 (136)	PPh_3 (−94)	Cl (24)	–	502
Ru	C_5H_4 (9, 7)	CO (−116)	PMe_3 (−3)	PMe_3 (119)	–	514
Ru[n]	Menthyl (2, 4)	CO (−77)	PPh_3 (−165)	I (77)	–	453(a)
Ru[o]	NM (9, 8)	CO (−9)	PPh_3 (117)	I (−145)	–	453(c)
Ru[p]	NM (6, 0)	CO (58)	PPh_3 (180)	NCMe (−64)	–	453(d)
Ru[q]	NM (7, 6)	CO (−35)	PPh_3 (96)	Me (103)	–	453(e)
Ru[r]	NM (10, 1)	CO (−45)	PPh_3 (−170)	SO_2Me (72)	–	453(e)
	(6, 5)	(−57)	(178)	(58)		
Co	PPh_3 (4, 8)	CO (91)	CO (−96)	–	–	542
Co	CO_2Me (1, 2)	PPh_3 (171)	Me (−67)	Me (49)	–	589
Co[s]	CO_2Me (2, 3)					590
Co	CO_2Me (−2, 4)	PPh_3 (−161)	$-(CH)_4-$ (−34)	(72)	–	590
Rh	CHO (−0, 3)	(η^4-2,4-$Me_2C_5H_6$)		–	–	537(a)
Rh	CO_2Me (0, 9)	(Cod)		–	–	136(c)

TABLE 50 (*continued*).

M	R ($\alpha^{a,b}$)	A ($\Phi^{b,c}$)	B ($\Phi^{b,c}$)	C ($\Phi^{b,c}$)	D ($\Phi^{b,c}$)	Ref.
Rh	NO_2 (3, 7)	CO (72)	CO (−111)	–	–	157(b)
Rh	PPh_3 (7, 6)		(Cod)	–	–	543
Rh	$(\eta^5\text{-}C_5H_4)Rh(CO)(PPh_3)$ (3, 2)	CO (158)	PPh_3 (−24)	–	–	557(b)
Ir	$C(Me){=}CH_2$ (1, 7)		(Cod)	–	–	540(d)

[a] Value given in parentheses is the angle, α, by which the substituent R deviates from the mean plane defined by the cyclopentadienyl ring (Fig. 10). A positive value indicates a deviation in the direction *away* from the metal and a negative value signifies bending *towards* the metal.

[b] Multiple values are given if the structure determination shows more than one crystallographic independent molecule.

[c] Value in parentheses is the torsional angle, Φ(C-cen-M-L); where C is the substituent-carrying cyclopentadienyl ring carbon, cen is the cyclopentadienyl ring centroid, M is the metal and L is the ligand A, B, C, D, or E. Negative and positive values indicate clockwise and counterclockwise rotations, respectively. With ligands bonding via more than one atom to the metal, the torsional angle given is that of the centre between the two extreme atoms.

[d] Five ligands attached to the metal.

[e] The (+)-(S)-isomer.

[f] The (−)-(S)-exo-isomer.

[g] The (−)-(S)-isomer.

[h] $X = (\eta^5\text{-}C_5H_4)Mn(CO)_2PPh_3$ (M = W); ($X = \eta^5\text{-}C_5H_4)W(CO)_3CH_3$ (M = Mn).

[i] (+)-(R)-α-(*N*-acetylamino)-ethylcymantrene.

[j] $X = (\eta^5\text{-}C_5H_5)Mn(CO)_2$.

[k] $X = (\eta^5\text{-}C_5H_4)Mn(CO)_3$.

[l] The torsional angles are given for each P atom in dppe, i.e. ϕ(C-cen-M-P).

[m] $X = (\eta^5\text{-}C_5H_4)Fe(CO)_2Et$.

[n] Configuration at Ru is (S)-(+)-.

[o] Configuration at Ru is (R)-(−)-.

[p] Configuration at Ru is (R)-.

[q] Configuration at Ru is (S)-.

[r] Configuration at Ru is (R)-.

[s] The compound is $(\eta^5\text{-}C_5H_4CO_2Me)Co(PPh_2\overline{C_5H_4)(\mu\text{-}C}Me)Co(\eta^5\text{-}C_5H_4CO_2Me)$

the metal and the cyclopentadienyl ring may become less symmetrical and steric interactions between the ligand and the cyclopentadienyl ring and its substituent become possible.

The simplest bonding type, η^5-bonding, implies total electron delocalisation over the five cyclopentadienyl ring carbon atoms. But even here, recent crystallographic data on "symmetrical" systems, e.g. $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ [8], reveal that the complex has lower symmetry than predicted.

Extended delocalisation from the ring into the substituent gives rise to a fulvene or ylene type η^6-bonding mode. X-Ray crystallography can be used to distinguish this type of bonding from other possibilities. Criteria used include the C–C bond lengths in the cyclopentadienyl ring, distances between the metal and ring carbons, and the distance between the cyclopentadienyl ring substituent and the metal. Compounds that have been analysed for η^5- versus η^6-bonding include the complexes $(\eta^5\text{-}C_5H_4R)Cr(CO)_3$, $R = SMe_2$, PPh_3, CHO, and $(\eta^5\text{-}C_5H_4NO_2)Rh(CO)_2$ [157(b),322,325].

The metal may also bond to the cyclopentadienyl ring at two moieties: a three-carbon η^3-allyl moiety and a two-carbon alkene moiety. This type of bonding has been proposed for $(\eta^5\text{-}C_5H_4CO_2Me)Rh(cod)$ [136(c)].

The ligand set in $(\eta^5\text{-}C_5H_4R)ML_x$ can adopt different conformational preferences relative to the ligand set. These conformers may be described in terms of the torsional angle, Φ, between the ring substituent and a ligand when viewed along the metal–cyclopentadienyl ring centroid axis. Figure 8 shows some of the expected (extreme) conformers that are possible when the metal is bound to two, three or four ligands, in addition to the cyclopentadienyl ring.

