AROMATIC TRANSITION METAL COMPLEXES - THE FIRST 25 YEARS

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ABSTRACT

The progress of the chemistry of aromatic transition metal
complexes is traced from the discovery of ferrocene and other
early work on π-complexes. The gradual elaboration of
metallocenes from most transition metals, then of mixed
cyclopentadienylmetal carbonyls and analogues with other or
additional ligands was followed by the recognition and
synthesis of bis-benzenechromium and in turn a varied range
of benzenoid complexes. The importance of successive
developments in preparative methods in making possible the
rapid expansion of this field is stressed and it is shown
how in turn the benzenoid complexes were followed by
tropylium, cyclobutadiene, cyclooctatetraene and cyclo-
propylium complexes, thus completing a range with 3-8 membered
carbocyclic aromatic systems. Knowledge of heterocyclic
analogues is much more restricted, but rapid expansion in this
and in the chemistry of triple-decker and other multinuclear
complexes is foreseen. Photochemical, electrochemical and
metal vapour methods of synthesis are expected to play a major
part in such further developments. Finally a brief account is
given of the increasing emphasis on understanding the effects
of transition metals on aromatic ligand reactivity, e.g. by
facilitating both electrophilic and nucleophilic reactions.
Many new organic synthetic procedures are being evolved which
utilize such effects on reactivity or the stabilization in
complexes of structures which have only transient existence
in the metal-free state; a few selected examples of these new
methods are given.

Non-benzenoid aromatic systems were still a rather new field and one in
which I had a strong interest, when, in 1950, R. D. Brown predicted that
fulvalene, 1, should belong in this class. I was fortunate therefore, when
early in 1951, Tom Kealy agreed to work with me and to try synthetic routes
to this molecule. After some unproductive attempts along relatively lengthy
routes I suggested that he try a very simple approach: the reaction of
cyclopentadienylmagnesium bromide with ferric chloride. As an 'allylic'

1

$C_5H_5MgBr + FeCl_3 \longrightarrow (C_5H_5) Fe_2$
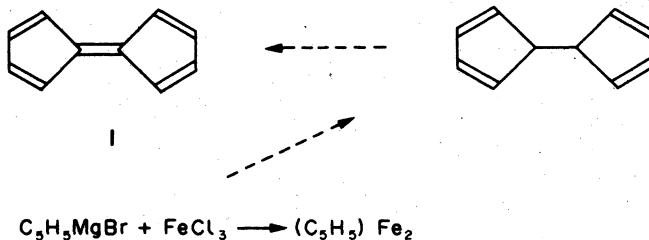
Grignard reagent C_5H_5MgBr was expected to undergo coupling when heated with transition metal halides; $FeCl_3$, if sometimes less effective than $CoCl_2$, had the advantage of being readily available in anhydrous form and might even cause immediate oxidation of the expected dihydrofulvalene to the desired aromatic system. I first saw the result of this experiment when a few drops of the ether solution ran down the outside of the separating funnel and left orange crystals. They proved to have the solubility characteristics and stability of the hoped-for aromatic hydrocarbon – but microanalysis showing 64.6% of carbon could only be accommodated by assuming the formula $C_{10}H_{10}Fe$. We could hardly believe that we had an organo-iron compound when much of the product was recovered unchanged from solution in conc. sulphuric acid; but on prolonged boiling with nitric acid or fuming with perchloric acid the presence of iron was duly confirmed both qualitatively and quantitatively.

This compound, now known as ferrocene had in fact been made somewhat earlier by Miller, Tebboth and Tremaine[2] by the vapour phase reaction of cyclopentadiene with an iron-oxide catalyst, but their publication of this discovery appeared after our own brief note.[3] You may well ask why these accidental discoveries should have led the organisers of this Conference to ask me to speak on the 'first 25 years' of aromatic transition metal chemistry. This is tantamount to asking why the discovery of ferrocene led to such a sudden surge of interest in organo-transition metal chemistry. I believe the answer lies in the timeliness which is an essential factor determining the impact of any chance discovery. It may be helpful therefore to set the scene by summarising the state of the art in 1951.

Ferrocene was far from being the first organo-transition metal compound. The first organometallic compound[4] was the ethylene-platinum compound known as Zeise's salt, $K[C_2H_4PtCl_3]$ described in 1827 – long before Frankland's alkyl zinc compounds and other 'conventional' organometallics. Alkyls of platinum and gold were also well-known, but there had been so many failures with other transition metals, that these substances were regarded as exceptions to a general rule that 'typical transition metals do not form stable organometallic compounds'. Indeed the coupling of Grignard reagents which we had tried to use had been one of the byproducts of such unsuccessful attempts. The carbonyls were other exceptions, regarded as sui generis, or despite their metal-carbon bonds not even thought of as organometallics. Reihlen's discovery[5] in 1930 of butadienetricarbonyliron, $(C_4H_6)Fe(CO)_3$, had been largely ignored. But perhaps most significant, the one known class of aromatic transition-metal complexes – Hein's so-called polyphenylchromium complexes '$[(C_6H_5)_nCr]X$' had obviously been discovered twenty years too soon[6]. Their existence was widely known and too well documented to be readily dismissed as fictional, but they had been allowed to remain a class of very puzzling compounds of unknown structure.

Against such a background we could have had no doubt that we had a most novel and remarkable compound on our hands and one whose true structure might not be what it appeared at first sight. We did not guess the correct structure – but we did initiate an attempt to have it determined crystallographically. The fact that that determination was delayed and later abandoned when three different groups of workers undertook similar work is irrelevant. The point I want to make is that ferrocene was discovered when X-ray techniques were sufficiently advanced and could give a rapid and firm answer – a situation very different from that which faced Hein in 1919. I have mentioned elsewhere that the correct structure of ferrocene was first suggested to me by W. E. Doering, to whom I described our compound shortly after we first made it. It is well known that the same structure was arrived at independently by E. O. Fischer,[7] by R. B. Woodward and by G. Wilkinson[8] when they first read our communication. Each sought and obtained evidence supporting this structure. Woodward went on to demonstrate[9] the aromatic nature of the beast and to coin the now familiar name, ferrocene. Fischer and Wilkinson directed their attention to the analogues of other transition metals and during the next few years such compounds were described in a rapid succession of communications, frequently simultaneously, from both their laboratories. There is ample evidence in the patent literature that several industrial laboratories in the U.S.A. were independently discovering many of the same compounds – further attesting to the range of interest aroused.

