

ORGANOMETALLIC COMPLEXES OF FIRST-ROW TRANSITION METALS: SOME RECENT ADVANCES

P. L. PAUSON

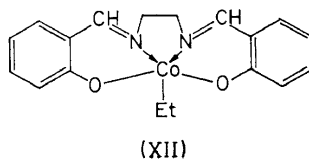
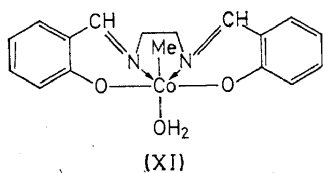
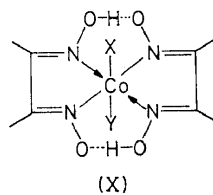
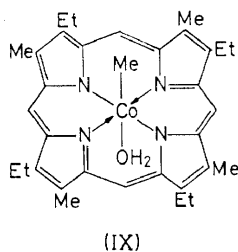
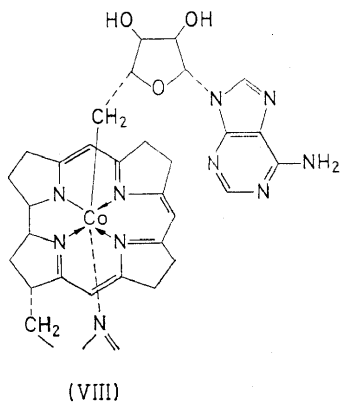
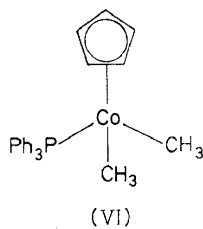
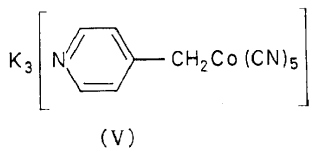
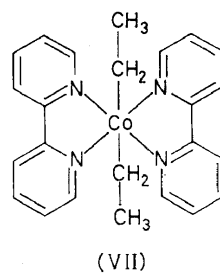
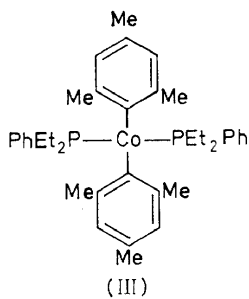
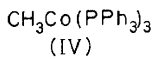
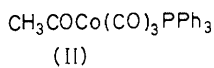
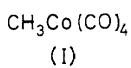
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The aim of this contribution is to set the background for that portion of the Conference (some 40 per cent of the papers) which deals with transition metal complexes. Topics to be covered by other plenary lectures are omitted. Even the remaining field is much too large and I have made no effort to cover it comprehensively. Instead, my choice of fields reflects my own current interests and allows me to deal in more detail with results recently obtained by my co-workers at Glasgow.

The neglect of organo-transition metal chemistry prior to 1950 was largely due to the earlier failures to obtain simple alkyls from these metals. It is appropriate therefore to begin by stressing our increased knowledge concerning alkyls. Although even simple alkyls of the earlier transition metals: Ti, V, Cr, Mn, have been isolated, their low stability readily explains the previous failures. But following the demonstration, 10 years ago, that π -complexing can greatly stabilize such alkyls — as for example in the alkylmanganese pentacarbonyl, $\text{RMn}(\text{CO})_5$, and the alkylcyclopentadienyl-iron dicarbonyl series $\text{RFe}(\text{C}_5\text{H}_5)(\text{CO})_2$ — the range of stable alkyls has grown steadily. A very wide range of other ligands appear capable of stabilising alkyls in addition to the carbonyl and cyclopentadienyl ligands of the early examples just mentioned.

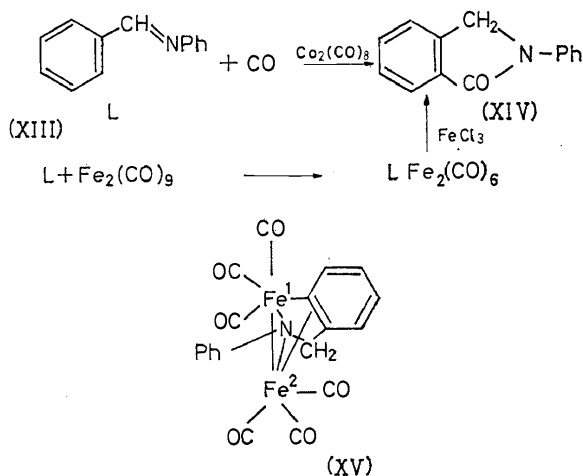
The high level of current interest in these compounds is justified by their importance in both *in vitro* and *in vivo* catalyst systems. There is strong evidence that transition metal alkyls are key intermediates in the reactions which account for the main catalytic uses of organometallic compounds: The Ziegler-Natta olefin polymerisation which is believed to involve titanium alkyls as the chain carriers; the olefin oxidations in which palladium alkyls must be at least transient intermediates; and the hydroformylation and related carbonylation processes which clearly involve alkylcobalt carbonyls.