The resulting conformation, determined by X-ray crystallography, is the result of electronic, steric and crystal packing forces [715(d)]. (See Table 50 for Φ values for a range of compounds.) The mode of bonding, e.g. η^5, η^6, $\eta^2+\eta^2+\eta^1$ or $\eta^3+\eta^2$ can influence, or be influenced by, conformations adopted by the ligand set. Steric considerations should also influence the ligand set on the metal towards adopting a conformation which minimises interaction between the ring substituent and the ligands. This will become more significant for large ring substituents and ligands (see, for example, refs. 307–310,443).

The steric interaction may also be expected to manifest itself in terms of the angle, α, by which the cyclopentadienyl ring substituent bends away from the cyclopentadienyl ring plane (see Fig. 9). This value is usually between 0 and 3° towards or 0 and 10° away from the metal atom (Table 50). The methyl substituent is relatively small and generally shows only a slight deviation from the plane, almost invariably in the direction away from the metal coordination sphere. A larger bending of the methyl substituent away from the metal (8.1°) is found for $(\eta^5\text{-}C_5H_4Me)Mo(CO)_2I_3$, and can be rationalised in terms of the large steric crowding introduced by the presence of five non-cyclopentadienyl ligands [344].

Another example of how steric interaction can be accommodated is revealed

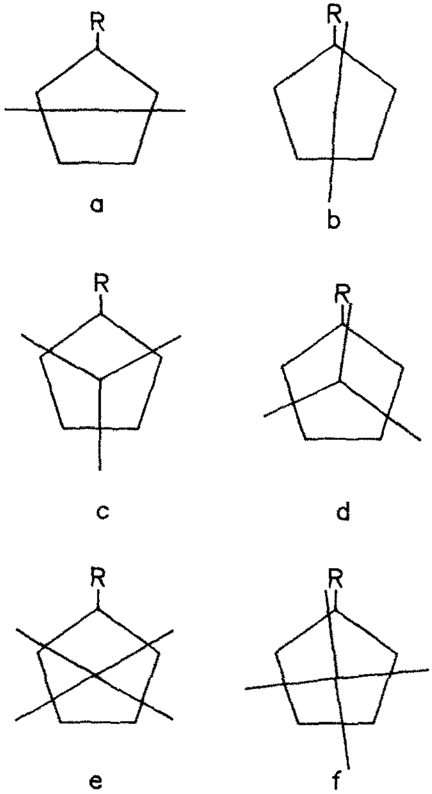


Fig. 8. Possible conformers for $(\eta^5\text{-}C_5H_4R)ML_x$ ($x = 2, 3, 4$) complexes. These conformers represent two possible extreme situations.

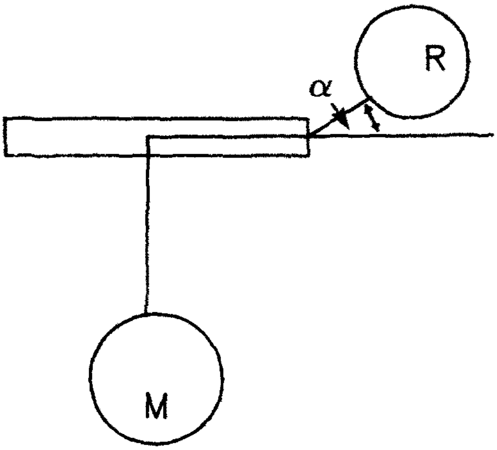


Fig. 9. Measurement of the degree of bending of the ring substituent, R, from the ring plane (α).

in studies on bimetallic bridging complexes in which the metals are not bound together. In the complexes $[(\eta^5,\eta^5\text{-}C_{10}H_8)Rh_2(CO)_2(PPh_3)_2][PF_6]_2$ [557(b)] and $\eta^5,\eta^5\text{-}C_5H_4C_2C_5H_4)Mn(CO)_2PPh_3W(CO)_3Me$ [394], the two metal coordination spheres are arranged in opposite directions.

The shape of the cyclopentadienyl ring substituent also determines the way in which steric interactions can be accommodated, e.g. substituents such as NR_2 and COR may take up a conformation co-planar with the cyclopentadienyl ring [e.g. 163,164,381(a)], which is not possible for groups such as *t*-Bu [443]. Less symmetrical substituents such as CHMe(NHCOMe) [653(b)] can take up a conformation in which the larger groups point away from the metal, and groups such as trityl may make use of "gearing" to establish more favourable conformations.

(iii) Theoretical studies

The electronic structure of $(\eta^5\text{-}C_5H_4R)ML_x$ $(x=2\text{–}4)$ complexes have been explored by using a fragment molecular orbital approach [683,685]. This has been achieved either by starting from the interaction of the C_5H_5 molecular orbitals with metal orbitals (and then adding a ligand set) [566,693], or from an interaction of the C_5H_5 ring molecular orbitals with the molecular orbitals associated with an ML_x fragment [694,698].

The generation of the C_5H_5 molecular orbitals has been well documented and most textbooks in inorganic chemistry give a description of the ring molecular orbitals [6]. In the usual approach, the σ framework orbitals are constructed by overlap of the p and/or s orbitals of the ring C and H atoms. This leaves a p orbital on each of the five C atoms which is not involved in the σ framework, and these five p orbitals generate the five π molecular orbitals shown in Fig. 10.

These orbitals have the correct symmetry to overlap with appropriate metal d (and s and p) orbitals, as shown in Fig. 10. The degree of overlap is dependent on the energies associated with the ring π orbitals and the metal orbitals. Studies have indicated that the dominant interaction is between the metal d_{xz} and d_{yz} orbitals, and the degenerate e_1 ring molecular orbitals.