We had been lucky in our choice of the water-soluble ferric chloride. The
other simple halides we might have used were all too insoluble to react
under the same conditions and our own first attempts to make cobalt and
nickel analogues were therefore quite unsuccessful. But improved techniques
were soon forthcoming, by way of more soluble metal derivatives and the more
reactive alkali metal cyclopentadienides: Thus Wilkinson[10] used the metal
acetylacetonates, while Fischer[11] employed sodium and potassium cyclopenta-
dienide in liquid ammonia and the metal hexammine chlorides. These and
similar innovations led to the whole series of bis-cyclopentadienyls of first
row elements from Ti to Ni - compounds of widely varying stabilities whose
redox and magnetic properties provided much of the initial interest and
stimulus to the theoretician. For not only was ferrocene timely in terms
of structure determination, but also and perhaps more so in terms of under-
standing. The early papers proposing the correct structure already con-
tained interpretations in M.O. terms and were soon followed by more refined
treatments. Hückel's theory of aromaticity and Dewar's suggestions concern-
ing π-bonding provided some of the essential background for such treatments
and the latter almost simultaneously led Chatt and Duncanson[12] to interpret
the related structural problem posed by Zeise's salt. Computers were not
yet available - theoretical treatments had to be largely qualitative and
controversy ensued mainly about the extent of involvement of different
orbitals. Moffitt's treatment[13] emphasising a single metal-ring bond was
too great an oversimplification, but a useful stimulus to further experi-
mental work. The Fischer-Ruch treatment[14] based on the donation of 6
π-electrons (3 pairs) from each cyclopentadienide and hence formation of a
typical 6-coordinate metal complex, while also oversimplified, had the
advantage, in common with later treatments, of emphasising the attainment
of a formal inert gas electron configuration by the metal. This continues
to be a most useful guide as to which complexes are stable. Indeed as the
field has expanded the exceptions to the 'inert gas rule' have become a
decreasing proportion.

Of the neutral bis-cyclopentadienyls of course only those of Fe, Ru and Os
could fit the rule. In the first row, manganese proved exceptional, forming
an apparently ionic analogue with 5 unpaired electrons. The paramagnetic V,
Cr and Co complexes have considerable thermal stability, but are very
sensitive to oxidation, while Cp_2Ni with two unpaired electrons shows
surprising stability in both respects. The cobalt complex could attain
inert gas configuration of electrons in the oxidised - cobaltocenium salt
form - one of the most stable of all cyclopentadienyl complexes. Other
metals could attain inert gas configuration by incorporating additional
ligands. Among early examples described the basic (!) rhenium hydride, 2,
and the unique carbonyl of titanium, 3 stand out. Even higher coordination
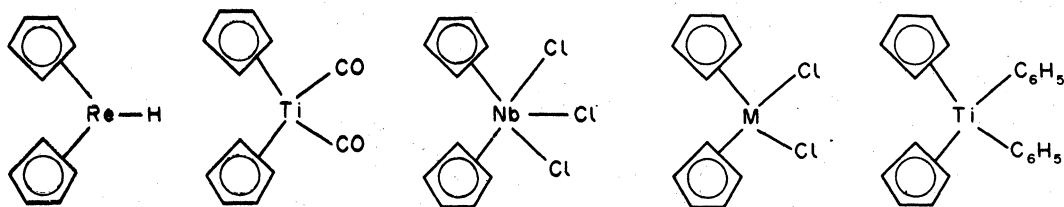
5: M = V
6: M = Ti, Zr, Hf

2   3   4   7

number was attained in the Nb compound, 4 and its Ta analogue while vanadium,
presumably because of its smaller size, gave the paramagnetic dichloride, 5.
The very stable dihalides of the Ti/Zr/Hf group, 6, are 16 electron complexes,
but since all outer electrons are bonding they are necessarily diamagnetic.
The titanium compound yielded[15] the first of the new stable transition metal
alkyls, 7.

Alongside such compounds were discovered the first of the mono-cyclopenta-
dienyl metal derivatives.   The examples shown (Fig. 8) illustrate the
varied types differing in counterligand.   We see that their wide range
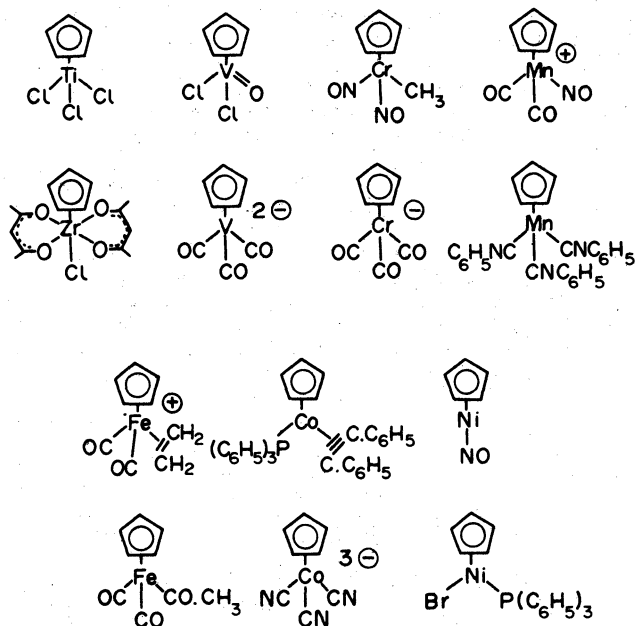included cationic and anionic derivatives.   The carbonyls (Fig. 9)

Fig.8

were reached either from the biscyclopentadienyl derivatives with carbon
monoxide or from the simple carbonyls with cyclopentadiene and included the
first binuclear cyclopentadienyls.   Again I must emphasise the important
contribution which the crystallographers made in establishing these struc-
tures and in some cases even the compositions.   Thus both the hexacarbonyl-
molybdenum (analogous to Cr) and the iron compounds had been formulated by
Wilkinson as pentacarbonyls before structure determinations[16,17] established
the compositions shown.
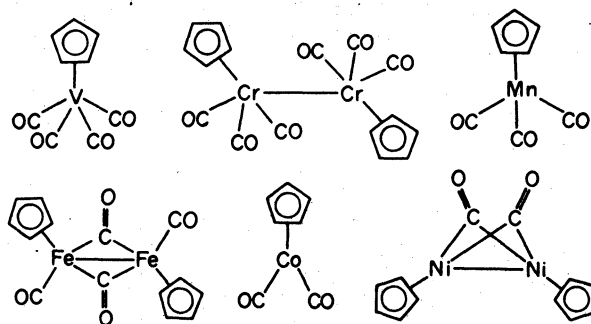
Fig. 9