Cobalt is again involved in the only known natural organometallic system, that of Vitamin B₁₂ in which an adenosyl group is linked through carbon to this metal. A survey of these and other cobalt alkyls (I–XII) provides excellent illustration of the wide range of ligands capable of exerting suitable stabilising influence. In compounds (I–IV) carbonyl or phosphine groups or both are used¹. The bulk of the mesityl groups in compounds of the type (III) helps stability², but is clearly not an essential factor. The 4-pyridylmethyl complex (V) is only one of numerous analogous



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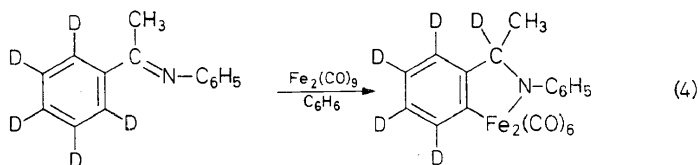
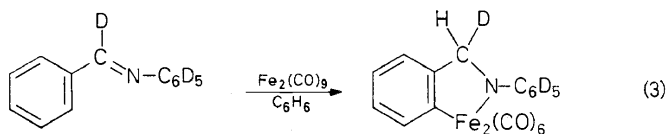
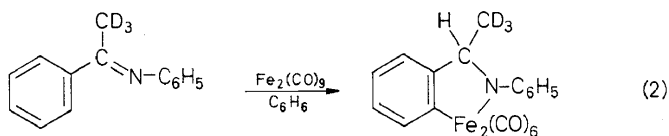
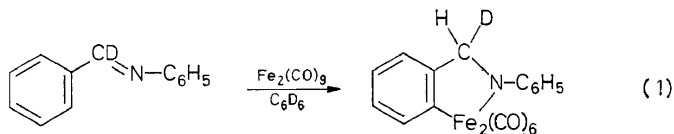
alkylcobalt pentacyanides³. In (VI) the cyclopentadienyl and phosphine ligands⁴ together stabilise two alkyl-cobalt bonds as do the two dipyrityls⁵ in the diethyl complex (VII). This is only one of numerous nitrogen chelates which stabilise alkyls. Chief interest has centred around vitamin B₁₂ of which formula (VIII) shows only the immediate surroundings of the cobalt atom⁶. Maintaining the *N*-chelated cobalt system the organometallic group as well as the sixth ligand (usually aquo or a nitrogen base) can be varied. Many such reactions have been studied in the model systems provided by the aetioporphyrin complexes⁷ (IX), the dimethylglyoxime complexes⁸ (X) and the salicylaldehyde-ethylenediamine Schiff base complexes⁹ (XI). A novel variant of the latter system is the 5-coordinate complex (XII). Whereas these nitrogenous ligands are better stabilisers than π -bonded groups like carbon monoxide, it is the intermediate stability and hence high reactivity which makes the alkylcobalt carbonyls suitable as catalysts or intermediates in catalytic processes. Some carbonylation processes have been postulated to involve chelated cobalt aryls¹⁰. One example is the carbonylation of benzaldehyde (XIII) to give *N*-phenylphthalimidine (XIV), first studied by Murahashi¹¹.



Our own interest in this particular process was aroused by the observation that the same ligand (XIII) reacts¹² under mild conditions with enneacarbonyldi-iron, $\text{Fe}_2(\text{CO})_9$, to give a stable complex (XV), which can be oxidised to the phthalimidine (XIV). A combination of mass spectral and p.m.r. data suggested the structure shown for this complex (XV) and x-ray crystallographic examination by Baikie and Mills¹³ has confirmed this.

We see that, the postulated¹⁰ substitution of metal into the aromatic ring undoubtedly takes place here. With respect to Fe^1 , the compound is an aryl of iron, stabilised not only by the carbonyl groups, but also by chelation through the nitrogen atom.

The mechanism of formation of such products (*e.g.* XV) is unknown. We have, however, established some features of the reaction by employing



deuterium labelled anils¹⁴. In particular the hydrogen transferred to the methylene carbon is clearly shown to be derived from the position attacked by the iron atom. Reaction (1) eliminates both the solvent and the methylene proton itself as sources of this hydrogen. Reaction (2) further eliminates the side chain methyl group in the acetophenoneanil case and reaction (3) excludes the *N*-phenyl protons. Finally in reaction (4) four deuterium atoms remain in the substituted ring whereas one is transferred and this can only derive from the substituted position. By reacting the last substrate

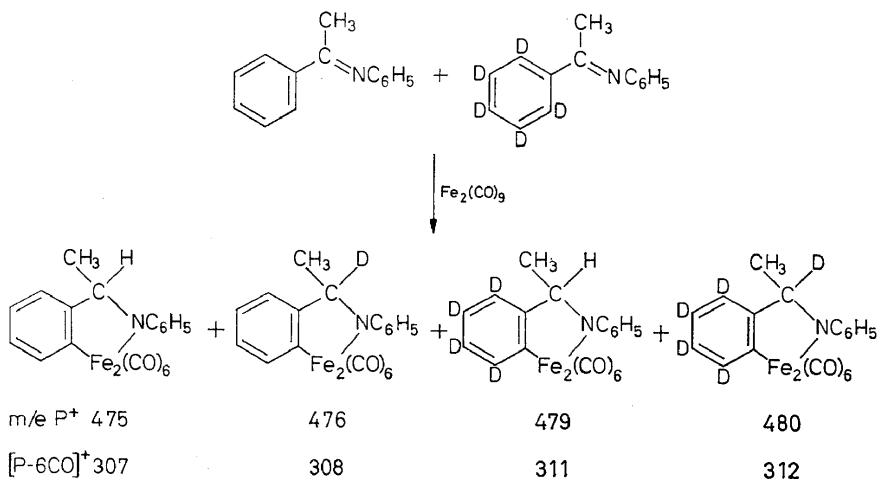
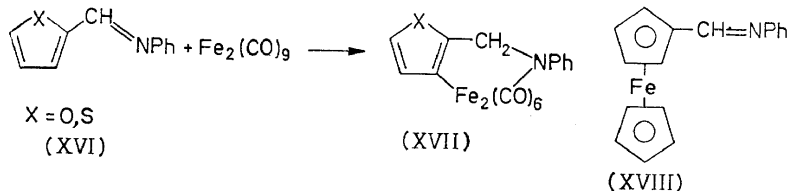