(a) $(\eta^5\text{-}C_5H_4R)ML_2$ complexes

An example of the interaction between a C_5H_5 ring and a metal, Co, is shown in Fig. 11 [693].

The degeneracy of the e_1 and e_2 orbitals can be lifted by reducing the symmetry of the ring, either by replacing one of the C atoms with a heteroatom or replacing one of the H atoms by a substituent, R [694].

An approach that has been adopted for investigating the influence of a ring substituent on the electronic structure of $(\eta^5\text{-}C_5H_4R)MnL_x$ complexes, is to consider the interaction of the ring MOs with the ML_x fragment orbitals, e.g. $ML_x = Co(CO)_2$ [694]. The fragment MOs for $Co(CO)_2$ have been well documented [683,685] and

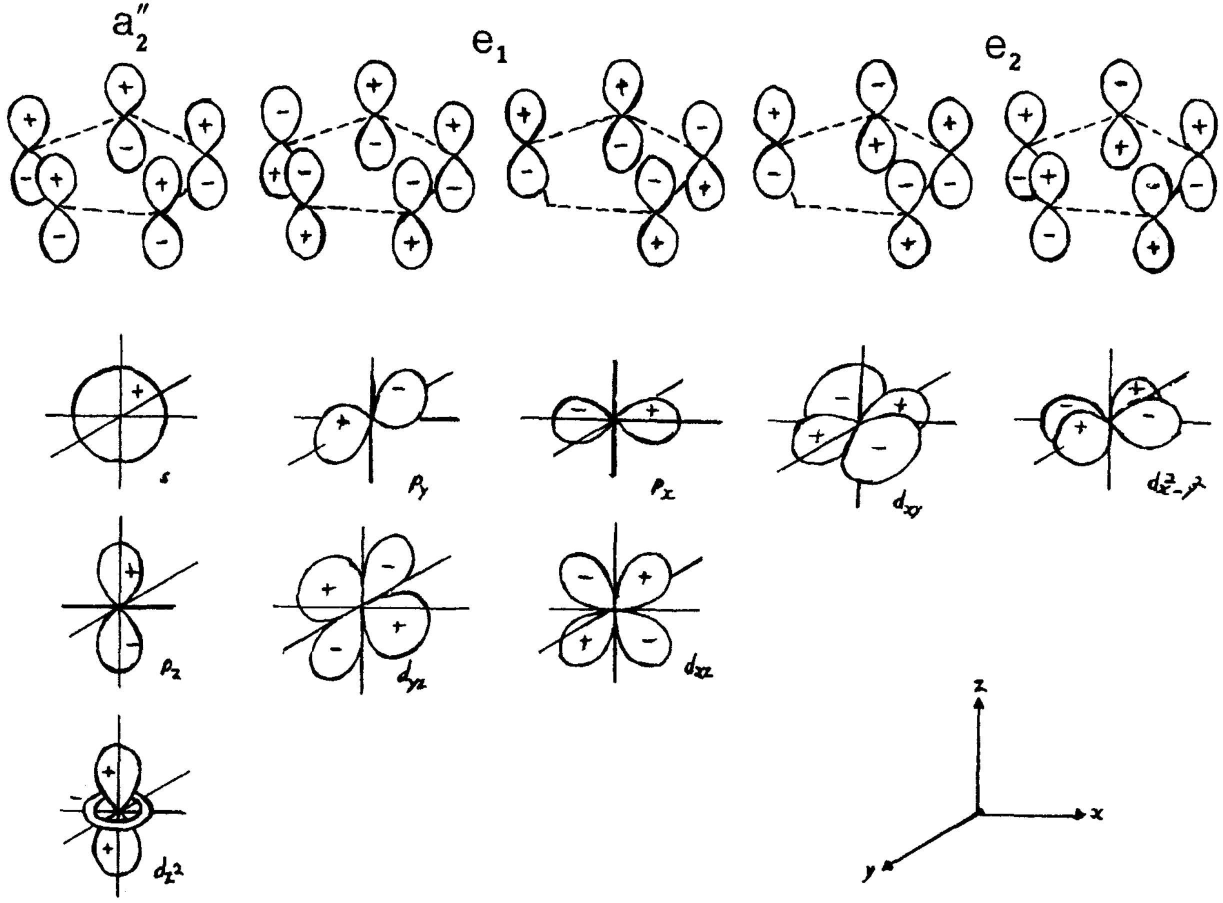


Fig. 10. Molecular orbital diagrams for $[C_5H_5]^-$ and atomic orbital diagrams for s, p, and d orbitals.

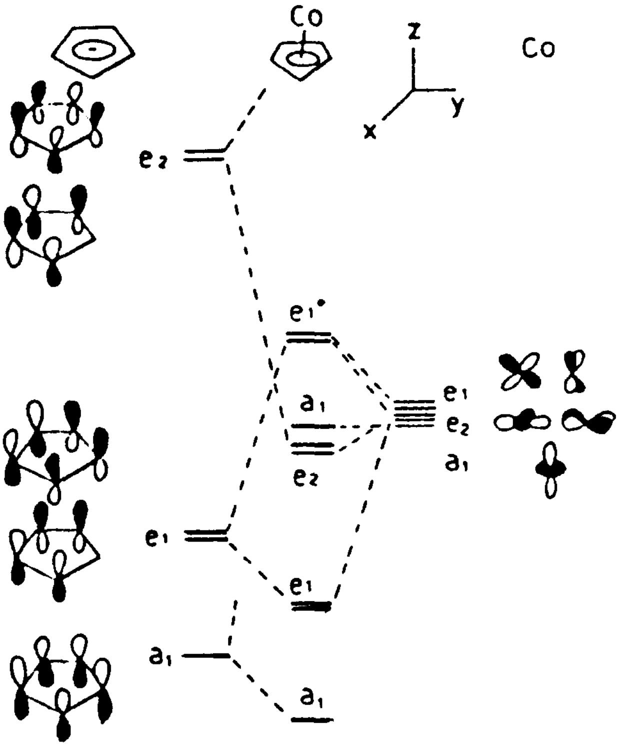


Fig. 11. Qualitative molecular orbital diagram of (η^5-C_5H_5)Co generated from the interaction of C_5H_5 and Co orbitals [693].

the relevant energies are shown in Fig. 12 [694]. The conformer generated in this study was **469**.