Bis(cyclopentadienylnickel-carbonyl) required a different preparative method
proving accessible[18] only by reaction of nickelocene with nickel carbonyl
(Fig. 10).   The binuclear complex is somewhat unstable losing more carbon
monoxide to give the paramagnetic $(C_5H_5Ni)_3(CO)_2$ – the first trinuclear
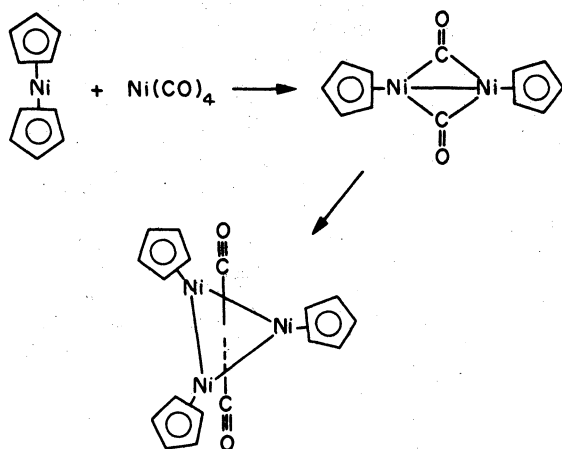complex of this type.

Fig. 10

If cyclopentadienyls seemed a unique class up to 1955 the dramatic develop-
ments of that year transformed the picture. Apparently several workers had
begun to speculate about the possibility of forming stable complexes from
benzene and its derivatives.   Positive results derive from two of these
speculations: Lars Onsager postulated that Hein's polyphenylchromiums were
in fact compounds of this type and stimulated experimental work by H. Zeiss
and his coworkers which ultimately confirmed this.[19]   Zeiss presented the
early experimental findings which strongly supported Onsager's idea in
several lectures given in Europe in the summer of 1955. But what appeared
to be highly suggestive results only acquired the aura of proof after the
independently undertaken synthesis of the parent bis-benzenechromium by
E. O. Fischer and W. Hafner.[20] I was fortunate to be a participant in a
half-day meeting of the Chemical Society in London where this result was
first presented. If anyone listening to Professor Fischer on that occasion
might have doubted that a whole new dimension had just been added to organo-
transition metal chemistry, there was, at the same meeting, the confident
prediction by Longuet-Higgins and Orgel that cyclobutadiene-metal complexes
should also be stable.[21]

So far as the benzenoid complexes are concerned intensive exploration in
E. O. Fischer's laboratory added complexes of many other metals (Fig. 11)
in the next 3 years and in 1958 the synthesis of the arene-tricarbonyl-
chromiums, independently achieved from the arenes and $Cr(CO)_6$ by his own
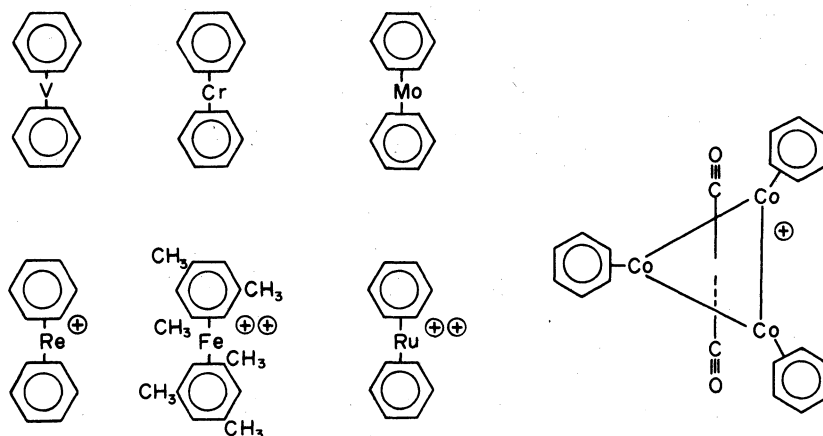group in Germany,[22] by Natta's group in Italy[23] and by Whiting and Nicholls

Fig. 11

in the U.K.[24] provided facile access to much more stable complexes and
opened up world-wide interest in the arene compounds. Independently
Wilkinson showed that the same reaction works with cycloheptatriene[25] and
since the complexes behaved like the free hydrocarbon in transferring
hydride to trityl cations, the first complexes containing the aromatic 7-
membered tropylium ring became available in this way.[26]

Development of suitable methods once again proved the key to many of these
advances. Fischer and Hafner[20] had invented the use of aluminium halides to
catalyse reaction between arenes and chromium(III) chloride and this proved
suitable for many other transition metals. Application to metal carbonyl
halides was first tried by Coffield and his coworkers at the Ethyl Corpora-
tion[27] and mixed cationic complexes such as $[C_6H_6Mn(CO)_3]^+$ and $[C_6H_6FeC_5H_5]^+$
resulted. Zeiss' group pioneered the formation of polysubstituted arene-
chromium complexes direct from acetylenes[19] while in E. O. Fischer's
laboratory K. Öfele[28] and later H. Werner[29] developed more and more sophisti-
cated methods of replacing carbonyl groups by arenes using labile complexes
of the type: $Cr(CO)_3L_3$ as intermediates from which the labile ligand (L)
could be displaced under sufficiently mild conditions to permit formation
of e.g. the iodobenzene, thiophene and even borazole complexes. As a result,
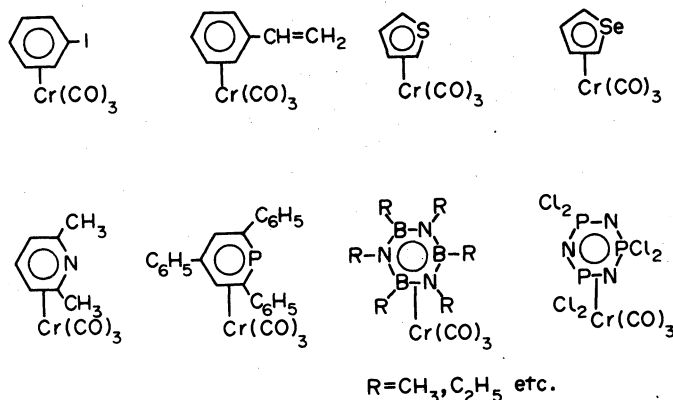
$R=CH_3,C_2H_5$ etc.

Fig. 12

a very wide range of such complexes is now known including the examples in
in Fig. 12.