Figure 1

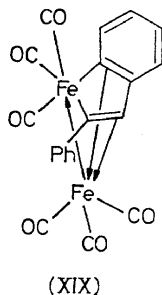
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together with an equal quantity of the unlabelled compound (*Figure 1*) it was shown that the process is intermolecular, giving equal amounts of the four products shown† whereas only the first and last of these would result from an intramolecular process. As indicated in the figure, adequate analysis of the product mixture is readily accomplished by high resolution mass spectroscopic examination of the product mixture and especially by the abundant $(P-6CO)^+$ ions produced.

Many ring-substituted anils have been employed in this reaction and only substitution in both the 2 and 6 positions (*e.g.* by Cl or Me) prevents complex formation¹⁴. The furan and thiophene analogues (XVI) give the corresponding complexes (XVII), but the anil (XVIII) of ferrocenealdehyde

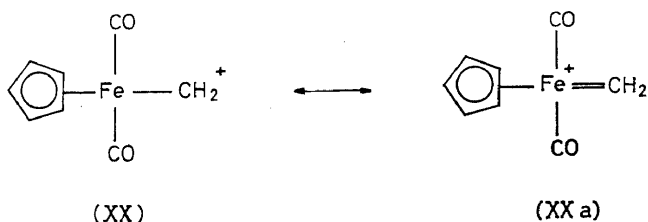


fails to react. This could be attributed to a mechanistic difficulty but is more likely to be due to the unavailability of the π -electrons of the ring for bonding to the second metal atom. With respect to this atom (Fe^2 in XV) the complexes are olefin complexes. The structural data¹³ show clearly that two and only two carbons of the benzene ring are involved and the close analogy of our compounds (*e.g.* XV) to the ferra-indene complex (XIX) described by Braye and Hübel¹⁵ and hence to the whole group of ferracyclopentadiene complexes justifies the view that the ring is participating as an olefin.

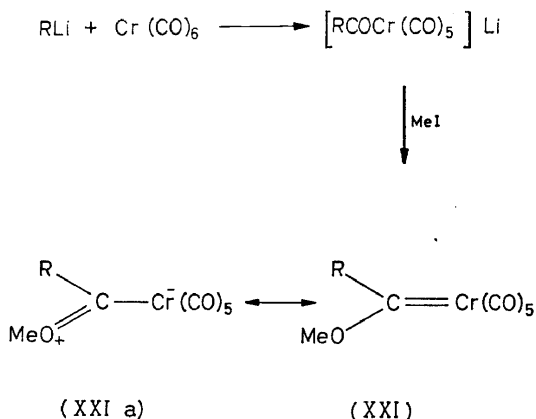


Whereas alkyls and aryls unambiguously involve a single bond between a carbon and a metal atom, the carbonyls may be thought of as involving at least partial double bonding between such atoms. The question whether other carbon compounds can be similarly linked by two bonds to one metal atom has given rise to a number of attempts to obtain carbene complexes. Both Green¹⁶ and Pettit¹⁷ have provided evidence to show that species like $C_5H_5Fe(CO)_2CH_2^+$ (XX) though not isolable, have distinct existence as

†*Note added in proof:* This result is misleading. Further experiments have shown wide variation in product composition with reaction time. This must result from side reactions leading to extensive redistribution of deuterium. An intramolecular mechanism is now preferred. The author thanks Dr H. Zeiss for valuable discussion.

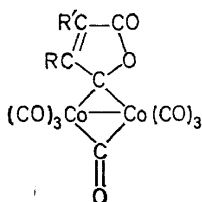


intermediates; the relative stability of this species compared to simple carbonium ions is most readily understood by assuming at least some participation from the structure (XXa). By far the strongest evidence for such groupings was obtained by Fischer and his co-workers with their isolation of several group VI metal carbene complexes¹⁸, which is illustrated by the preparation of the chromium compounds (XXI).



Even in these it must be admitted that 'double bonding' need only be partial since the observed bond distances suggest significant participation of charged structures of the type (XXIa).