The primary interaction, shown in **469**, is between the $1b_1$ and the $1\pi_a$ orbitals. Rotation of conformer **469** to the in-plane conformer **468** results in $1b_1$ interacting with $1\pi_s$ (the $1\pi_s$ and the $1\pi_a$ orbitals are degenerate). Thus, for the unsubstituted ring, the difference in energy between the two different conformers **468** and **469** of (η^5-C_5H_5)Co$(CO)_2$ is zero, although the energy barrier between conformers will be non-zero [694]. This energy barrier is calculated to be non-zero even prior to interaction with the metal.

However, when a substituent, R, replaces a ring H atom, this is no longer true. For example when $R = BH_2$ (or COR), the conformer **469** is favoured over conformer **468** by 12.1 (or 24.7) kJ mol^{-1}, respectively. It appears that π acceptor substituents lower the $1\pi_s$ orbital, but do not affect the $1\pi_a$ orbital [694]. Hence, the energy difference between $1b_1$ and $1\pi_a$ is less than between $1b_1$ and $1\pi_s$, and rationalises the conformational preference observed. The analysis also suggests that a ring slippage of the "Co$(CO)_2$" unit towards R should occur.

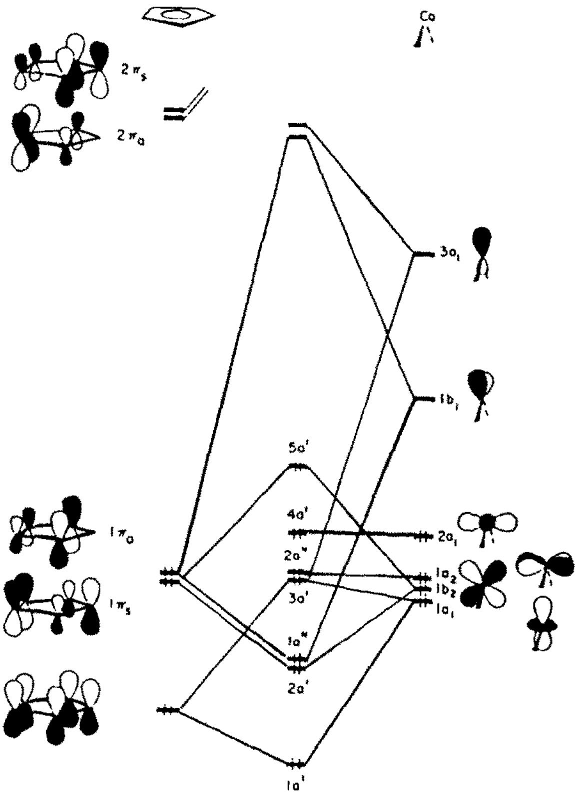


Fig. 12. Qualitative molecular orbital energy diagram for (η^5-C_5H_5)Co(CO)$_2$ generated from $C_5H_5^-$ and Co(CO)$_2^+$ molecular orbitals [694].

468

469

Theoretical studies on (η^5-C_5H_5)PtL_2 complexes have also been reported (ref. 695; see also ref. 696).

Extended Hückel calculations with self-consistent charge iterations have been performed on some related (η^5-C_5H_4R)Rh(diene) (R = CHO) complexes [537(a)]. The analysis was carried out to assess the influence of R and the diene on ring distortions in the complex. If the cyclopentadienyl ligand has a full +1 charge, both the e_1 orbitals will be fully occupied. Calculations show that this is not observed. The charge on the Rh atom, for R = H, is +0.21 (for R = CHO, 0.24) and on the rings

-0.18 (R = CHO, -0.30). Thus, only ~ 3.2 electrons are available to be distributed between the two e orbitals. The substituent, R, can influence the ring system via

(a) its electron-donating/withdrawing ability, or

(b) by extending the π system.

From the analysis, predictions can be made as to whether an allyl-ene or di-olefin ring distortion is possible. Unfortunately, the di-olefin distortion predicted when R = CHO is not observed and the authors concluded that this result cannot be described by a simple mechanism. An analysis of the diene–ring interaction was also carried out and the results indicate that if the diene is sufficiently electron-withdrawing, then an allyl-ene ring distortion can be expected.

(b) (η^5-C_5H_4R)ML_3 complexes

Theoretical studies have been performed on (η^5-C_5H_5)ML_3 complexes, based on a fragment orbital approach [683,685]. The molecular orbitals of the ML_3 fragment are known. For example, the MO diagram for the interaction of $C_5H_4Me^-$ with $TiCl_3{}^+$ to give (η^5-C_5H_4Me)$TiCl_3$ has been reported [249]. The MO interaction diagram for $C_5H_5{}^-$ with $Mn(CO)_3{}^+$ is now found in general chemistry textbooks (see, for example, ref. 703). MO diagrams for the addition of L′ ligands to (η^5-C_5H_5)ML_2 to give (η^5-C_5H_5)ML_2L' have also been reported [700].

The ML_3 fragment has two degenerate e_a orbitals, and a small energy barrier is predicted for ring rotation [697]. No ring slippage is predicted for 13 electron ML_3 fragments [694]. If, however, asymmetry is created in the ligand set, for example, by using an ML_2L' fragment, the e orbitals will have different energies, and ring slippage becomes possible.