While on the subject of heterocycles, I may mention that K. Joshi, working
in my laboratory was convinced that π-pyrrolyl complexes comparable to
cyclopentadienyls should exist and correctly chose $C_5H_5Mn(CO)_3$ as the most
stable mono-cyclopentadienyl to imitate.   He therefore heated pyrrole with
manganese carbonyl to achieve the first success[30] with a heterocyclic
cyclopentadienyl analogue, 13.

In the meantime, the predicted stability of cyclobutadiene complexes had not
failed to arouse interest; the dramatic proof of the correctness of this
prediction was obtained by Criegee and Schröder,[31] who in 1959 prepared the
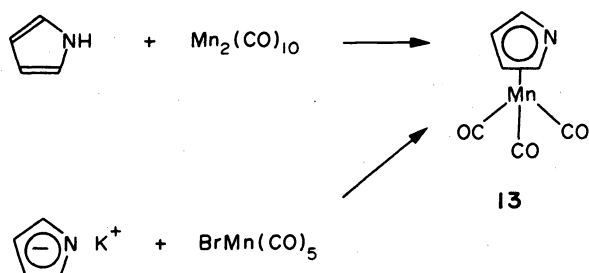
tetramethylcyclobutadiene nickel chloride complex by treating nickel carbonyl with dichlorotetramethylcyclobutene (Fig.14). Independently Hübel and Braye tentatively identified one of the products from iron carbonyls and tolane as the tetraphenylcyclobutadiene iron tricarbonyl.[32] These two approaches have remained the principal routes. Thus Pettit returned to the former method to
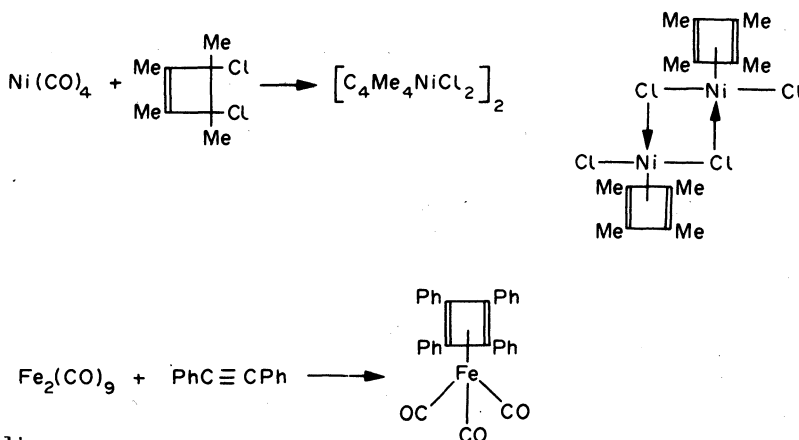

Fig.14

obtain[33] the unsubstituted iron complex in 1965 and the facile formation of tetraphenylcyclobutadiene palladium complexes from tolan, elucidated by Blomquist and Maitlis,[34] gave much impetus to further studies in the field including similar reactions of other metals. Maitlis[35] moreover developed an important secondary method when he showed that the Pd and Ni complexes readily transfer their cyclobutadiene ligands to other metals including Co, Fe and Mo.

Complexes of the smallest aromatic, the cyclopropenyl system have proved elusive – with the exception[36] of the single authenticated type exemplified by $Ph_3C_3NiC_5H_5$, 15, and its precursors $[Ph_3C_3Ni(CO)Br]_2$ and $[Ph_3C_3NiBr(py)_2]$.
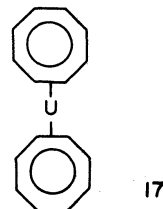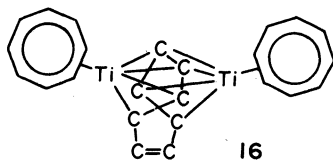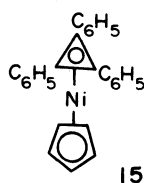

At the other end of the scale C_8H_8 is the largest ring known to form stable and aromatic transition metal complexes. The first examples of cycloocta-tetraene-titanium derivatives, e.g. 16, with flat 8-membered rings were described by Breil and Wilke,[37] but even greater interest was aroused by Streitwieser's discovery[38] of the uranium and related sandwiches, e.g. 17.

What fascinates the organic chemist in such systems is the formation of the stable planar aromatic system in cases where the free ligand is unknown, unstable, non-planar and/or non or even anti-aromatic. Before those of cyclobutadiene and cyclooctatetraene the complexes of the potentially anti-aromatic cyclopentadienone were known, while more recently, examples of complexes derived from fulvalene and pentalene have become known in steadily growing numbers.

Equally surprising at first was the realization that metals can have
the converse effect of stabilising non-aromatic forms: fixing double bonds.
A splendid illustration is provided by the stabilisation of the ketonic form
of phenol in e.g. complex 18, but the most startling examples are the arene
complexes in which benzene rings are bent and linked as 4-electron donors
with one clearly localised double bond, e.g. 19.

I have kept rather close to the term 'aromatic' in my title, but so many
interrelated developments have marked the progress in this field that it is
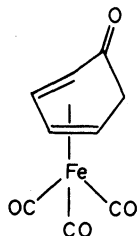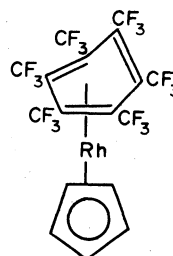
18   19

impossible to draw the line.   Perhaps my dilemma is best illustrated by
what may be the most remarkable of all the complexes – the carborane
derivatives.   Surely no conventional definition of aromaticity is applicable
– yet in many ways they are closely similar to the cyclopentadienyls.   They
exploded upon the chemical world with Hawthorne's first descriptions (in
1965)[39] and in the rapid stream of publications which has followed, what has
fascinated us is the architectural beauty of the structure of these molecules,
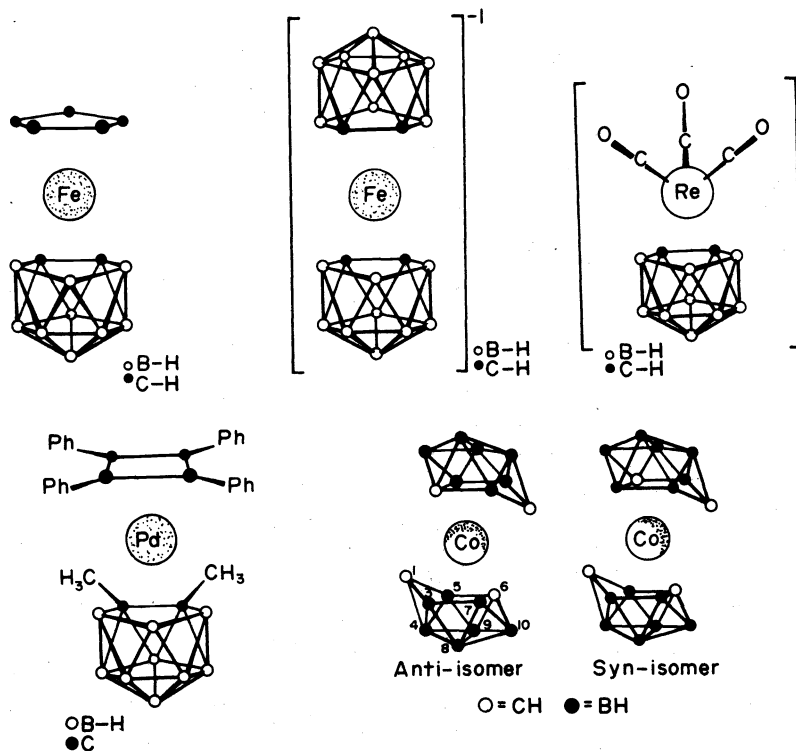their variety and their unprecedented rearrangements (Figs. 20, 21).