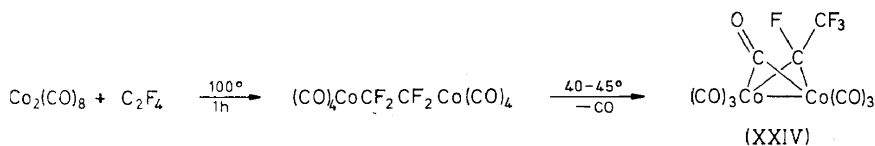
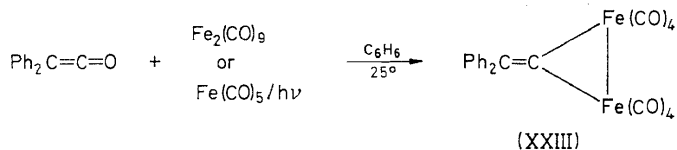
Several examples are known of carbenes bridging two metal atoms in a manner similar to bridging carbonyl groups. The first were the lactone cobalt complexes (XXII) obtainable from acetylenes $\text{RC}\equiv\text{CR}$ ¹⁹. More recently the unsaturated carbene complex (XXIII) was obtained by us²⁰ from the reaction of iron carbonyl with diphenylketene. Although formally



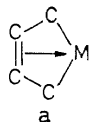
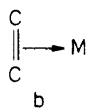
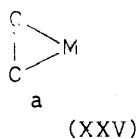
(XXII)

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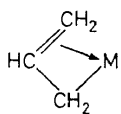
this product is an analogue of $\text{Fe}_2(\text{CO})_9$, the unsaturated carbene is the only bridging group, all the carbonyl groups being terminal, as shown both by the infrared spectrum and by the structure determination of Mills and Redhouse²⁰. This contrasts with the cobalt compounds (XXII) in which one of the bridging carbonyl groups of octacarbonyldicobalt is replaced by the carbene. A related complex (XXIV) with a perfluoroethylidene group was recently obtained by the reactions shown²¹.



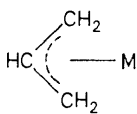
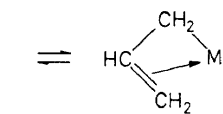
The linkage of one metal atom to two adjacent carbons (XXVa) must be considered equivalent to the formation of a μ -bond from an olefin to a metal (XXVb). The second formulation is, in general, preferable, although we may agree that the actual bonding is normally intermediate between these extremes. Although individual cases may tend more to one extreme or another, I doubt whether the subject is advanced by authors who attempt to reopen the controversy by postulating essentially pure σ -bonding in special cases. There is an exactly parallel situation with the conjugated diene complexes for which the formulations (XXVI a and b) have been much debated. Again there is reason to believe in an intermediate status with the balance of evidence²² in favour of using the π -complex formulation



(XXVI)



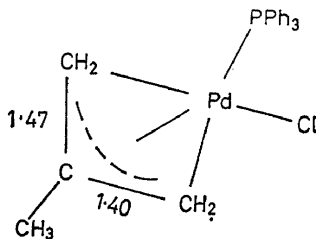
(XXVIIa)



(XXVIIb)

(XXVIb). Most notably perhaps, u.v. data have been used convincingly²³ to show that such a grouping in the middle of an extended conjugated chain reduces, but does not effectively interrupt conjugation.

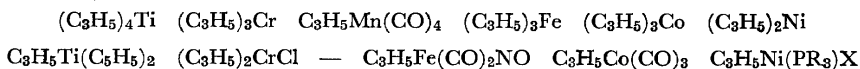
There is at first sight more justification for examining the reality of a difference between the extreme formulations (XXVIIa and b) for allylic complexes since in this case one can look for evidence for non-equivalent methylenes. Here too, I can only advise caution. The variety of interpretations put forward for temperature variations in the n.m.r. spectra of allylic complexes by different authors²⁴ strongly suggests that it is not easy to reach an unambiguous decision on this basis. Even in cases where x-ray



(XXVIII)

crystallographic evidence has shown²⁵ a difference between the methylenes as in the palladium complex (XXVIII), we have the choice of writing a π - and a μ -bond or of attributing the difference in bond length to the different effects of the PPh₃ and Cl groups to which the methylenes are *trans*.

More positive progress has been made on the preparative side of the chemistry of π -allyl complexes. Typical examples are tabulated below and



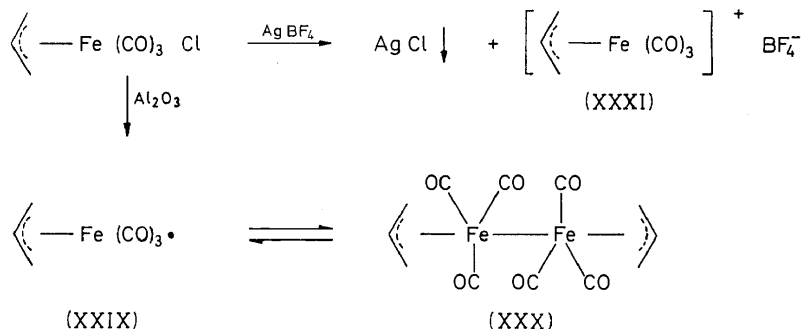
show that these now include all the first-row transition metals, except vanadium[†]. There is a noticeable tendency for allyls to be stable with less than an inert gas complement of electrons about the metal atom. Nickel is particularly prone to do this and both examples shown fall in this category, although there are also complexes with a second phosphine ligand [$\text{C}_3\text{H}_5\text{Ni}(\text{PR}_3)_2\text{CN}$] which attain the inert gas configuration²⁷. The availability of free metal orbitals in the allyl-nickel complexes may account for some of their reactivity. An interesting example is provided by the facile alkylations recently described by Corey²⁸. For instance:



[†] The unstable allyl dicyclopentadienylvanadium briefly reported by Martin and Jellinek^{26a} is now known to be a σ -allyl compound^{26b}.