Another approach to studying ring rotational effects is by using molecular mechanics calculations [702]. This approach has been used to study the energy barrier to ring rotation in (η^5-C_5H_4R)Fe(CO)[P(OMe)$_3$]I (R = Me, *t*-Bu) [7,443(a)] and low-energy ring rotational barriers were found (<20 kJ mol^{-1}). This method predicted the conformation observed by X-ray crystallographic analysis, and no potential energy wells were observed.

(c) Photoelectron spectra

The above analysis of M–L bonding schemes has, in part, been made possible by the availability of PES (XPS and He I/He II UPS) data. Quantitative information on the influence of R (and M) on the electronic spectra of a variety of (η^5-C_5H_5)ML_x complexes has been obtained by this technique.

(1) (η^5-C_5H_4R)ML_2 complexes. Studies have been carried out on a series of (η^5-$C_5H_{5-n}Me_n$)M(CO)$_2$ ($n = 0, 1, 5$; M = Rh, Co) complexes, and comparisons of the influence of the metal and the degree of methyl substitution have been reported [698,701]. Major differences in the valence, but not the core, ionisations were detected, as shown in Fig. 13.

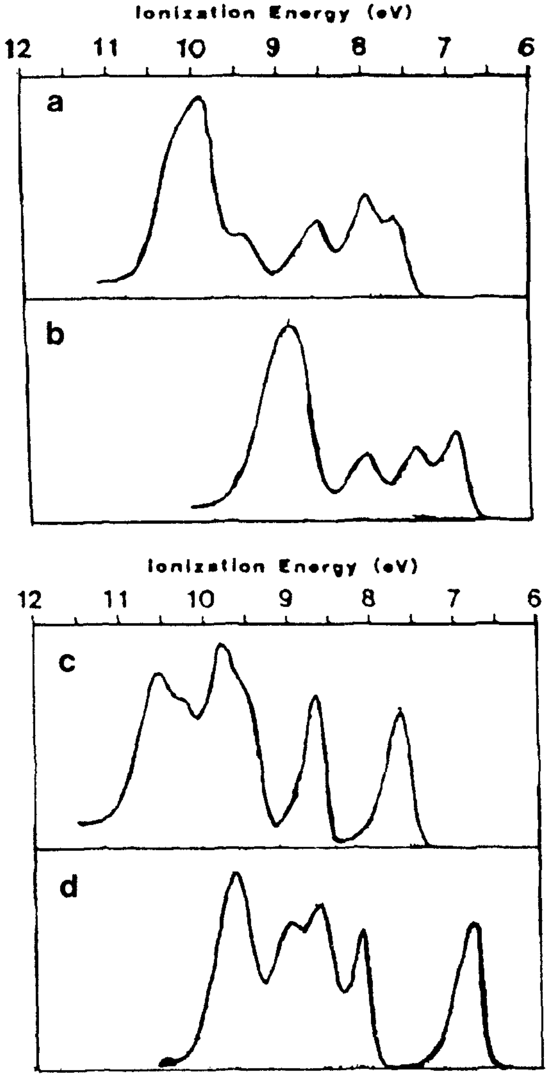


Fig. 13. He I close-up spectra for (a) (η^5-C_5H_5)Co(CO)$_2$, (b) (η^5-C_5Me_5)Co(CO)$_2$, (c) (η^5-C_5H_5)Rh(CO)$_2$ and (d) (η^5-C_5Me_5)Rh(CO)$_2$ [701].

The valence shell ionisation data were interpreted in terms of ring–metal orbital overlap, with large differences between the two e_1–$1b_2$ metal orbital interactions, especially for the Rh complex. (In this study the MO energy diagram for conformer **468** was determined.) This is ascribed to excited state effects associated with relaxation in the positive ion. He I PES were also obtained for (η^5-C_5H_4R)Co(COD) (R = H, COOMe, $COCF_3$) [566]. Introduction of the R group results in the ionisation bands being moved to higher potential due to their electron-withdrawing properties. A consideration of the MOs (generated from the (η^5-C_5H_4R)Co and COD fragment MOs) suggests that the HOMO is stabilised by ~0.5 eV when H is replaced by $COCF_3$, suggesting a through-space interaction between R and the metal.

(2) (η^5-C_5H_4R)ML_x ($x=3, 4$) complexes. Spectral comparisons have been carried out for (η^5-$C_5H_{5-n}Me_n$)$Mn(CO)_3$ ($n=0$, 1, 5) [701]. Addition of methyl groups to the ring results in shifts in the PE spectrum, which are larger for the ring e″ ionisations than for the metal ionisations. This is a consequence of the large orbital overlap between the Me and the ring e″ orbital, shown in Fig. 14.

This technique, thus, unambiguously separates inductive effects from bonding contributions in these complexes. Ring methylation is additive for both core and

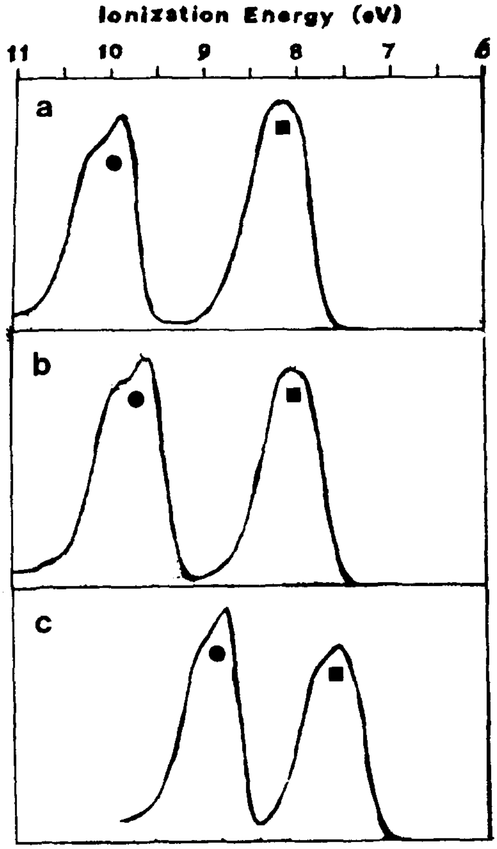


Fig. 14. He I close-up spectra for (a) (η^5-C_5H_5)$Mn(CO)_3$, (b) (η^5-C_5H_4Me)$Mn(CO)_3$ and (c) (η^5-C_5Me_5)$Mn(CO)_3$ [701]. ●, Valence ionisations; ■, core ionisations.

valence ionisations (~0.24 eV per Me) and arises from reduced overlap of the filled Me orbital with the ring π orbitals.