Anti-isomer   Syn-isomer

O = CH   ● = BH

Fig.20   oB–H
                          ●C

Many other if less spectacular developments took place in parallel –
influenced by and in turn influencing the development of the aromatic
complexes: The work on cyclopentadienyls led directly to our reformulation[40]
of Reihlen's butadienetricarbonyliron and in the same year Jonassen[41] pre-
pared the first π-allyl complex from butadiene and HCo(CO)$_4$.   This was soon
followed by general routes which made such π-allyls widely available.[42] Also
around 1960, the first cyclohexadienyl complexes were prepared, both by
hydride abstraction (22) from diene complexes[43] and by nucleophilic addition[44]
to cationic arene complexes 23.   They turned out to be merely the first
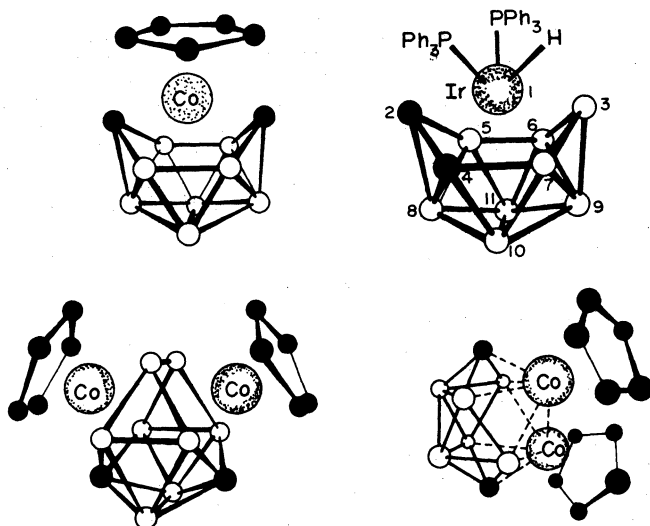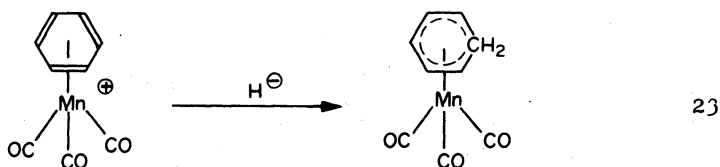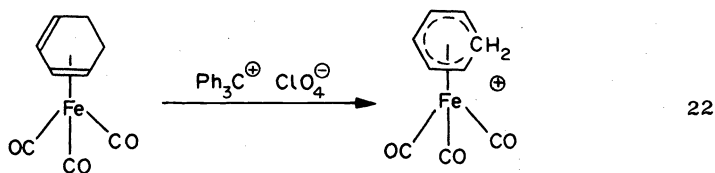examples of a range of dienyl complexes which so closely resemble the

Fig.21

corresponding cyclopentadienyls that the description 'pseudo aromatic' suggests itself for such ligands.

22

23

And a little further away from the aromatic complexes there has been a great volume of intriguing literature on complexes of alkenes and non-conjugated dienes and in the last 12 years the pioneering work of E.O. Fischer on carbene and carbyne complexes and the discoveries, led by Wilkinson and by Lappert of many remarkably stable simple alkyls. Throughout the 25 year period under review some of the most unpredictable results have come from studies of the reaction of acetylenes with metal carbonyls. Indeed these studies go back to the early nineteen forties, when Reppe's group first isolated several iron and cobalt complexes during their work on carbonylation. The astounding structural diversity which results from acetylenes on complexation seems to be unending – (I have already mentioned cyclobutadiene and cyclopentadienone complexes) – and is far beyond the scope of this account. Perhaps I may give a solitary example to show that almost every X-ray determination reveals a new type. The compound 24 was first made 17 years ago,[45] but its complete purification and structure analysis has only just been completed.[46] It is the product of successive treatment of $Co_2(CO)_8$ with PhC≡CH, then CO and then MeC≡CH and illustrates σ-bonding, π-olefin and π-allyl-bonding within the same molecule.