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A remarkable example of the stability of allyl complexes which fail to conform to the E.A.N. rule is provided by Murdoch's tricarbonylallyliron²⁹ which exists as a stable radical (XXIX) in equilibrium with the iron-iron bonded dimer (XXX) as well as forming³⁰ a stable cation (XXXI).



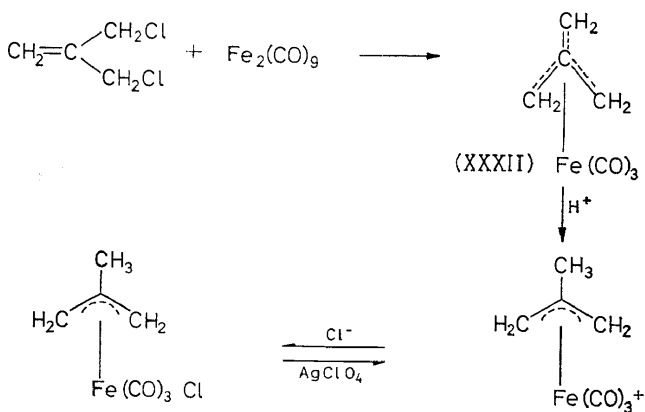
A convenient classification of transition metal complexes is by the number of electrons donated by the hydrocarbon ligand — or — and this is equivalent, by the number of carbon atoms linked to the metal atom. On this basis the examples mentioned above include

- 1 carbon ligands: the alkyls
- 2 carbon ligands: the olefin complexes
- 3 carbon ligands: the allyl complexes

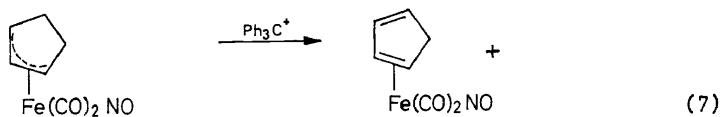
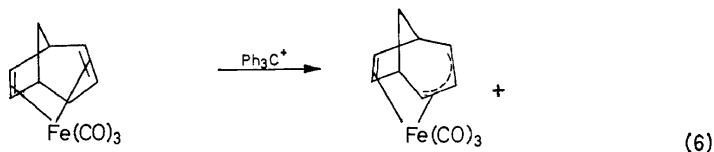
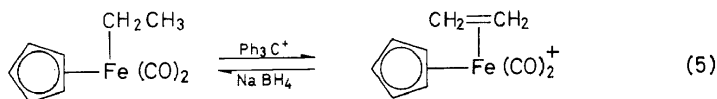
and 4 carbon ligands: the conjugated diene complexes

To the latter Emerson³¹ has added an interesting new type of 4-carbon ligand—the branched four carbon ligand obtained as the tricarbonyliron complex (XXXII). Its protonation leads, as shown, to related methallyl complexes and confirms the structure.

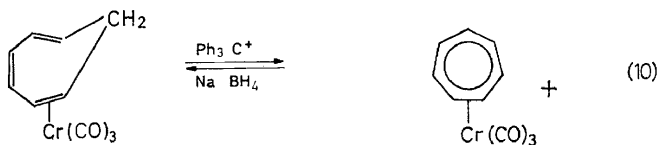
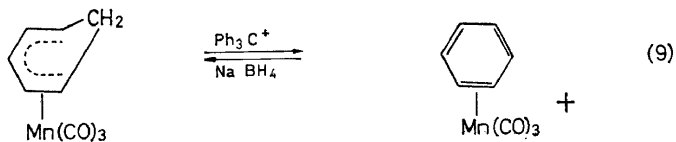
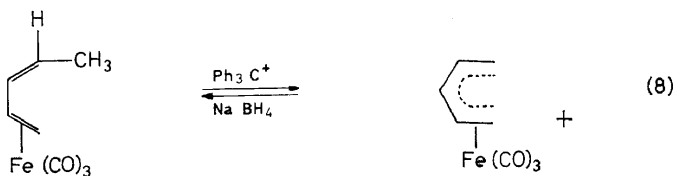
Transitions from one complex to one with either one more or one less metal-carbon link have become important preparative methods. For



increasing the number of links, triphenylmethylcarbonium salts acting as abstractors of hydride ion have been most widely used and may well be most versatile. The reverse addition of hydride is effected by NaBH_4 or LiAlH_4 . Green and Nagy³² have used these methods to interconvert alkyl



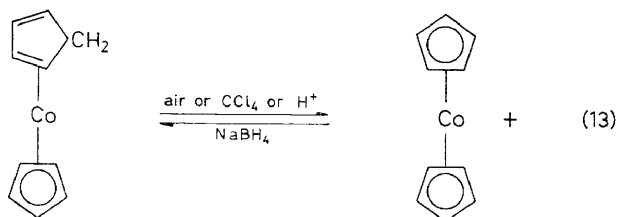
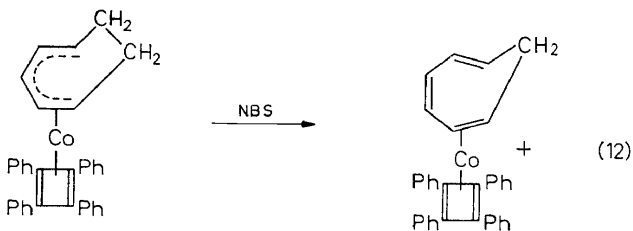
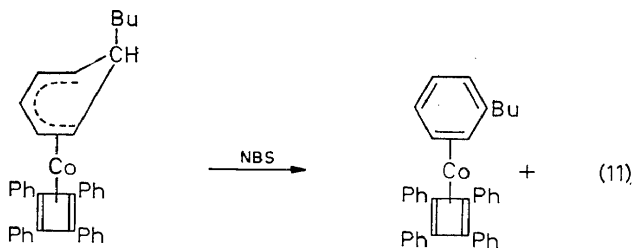
and alkenyl derivatives (see *e.g.* equation 5). An interesting example (equation 6) of the conversion of an alkene to an allyl complex was described by Margulis, Schiff and Rosenblum³³; we employed the same technique in transforming³⁴ the neutral nitrosyliron allyl to an unstable cationic diene complex (equation 7).