Numerous $(\eta^5\text{-}C_5H_4R)MnL_2(SiR_3')H$ complexes have been studied, in which R′ [699(c)], L [699(b)] and R [699(c)] have been varied. These studies have provided information on the degree of Si–H bond cleavage in the $SiR_3'H$ unit when attached to Mn [699(d)]. Electron-withdrawing groups on Si, and electron-donating groups on Mn, favour an oxidative addition reaction in which the Si–H bond is cleaved. The influence of R on the PE spectra, e.g. by varying the ring methylation, is more complex, as has been reported for $(\eta^5\text{-}C_5H_{5-n}Me_n)Mn(CO)_2(H)(SiHPh_3)$ ($n = 0, 1, 5$) [699(a)]. It was observed that the degree of methylation ($n = 0, 1$) gives small, but predictable, increases in the degree of Si–H bond cleavage (Me > H). For $n = 5$, an anomaly is observed; here, the Si–H σ^*–M orbital interaction is reduced, a phenomenon ascribed to steric effects.

The He I and He II PES of $(\eta^5\text{-}C_5H_{5-n}Me_n)TiX_3$ ($n = 0, 1, 5$: X = Cl, Br) have also been reported [249].

To our knowledge, no pertinent studies relevant to this review have been performed on $(\eta^5\text{-}C_5H_4R)ML_4$ complexes [704].

(iv) Ring rotation studies

A variety of techniques have been applied to the study of ring rotation in $(\eta^5\text{-}C_5H_4R)ML_x$ complexes. In principle, any technique that can measure motions in the 10^4–10^{11} s^{-1} range can be used. Results obtained from NMR studies (Sect. E.(i)(d)(3)) and theoretical studies (Sect. E.(iii)) have already been mentioned.

Other techniques which have been employed include Raman spectroscopy [678], quasi-elastic neutron scattering [684] and mechanical spectroscopy [705,706]. Mechanical spectroscopy involves subjecting a solid to a mechanical stress at a fixed frequency. The energy dissipated by the solid is then measured as a function of temperature. Energy dissipation occurs when the frequency of the molecular motion of the solid molecules corresponds to the frequency of the stress. Eisenberg and coworkers have applied this technique to a series of $(\eta^5\text{-}C_5H_5)PtL_3$ complexes and measured rotational barriers in the range 20.5–25.9 kJ mol^{-1}. The values varied with the size of L (L = Me, Et, COMe), which suggests that the method could be applied to studying the influence of R substituent size in $(\eta^5\text{-}C_5H_4R)ML_x$ complexes.

(v) Steric effects

(a) Introduction

Very little data are available on the quantitative analysis of steric effects associated with the cyclopentadienyl or substituted cyclopentadienyl ring. The only available data on a measure of the size of the ring are based on the Tolman cone angle concept [707]. The procedure for measuring the ring size is the same as that used to measure the size of phosphines and phosphites, i.e. a cone is generated with the metal as the apex atom. Using this procedure, Tolman reported a cone angle, θ, for the unsubstituted cyclopentadienyl ring of 136° (θ_1, see Fig. 15(a), below), based on a metal–ring (centroid) distance of 2.03Å. To our knowledge, only two other ring size measurements have been reported. Maitlis [708(a)] reported cone angle measurements for some Rh complexes, with the values of: $C_5H_5Rh(I)$, $\theta = 150°$; $C_5Me_5Rh(I)$, $\theta = 182°$; $C_5H_5Rh(III)$, $\theta = 148°$; $C_5Me_5Rh(III)$, $\theta = 188°$. Mingos [708(b)] reported "cluster cone angles" for $(C_5H_5)M$ fragments in which the M–M bonds in a cluster were varied. Values for the unsubstituted ring cone angle varied between 82° and 97°.

A number of studies have appeared in the literature in which the size of the ring has been regarded as fundamental to an understanding of the chemical and physical properties of cyclopentadienylmetal complexes. Although no specific measurement of a cone angle may have been given, it is apparent in these studies that the steric and not the electronic properties of the ring correlates with the properties of the complex. Pertinent studies are described below.

(a) Li Xing-Fu and Guo Au-Ling [709] have reported on the use of spherical trigonometry to determine steric hindrance in $(\eta^5\text{-}C_5H_5)_3UL$ complexes. Their procedure entails the determination of differences between the required and available space when a ligand is added to a fragment molecule. The difference between the two values can be used as a measure of steric hindrance. Although no explicit mention is made about the role of ring substituents in the analysis, it is apparent that this procedure can readily be adapted to incorporate this variable.

(b) Dämmgen and Bürger [243] have reported on the ^1H and ^{13}C NMR spectra of a series of $(\eta^5\text{-}C_5H_4R)Ti(NR_2'')_3$ and $(\eta^5\text{-}C_5H_3RR')Ti(NR_2'')_3$ complexes (R, $R' = H$, alkyl, $SiMe_3$, $GeMe_3$; $NR_2'' = NMe_2$, piperido). As the size of R, R′ and R″ are varied, it was suggested that the ring moved from an η^5 to an η^2 bonding mode via a ring-tilt mechanism. The authors' analysis was based on the steric size of the R and R′ groups and the diagrams in their publication explicitly indicate the steric interactions between R and R′, and the NR_2'' ligand. No quantitative analysis of the size of the ring–ligand interaction was, however, given.