But what of the 1970s and beyond? I should be foolhardy to risk wild predictions and have no intention to gaze into a crystal ball. But a look at recent advances and current trends may give us some hint of where rapid progress is most likely. Each new method of preparing complexes has added to the range and variety. In the seventies the most impressive example has been the atomic vapour method based on P.S. Skell's work and brilliantly
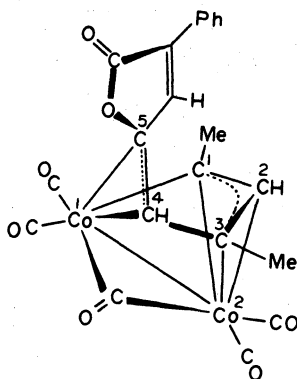
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developed by Timms and more recently also Green in the transition metal
field.   Much is still to be expected not only from this method, but also
from the development and more systematic application of both electrochemical
and photochemical techniques.   The power of the latter has long been recog-
nised, but application has been sporadic despite the success in obtaining
unusual structures not readily available otherwise.   A few examples may serve
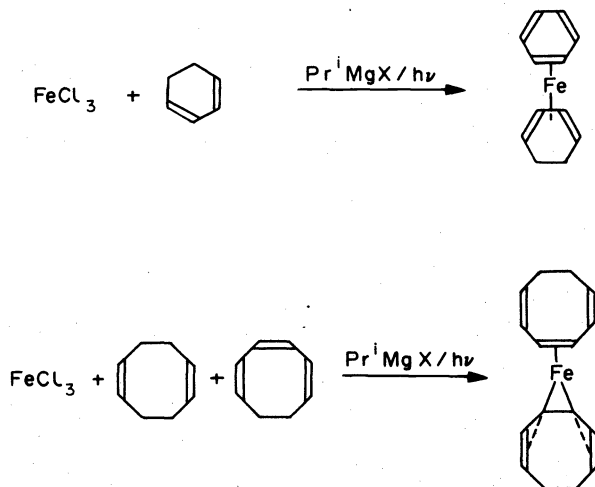to illustrate this:
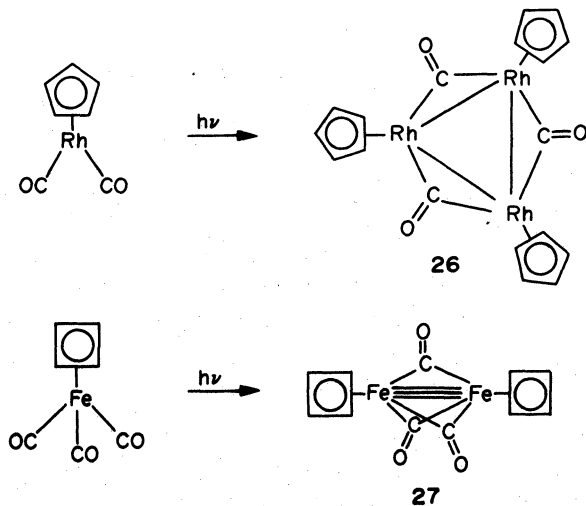

Fig.25

Fischer and Müller[47] employed irradiation to promote reactions of metal
halides with unsaturated hydrocarbons in the presence of $(CH_3)_2CHMgBr$ as
reducing agent (Fig. 25).   Yet the way irradiation assists this versatile
synthetic reaction remains obscure.

26

27

Many workers have used irradiation to induce dissociation of carbonyl groups.
Results include the formation of cluster compounds, e.g.[48] 26, themselves the
centre of much recent interest and surely offering great scope for further
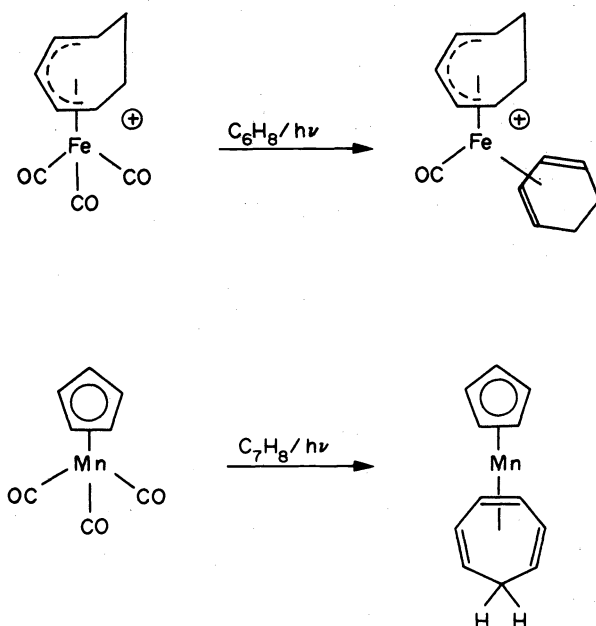exploration. Other photolysis products include multiply metal—metal bonded

Fig. 28

systems, e.g.[49] 27, and irradiation has made possible the simultaneous
substitution of two or three CO groups from otherwise very stable complexes
e.g.[50] (Fig. 28).

If triple deckers have been the subject of speculation for 20 years the
isolation of the first examples[51,52] (Fig. 29) undoubtedly opens up not only
the likelihood of finding analogues with rings other than 5-membered – but
the possibility of multilayered structures.

$[(C_5H_5)_3Ni_2]^+ BF_4^-$ $(C_5H_5)_2Co_2C_2B_3H_5$ isomers

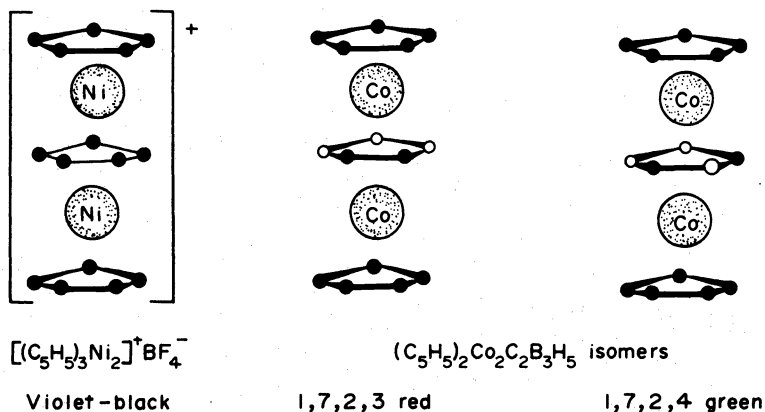Violet - black   1,7,2,3 red   1,7,2,4 green

Fig. 29

Heterocyclic complexes are still rare, but I doubt that this reflects their
inherent instability rather than insufficient effort to make them both by
applying known techniques and by devising new ones specifically suited for
this purpose. In the former category application of the metal vapour method
may prove rewarding, while a new approach has been pioneered by Herberich who
obtained a series of borabenzene complexes by ring expansion reactions,[53]
e.g. 30. It is one example of how studies of reactivity of complexes have in
fact contributed to the syntheses of new types of organometallics. There are

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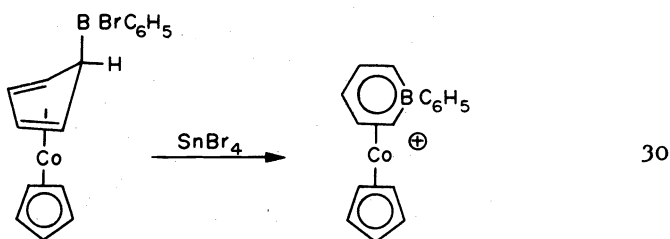
many others – including a variety of ring expansions and contractions.
Fischer and Breitschaft's early observation[54] that attempted Friedel–Crafts
acylation of benzenecyclopentadienylchromium or –manganese gives the
corresponding tropylium complexes (Fig. 31) has remained one of the most
fascinating examples perhaps not least because no satisfying mechanism has
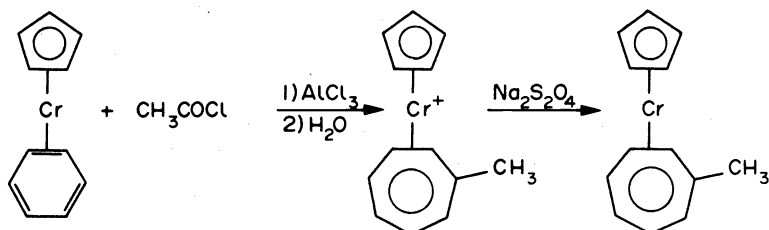ever been advanced to rationalize it.