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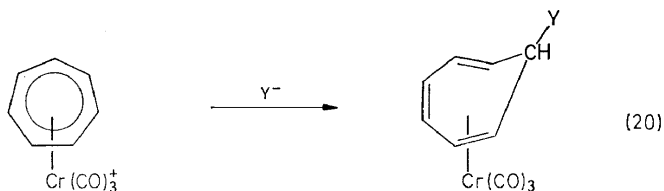
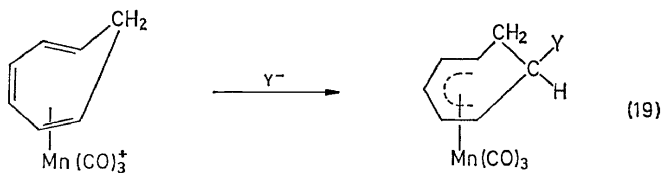
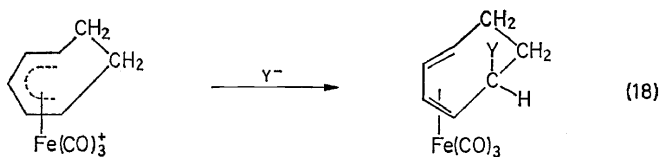
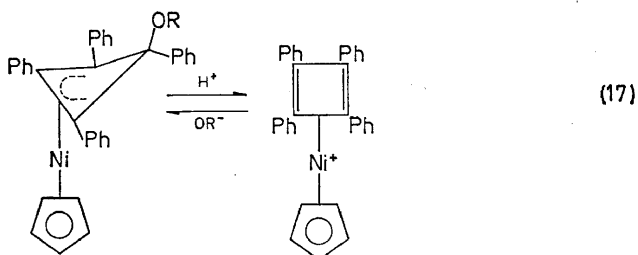
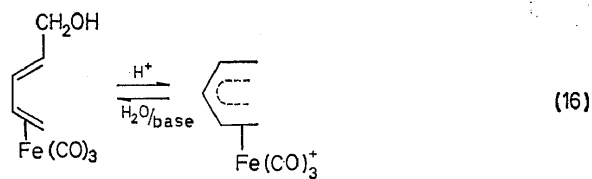
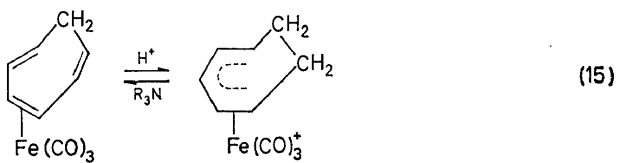
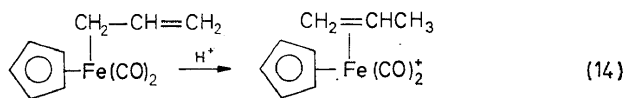
Examples of similar interconversion at the diene-dienyl-triene-trienyl levels using iron³⁵, manganese³⁶ and chromium³⁷ complexes respectively are shown in equations 8–10.

As an alternative oxidant Efraty and Maitlis³⁸ employed *N*-bromosuccinimide for the cobalt complexes shown (equations 11, 12). In contrast to Ph_3C^+ which appears, admittedly on rather limited evidence, to be stereospecific for removal of *exo*-hydrogen, this reagent can apparently remove the *endo*-hydrogen (equation 11). One of the earliest examples—the rather special one of $\text{C}_5\text{H}_5\text{CoC}_5\text{H}_6$ suffers dehydrogenation so readily³⁹ that even air oxidation suffices (equation 13).



Another approach is possible when a carbonium ion can be created α - to the metal–carbon bond by protonation. In addition to the protonation of compound (XXXII), four examples^{35, 40, 42} are shown in equations 14–17. The last two of these introduce, in the reverse reaction, the addition of other anions^{38, 42}, e.g. OH^- , OR^- ; these weaker nucleophiles will not add to cationic complexes in which addition is to C_5H_5 or benzenoid residues. Only H^- and R^- (as RLi or RMgX) are effective here. But when the ligand has less aromatic stability a wide variety of anions can be added.

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ORGANOMETALLIC COMPLEXES OF FIRST-ROW TRANSITION METALS

In my own laboratory we have been especially interested in the iso-electronic series of 7-membered ring complexes of iron⁴³, manganese⁴⁴, and chromium^{37, 45} shown in equations 18–20. We have studied malonate, alkoxide and cyanide addition in each of these systems and various other anions in the chromium case.

The stereospecificity of all such additions is not in doubt, single products being obtained consistently. Since in three cases, the phenyllithium addition to cobalticinium salts⁴⁶ and to the tricarbonyl tropylium-chromium salts⁴⁷ and the hydride addition to a tricarbonyl hexamethylbenzenerhenium salt⁴⁸ *exo*-addition has been demonstrated crystallographically, the assumption that this is the mode followed in all cases seems justified.