(c) Razuvaev and co-workers [713] have analysed the electron donor ability of $(\eta^5\text{-}C_5H_4R)_2WX_2$ (R = alkyl, X = Cl, Br, I) complexes by UV spectroscopy. Interaction of $(\eta^5\text{-}C_5H_4R)_2WX_2$ with strong π acids, such as TCNE, give 1 : 1 ion-radical salts and the formation of these ion-radicals was influenced by the steric size of both the R and X groups. It was proposed that the steric influence of C_5H_4R and X results in a shielding of the W atom from the π acid, which reduces the possibility of the electron-transfer reaction. The degree of ion-radical formation was measured, in equilibria studies, and the data obtained plotted against the Charton steric constants [714]. To further refine the analysis, the data were plotted against a so-called exocyclic angle, q, measured from the W atom. The q values were obtained by "plotting the molecular projection in the spheric coordinate system on the sphere of unit radius, the atoms being represented as rigid balls with the corresponding Van der Waals radii" [713]. Data for C_5H_4Me and C_5H_4Et sizes were based on a W–C (ring centroid) distance of 2.36 Å. Other exocyclic values were derived from these data. The orientation of the R groups was based on minimal steric interactions. The q values obtained for C_5H_4R were: C_5H_4Me, 4.25; C_5H_4Et, 4.29; C_5H_4Pr-i, 4.49 and C_5H_4Bu-*t* 4.76 steradians.

(d) Coville and co-workers [7,443(a)] have established that NMR spectroscopy can be used to assess the steric size of ligands, L, and ring substituents, R, in $(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I$ (L = Group 15 ligands). Since the Fe atom is a chiral centre in the complex, four ^1H and five ^{13}C resonances are expected in the NMR spectrum. A correlation was found between the size of L and Δ(H2–H5) where H2 and H5 are the ^1H NMR absorptions associated with the protons adjacent to the ring substituent. The value of Δ(H2–H5) also increased when the size of R increased from Me to *t*-Bu [443(a)]. A correlation was also noted between Δ(C2–C5) and the cone angle of L (R = Me) [443(c)]. Similar results were obtained for $(\eta^5\text{-}C_5H_4R)Ru(CO)(L)I$ [443(b),(g)]. It was suggested that a cone angle, measured from the ring centroid (Fig. 15(b)), could be associated with the ring substituent. No quantitative data were reported.

(e) Another pertinent study, in which the steric size of arene ligands were reported, should also be mentioned. Hunter et al. [712] have reported the VTNMR spectral results of $(\eta^6\text{-}C_6R_6)Cr(CO)_2PR_3'$ (R′ = Me, Et, *n*-Pr) complexes. In the analysis of the data, it was proposed that cones could represent both the size of the PR_3' and the arene ligand. The metal was the apex atom for both cones.

(f) Finally, the recent studies by Giering and co-workers [710] and Poe [711] have further refined the concept of steric size by introducing the concept of steric threshold. Although these studies have concentrated on the steric size of Group 15 donor ligands, the basic ideas should also apply to cyclopentadienyl rings.

In summary, it can be seen that little quantitative data is available on the steric size of C_5H_5 and C_5H_4R rings. Two types of measurement have been proposed to measure the size of the ring (see Fig. 15) but the literature data do not suggest which is the better measure.

(b) C_5H_4R cone angle data

We have recently calculated the cone angles of a series of C_5H_4R ligands using the Tolman cone angle concept [715]. The cone angles have been measured from both the metal and the ring centroid (Fig. 15) and the calculated data are shown in Table 51.

Certain assumptions were made in the calculation of the cone angles.

(a) The C_5H_5–M distance was chosen as 1.73 Å, and corresponds to a typical Fe–C (ring centroid) bond distance.

(b) The ring is assumed to be planar with idealised bond lengths and bond angles. Calculations show that non-ideality has little influence on the cone angle values [715(c)].

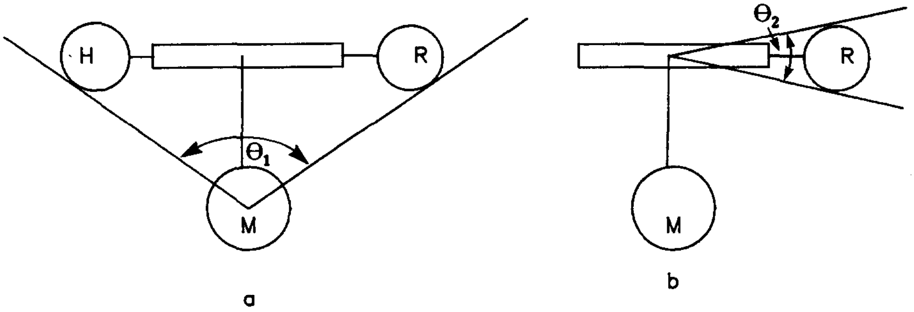


Fig. 15. C_5H_4R cone angle measurements (a) measurement from the metal atom (θ_1) and (b) measurement from the ring centroid (θ_2).

TABLE 51

Maximum cone angles, θ_1 and θ_2, for C_5H_4R

R	θ_1/degrees[a]	θ_2/degrees
H	128	55
CH_3	141[b]	64
CH_2CH_3[c]	146	85
$CH(CH_3)_2$[d]	150	107
$C(CH_3)_3$	154	128
$Si(CH_3)_3$	158	138
$CH_2CH_2CH_3$	178	172
CH_2Ph[e]	150	102
$CHPh_2$[f]	158	140
$C(CH_3)Ph_2$[g]	163	161
$C(CH_3)_2Ph$[h]	158	144
CPh_3	167	178
Ph[i]	133	71
$CH{=}CH_2$[j]	151	39
CO_2CH_3[j]	132	47
$COCH_3$[j]	142	47
OCH_3	155	132

[a] Calculated from $0.8(C_5H_5)+0.2(C_5R_5)$.