Fig.31

I have chosen to concentrate on preparative aspects in order to illustrate
the multitude of structural types which have become known. Many other
aspects could and should perhaps have been stressed and I can only mention
them very briefly. Stereochemical features of the structures have been a
persistent source of interest and the elegant studies of Brunner and of
Tirouflet have provided a multitude of examples of metal chirality and aided
study of reaction mechanisms. The observation of single proton resonances
in σ-cyclopentadienyls and in cyclooctatetraenetricarbonyliron – in
apparent conflict with solid state structures – first drew attention to the
remarkable fluxionality of numerous complexes, so elegantly elucidated and
widely studied by F. A. Cotton.[54a]

The reactivity of the organic ligands in complexes rather than mere prepara-
tion of the complexes has increasingly become the main centre of attention
and presents problems which will continue to offer an interesting challenge
for many years. Ligands may be split off or exchanged; they may undergo
novel additions while still bound to the metal or at the moment of liberation
as in the elegant work of Pettit on the $C_4H_4Fe(CO)_3$ system. They may be
activated towards electrophilic or nucleophilic attack. The former is the
basis of the extensive aromatic chemistry of ferrocene and of $C_5H_5Mn(CO)_3$ –
a subject which would have merited a review lecture of its own in a more
organically oriented symposium. It has been contributed to by many, but
most consistently, indeed massively by the group at the Institute of Organo-
Element Chemistry in Moscow under the leadership of Academician A. N.
Nesmeyanov.

Nucleophilic attack has been equally widely studied – but even the simplest
reactions still provide problems of interest. I shall illustrate this
largely from our work. Strong activation of halobenzenes by the $Cr(CO)_3$
group was first demonstrated by Whiting who showed that nucleophilic
substitution by alkoxide occurs under mild conditions.[24,55] Nesmeyanov
demonstrated that even greater reactivity is observed in substituting the
cationic complexes of the type $[C_5H_5FeC_6H_5Cl]^+$ (Fig. 32) and used a wide
variety of nucleophiles to do so.[56] Our recent studies[57] of
$[(C_6H_5Cl)Mn(CO)_3]^+$ showed a marked further increase in reactivity emphasising
the effect of the counterligand. With strong nucleophiles, e.g. hydride or
carbanions, addition is always preferred to substitution and occurs regard-
less of the nature of the benzene substituents, although these were shown to
exert interesting directive effects, e.g. 33. The cyclohexadienyl complexes
formed by addition of carbanions were shown[58] to undergo hydrogen migrations
on heating, e.g. 34, probably via Mn–H derivatives. Similar migrations had
previously been studied in the $C_7H_8Cr(CO)_3$ series.

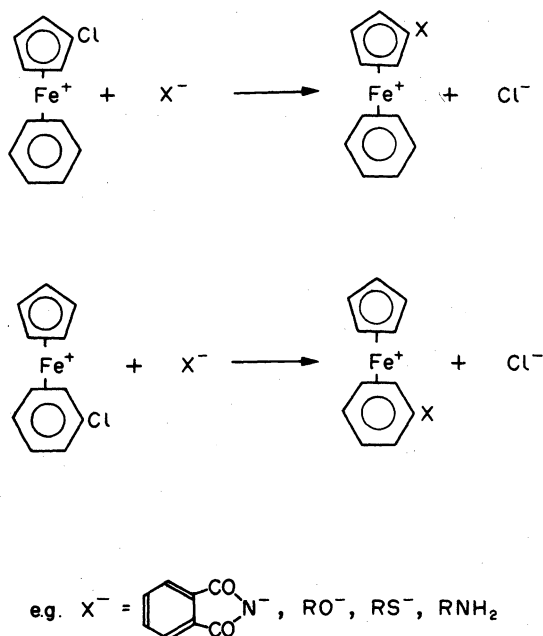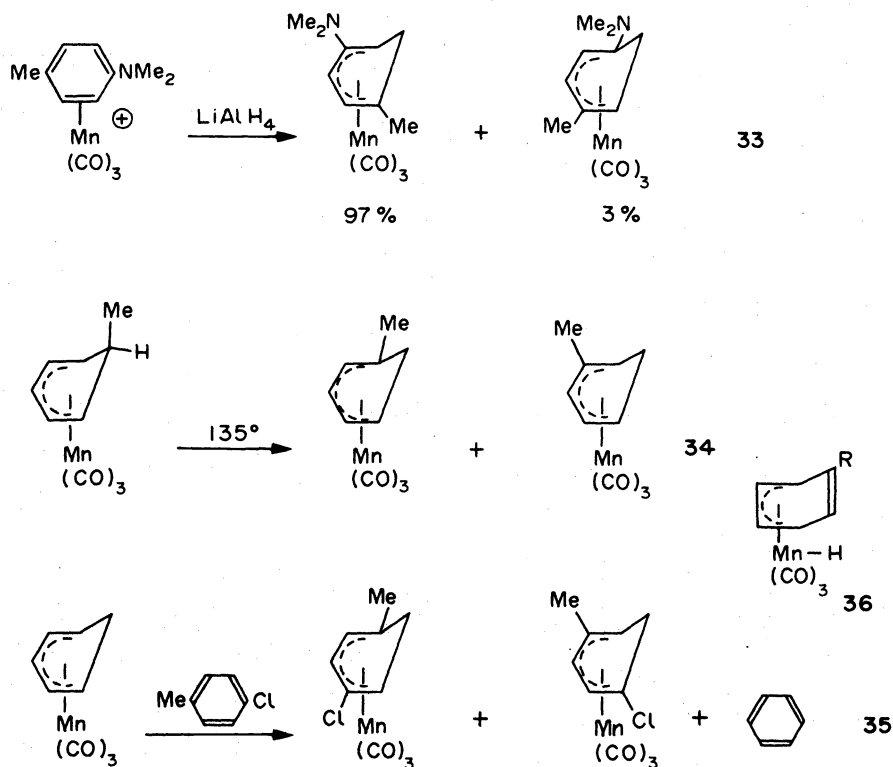e.g. $X^- = $ N^-, RO^-, RS^-, RNH_2

Fig.32

The Mn complexes also undergo ligand displacements <u>with</u> hydrogen transfer, 35 – perhaps via the same intermediate, 36. Simple ligand displacements, 37, were long known in the ArHCr(CO)$_3$ series,[59] but displacement preferences

are unknown and are currently under investigation. If displacement of e.g. alkoxy-benzenes with chloro-or fluorobenzene can be effected sufficiently efficiently, the cyclic process, 38, becomes an attractive method of phenyla-tion in which the relatively expensive chromium carbonyl component can now be seen in an essentially catalytic role.