So far the chromium series is the only one where the other stereoisomer is also accessible⁴⁹. Apparently the preferred equatorial conformation of most 7-substituents is preserved during complex formation even at relatively

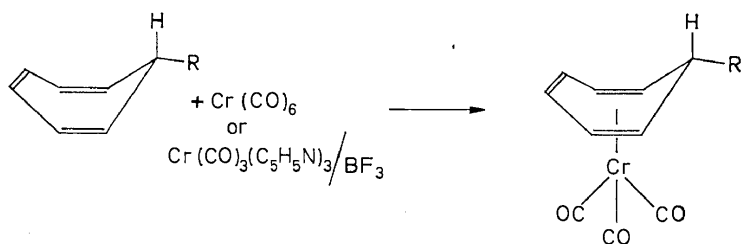
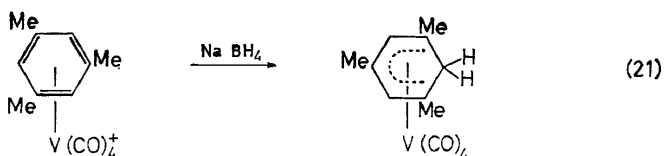


Figure 2

high temperature, allowing the reactions with chromium carbonyls (*Figure 2*) to occur with a high degree of stereospecificity. As a logical extension of such studies, the direction of addition of anions to unsymmetrical systems becomes of interest. To gain information about substituent effects on such addition it is easiest to work with the cationic benzene complexes. This effectively restricts the choice of anions to alkyl or hydride, but both are convenient since the products lend themselves to structure determination by nuclear resonance techniques.

Calderazzo⁵⁰ has shown that hydride addition to tetracarbonylarenevanadium occurs at unsubstituted positions in a series of polymethylbenzene derivatives. (*e.g.* equation 21). Since *exo* attack at a substituted position would require the substituent to be pushed towards the metal atom, the observed mode of attack is clearly favoured sterically. This assumes that the transition state is not too unlike the starting material since no marked hindrance is expected in the product—and indeed when no unsubstituted position is available, normal attack still occurs^{48, 50}.

We are engaged in a more extensive investigation of this addition reaction in the $\text{C}_5\text{H}_5\text{FeArH}^+$ series. Here, the same preference for unsubstituted



positions was noted by us some time ago⁵¹ and we can now further report that methyl groups appear to exert little or no other directive effect, attack being statistically distributed⁵² over the available unsubstituted positions in toluene and xylene complexes, *e.g.* as shown in *Figure 3*. On the other hand,

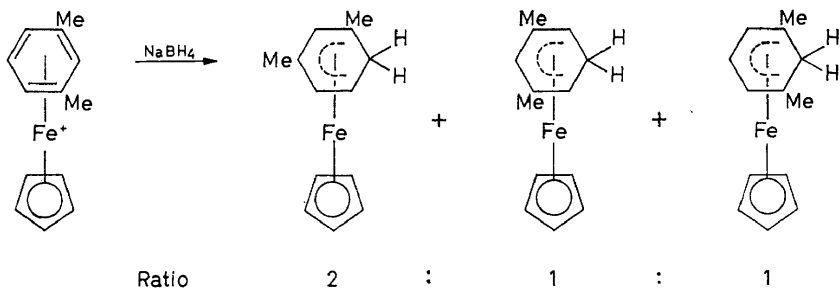
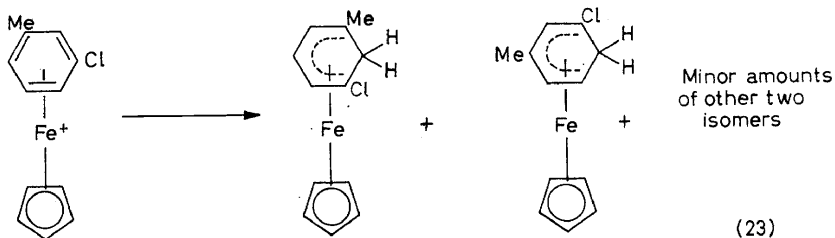
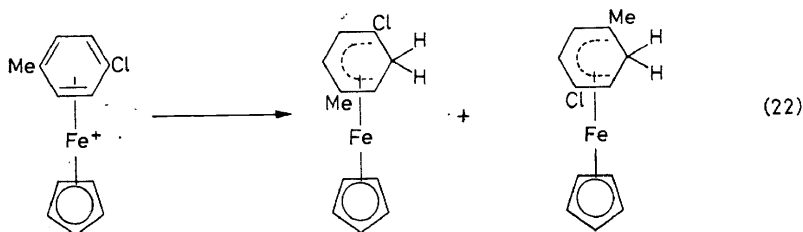


Figure 3

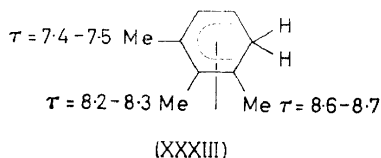
halogens have a very pronounced *o*-directing influence illustrated by the examples shown (equations 22, 23). Similar results are obtained with dichlorobenzene and with the bromo-analogues⁵². Whereas we can attribute this result to the inductive effect of chlorine enhancing the positive charge



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at the *ortho* position, it is somewhat surprising that the opposite effect of CH_3 is not sufficiently strong to be noticed. We are now studying other substituents in the hope of obtaining a more complete picture.