[b] The cone angle for $Fe{-}C_5Me_5$ (Fe–centroid distance = 1.73 Å) is 194°.

[c] Calculated from $\frac{1}{3}(t\text{-Bu})+\frac{2}{3}(CH_3)$.

[d] Calculated from $\frac{1}{3}(CH_3)+\frac{2}{3}(t\text{-Bu})$.

[e] Calculated from $\frac{1}{3}(CPh_3)+\frac{2}{3}(CH_3)$.

[f] Calculated from $\frac{1}{3}(CH_3)+\frac{2}{3}(CPh_3)$.

[g] Calculated from $\frac{1}{3}(t\text{-Bu})+\frac{2}{3}(CPh_3)$.

[h] Calculated from $\frac{1}{3}(CPh_3)+\frac{2}{3}(t\text{-Bu})$.

[i] Assuming the aryl and cyclopentadienyl rings are mutually at 45°.

[j] Calculated assuming the substituent and cyclopentadienyl rings are coplanar.

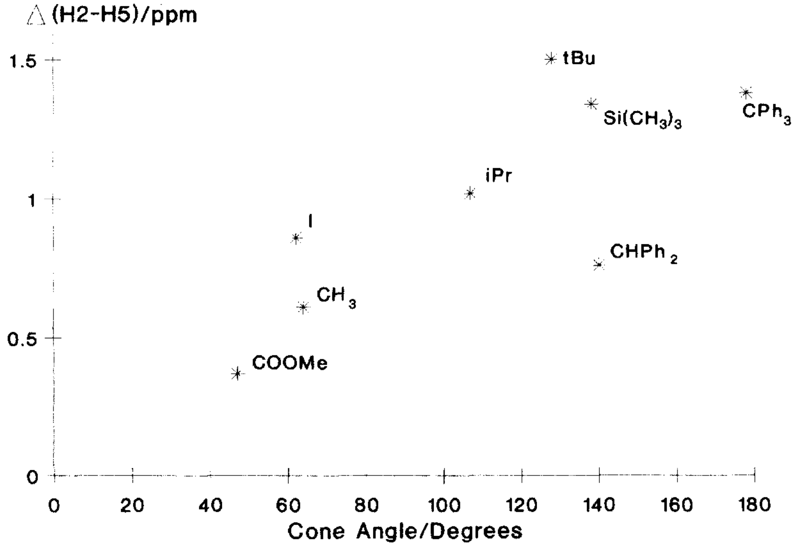


Fig. 16. Plot of C_5H_4R cone angle, θ_2, against Δ(H2–H5) for a series of (η^5-C_5H_4R)Fe(CO)[P(OMe)$_3$]I complexes. NMR data recorded in C_6D_6 versus TMS.

(c) The COOMe group cone angle has been measured with the group co-planar to the cyclopentadienyl ring. All crystal structure determinations performed on (η^5-C_5H_4COOMe)ML$_x$ support this geometry (see Sect. E.(ii)).

(d) The cone angle of the phenyl ring was measured with the ring at 45° to the cyclopentadienyl ring. Crystallographic data are presently not available to confirm this choice.

(e) Anisotropic effects have been neglected.

(f) In the calculation, the *ipso* ring C atom size has been ignored.

(g) Averaged values of the groups attached to the substituent have been used for non-symmetrical substituents (see Table 51).

Recently, we have synthesised a range of (η^5-C_5H_4R)Fe(CO)(L)I complexes in which the L group (P(OMe)$_3$, PPh$_3$) has been kept constant [715(c)] while R has been varied. The influence of R on the NMR spectrum has been analysed. Attempts were made to correlate Δ(H2–H5) with various Hammett functions, other electronic parameters, and θ_1 and θ_2. The best correlation observed was between θ_2 and Δ(H2–H5). This is shown in Fig. 16 for (η^5-C_5H_4R)Fe(CO)[P(OMe)$_3$]I.

Whether θ_2 will prove, in general, to be a better measure than θ_1 of cyclopentadienyl ring size, must await further studies.

F. CONCLUSION

This review has outlined various facets of monosubstituted half-sandwich transition metal complexes. An attempt has been made to be comprehensive, especially with respect to the synthesis of substituted cyclopentadienes and (η^5-C_5H_4R)ML_x complexes. It is apparent from the review that synthetic strategies to these compounds constitute a well-established area of chemistry. Numerous physical properties of (η^5-C_5H_4R)ML_x complexes have been measured and these have been mentioned in Sect. E. No discussion of the uses of these types of complex has, however, been given; suitable examples are to be found throughout the text.

Very few (η^5-C_5H_4R)ML_x complexes in which the metal is in a high oxidation state have been reported. The current interest in this area of chemistry suggests that the influence of ring substituents on the properties of these complexes could be important [720].

Finally, it is to be noted that cyclopentadienyl complexes with more than one ring substituent have not been covered in this review. From the discussion of steric effects in Sect. E(v), it can be expected that multiple ring substitution should provide an even larger steric influence on the properties of cyclopentadienyl-containing complexes. Data scattered throughout the literature suggest that this is a correct assumption, but a more comprehensive investigation is needed to confirm this proposal.

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NOTE ADDED IN PROOF

Since this manuscript was submitted in January 1991, more than 100 articles which pertain to the content of this review have been published. Some of the more pertinent articles which will enable the interested reader to cover some of the latest developments in the field are given in the reference list (refs. 721–748).

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