In contrast to the cationic complexes which add nucleophiles so readily, few

$$ArH + (Ar'H)Cr(CO)_3 \rightleftharpoons Ar'H + (ArH)Cr(CO)_3$$
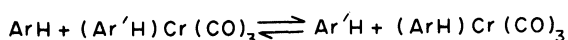
37
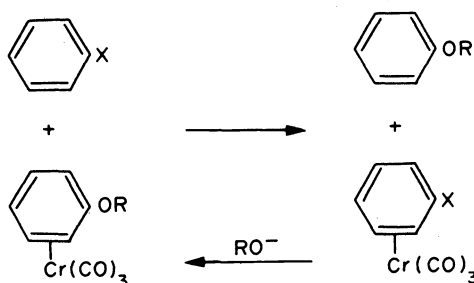
38

X = Cl or F

additions to neutral complexes are known. But Semmelhack[60] has shown that
many carbanions add smoothly to $C_6H_6Cr(CO)_3$ giving unstable adducts, but
high yields of the free substituted arenes on oxidation. We have encount-
ered another amusing example of addition to a neutral complex. During
preparation of the above cyclohexadienyl-manganese tricarbonyls we noted
that excess $LiAlH_4$ gave two by-products.[61] One of these had been isolated
by Winkhaus,[62] who on i.r. evidence alone formulated it as 39. Its n.m.r.

40

39   41
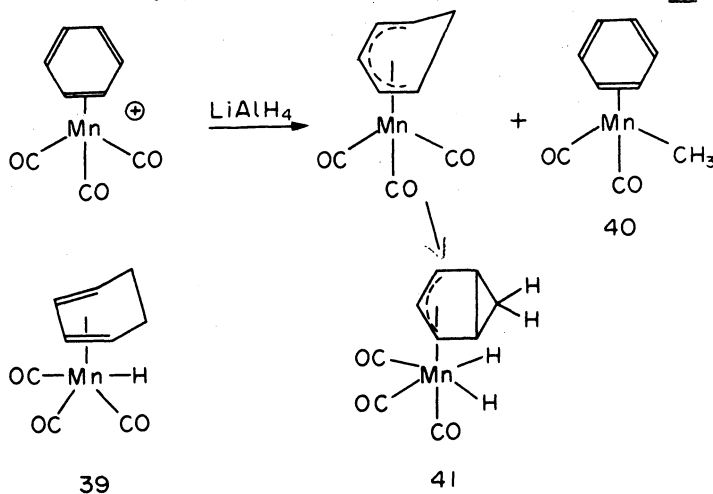
spectrum in fact shows clearly that it is the dicarbonyl-methyl, 40. But
the second product is of greater interest. It can be obtained in high yield
by first preparing the cyclohexadienyl complexes and then subjecting them to
further hydride reduction. ¹H nmr suggests the formulation 41. The
spectrum shows coalescence of the signals on warming, corresponding to rapid
interchange of all the protons in two groups: an 'exo'-pool of six and an
'endo' pool of three hydrogens - possibly via e.g. 39.

These rather arbitrarily chosen examples are designed to show how much we
can still learn about apparently simple reactions. Other examples would
provide better evidence of the steadily increasing value of transition metal
organometallics to the synthetic organic chemist, although most are again
further removed from the 'aromatic' class. I think particularly of the
well known and elegant work of Wilke on the cyclooligomerization of buta-
diene and many related reactions of allyl-Ni complexes. I think of a wide
range of fascinating condensation reactions studied by Heck[63] in America, by
Chiusoli[64] in Italy and by Tsuji[65] and others in Japan. These reactions
in which quite simple molecules are combined in one step to produce much
more complex products have already been exploited by Corey and others in
natural product and other organic syntheses. In my own laboratory we are
still perfecting a cyclopentenone synthesis[66] which, illustrates well how
much can be achieved in one step (Fig. 42). Methods such as these, or the
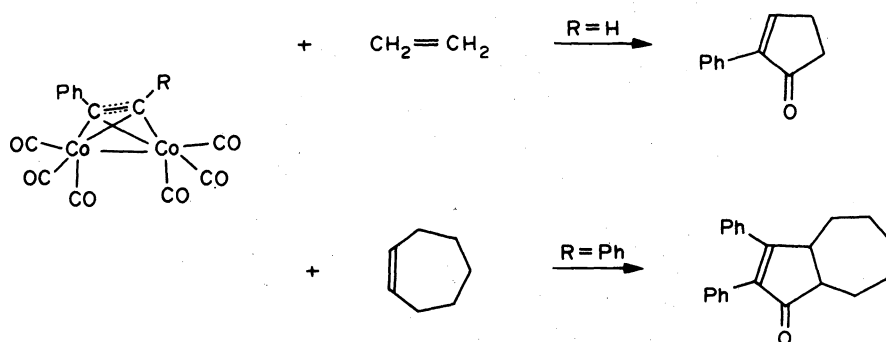reactions of cyclopentadienyldicarbonyliron complexes explored by

Fig 42

Rosenblum,[67] the dienyliron complexes studied by Birch,[68] and the synthetic methods using tetracarbonylferrate developed by Collman[69] are rapidly taking their place among the standard methods of the organic chemist and I believe that we will soon see such organometallic reagents as widely accepted as say organolithium compounds. Finally the effect which all this chemistry has had on the development of homogeneous catalytic methods will I hope become clear from some of the later lectures in this symposium since neither the time nor the scope of my lecture permits me to touch on this vast field.

I have given what is clearly a highly personal account of the developments as they have impressed themselves on my memory in the last 25 years. I would like to thank the organisers for inviting me to give this account and my coworkers who have enabled me to play a small part in these developments.

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