Although in many of these products the n.m.r. spectra can be analysed completely, it is worth remarking that the methyl groups provide a particularly convenient indication of structure. We find that the methyl



signals are highly dependent on the position of the group in the dieny system. Partial formula (XXXIII) shows typical values observed when no other substituents are present. Clearly these values reflect the electron distribution in the dieny system.

Viewed as simple analogues of cyclopentadienyl, the other dieny systems yield complexes which are less stable, but not to such an extent that there should not exist a very wide range of such compounds. Thus it should prove possible to obtain open-chain and cyclic dieny analogues of a large number

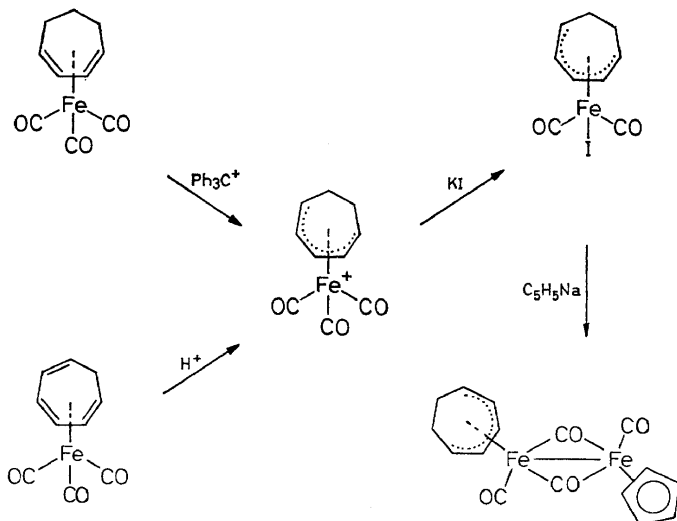
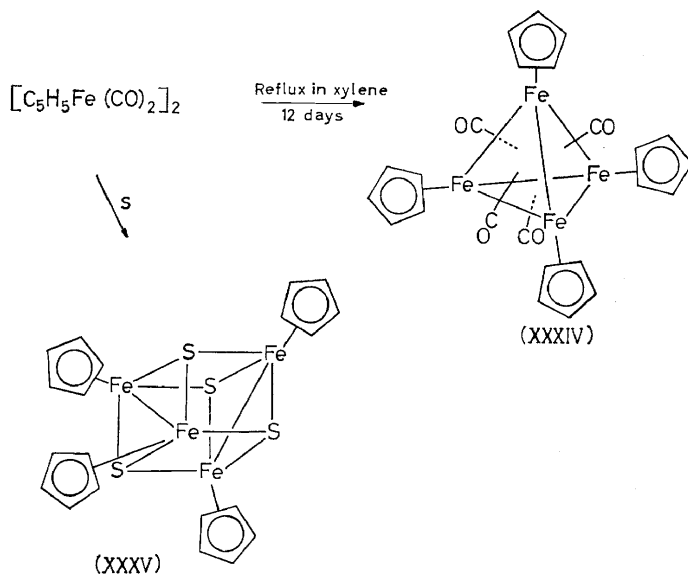
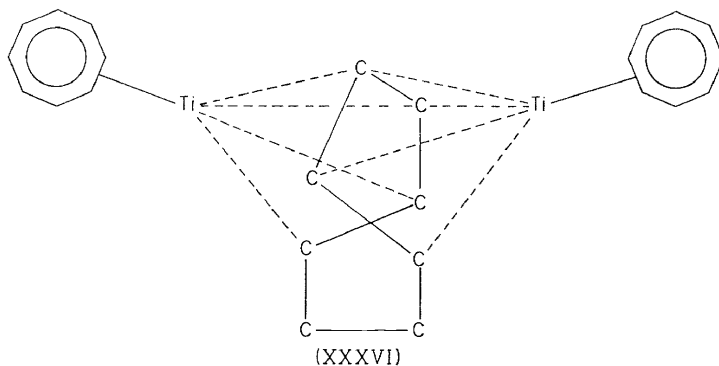


Figure 4

of cyclopentadienyl complexes. In the iron series we have made a few analogues of known carbonyl cyclopentadienyl derivatives⁴³, *e.g.* those shown in Figure 4 but for many transition metals not even this small beginning has been made. A similar range of possibilities awaits exploration with the heterocyclic analogues of cyclopentadienyl compounds, of which only a few azaferrocenes and tricarbonylpyrrolylmanganese derivatives have been prepared⁵³.



Even among the cyclopentadienyls themselves, well-studied though they have been in the last 15 years, surprising new additions continue to appear. Examples which come to mind include two iron clusters (XXXIV and XXXV), both derived from $(\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2)_2$, one by simple heating⁵⁴, the other by reaction with sulphur⁵⁵.



Although I have talked much about systems in which a metal atom is linked to either one or five carbon atoms, I have also touched on examples with 2, 3, 4, 6 and 7. I would like to end by mentioning Professor Wilke's discovery⁵⁶ of the first 8-carbon complex—his tricyclooctatetraenyldi-titanium (XXXVI), in which for the first time a metal atom is bonded symmetrically to 8 carbon atoms, despite the strain imposed by making the ring planar.

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