Pure & Appl. Chem., Vol.56, No.1, pp.63-80, 1984.
Printed in Great Britain.

0033-4545/84 $3.00+0.00
Pergamon Press Ltd.

REACTIVE ORGANOMETALLIC COMPOUNDS FROM METALLOCENES

Klaus Jonas

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1
4330 Mülheim a. d. Ruhr, Germany

Abstract - Metallocenes can be converted into reactive organometallic compounds having readily accessible coordination sites by removing one or both of the C_5H_5-ligands: two types of reaction are discussed by which this can be achieved. Both these reactions permit the preparation of numerous new organometallic compounds, many of which are important precursors for organometallic syntheses.

Aspects to be covered include the synthesis of $(C_5H_5)Co(C_2H_4)_2$ and its application as a catalyst precursor for the cobalt-catalysed alkyne cyclooligomerization and the cotrimerization of alkynes and nitriles. Also reported are the alkali metal cobaltates $M_A[Co(C_2H_4)_4]$ and $M_A[Co(cod)_2]$ (M_A = alkali metal) which can be used as starting materials for the preparation of new catalysts for the hydrogenation of olefins and arenes. Finally, a series of novel binuclear complexes of Co, Fe and V is presented that are the first examples in which η^6-arene ligands are bonded to two metal centres.

INTRODUCTION

Some years ago, our investigations on the "Nickel Effect" (1), based upon studies of the organic chemistry of nickel carried out by Wilke and his coworkers, prompted us to examine the behaviour of nickel(0)-olefin complexes towards the hydrides and organometallic compounds of the alkali metals (2, 3). From the reaction of cyclododecatriene-nickel(0) [Ni(cdt)] with dinitrogen and either lithium phenyl or a mixture of sodium and lithium phenyl, we obtained $[(LiPh)_6Ni_2N_2(Et_2O)_2]_2$ (4) and $\{Ph[Na(Et_2O)]_2(Ph_2Ni)_2N_2NaLi_6(OEt)_4(Et_2O)\}_2$ (5), respectively. These two compounds, for which the crystal structures have been determined (5, 6), are the first examples of transition metal N_2 complexes in which dinitrogen molecules are bonded side-on. A third example, that of a Ti_4 dinitrogen complex, has recently been reported (7).

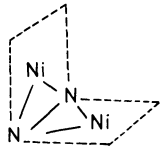


Fig. 1. Side-on coordination of dinitrogen to two nickel centres in $[(LiPh)_6Ni_2N_2(Et_2O)_2]_2$ (6).

Shortly afterwards we were able to demonstrate that nickel(0)-olefin complexes can react with the elemental alkali metals when lithium is used as the reducing agent. In this way, bimetallic compounds with two lithium atoms per nickel were obtained, e.g., $[Li(TMEDA)]_2[Ni(cdt)]$ and $[Li(THF)_2]_2[Ni(cod)_2]$ (2, 3, 8). This raised the question whether compounds of this new type could also be prepared with other transition metals. Since it was already known that certain metallocenes can be reduced by alkali metals to give elemental transition metals and alkali metal cyclopentadienides (9), we considered it likely that the addition of suitable olefins could be a promising route to new alkali metal-transition metal-olefin complexes. In 1976 the first results of these investigations were reported - the reaction of cobaltocene with lithium and 1,5-cyclooctadiene to give $[Li(THF)_2][Co(cod)_2]$ (10).

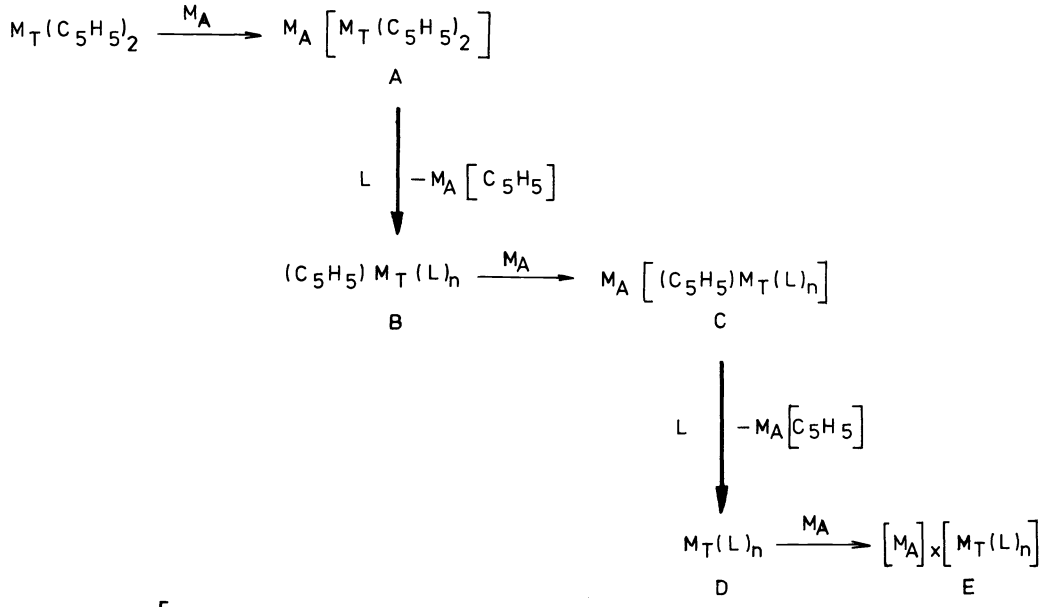
$$Co(C_5H_5)_2 \xrightarrow[-Li[C_5H_5]]{Li,\ cod} (C_5H_5)Co(cod) \xrightarrow[-Li[C_5H_5]]{2\ Li,\ cod} Li[Co(cod)_2] \qquad (1)$$

Since then we have been particularly interested in the use of metallocenes as precursors for the synthesis of reactive organometallic compounds.

A. METALLOCENES AS STARTING MATERIALS FOR THE SYNTHESIS OF REACTIVE ORGANOMETALLIC COMPOUNDS

The metallocenes can be converted into reactive organometallic compounds having readily accessible coordination sites by removing one or both of the C_5H_5-ligands. We are looking at both the following types of reaction A.1. and A.2. to achieve this under mild conditions.

A.1. Reductive abstraction of C_5H_5-ligands by alkali metals

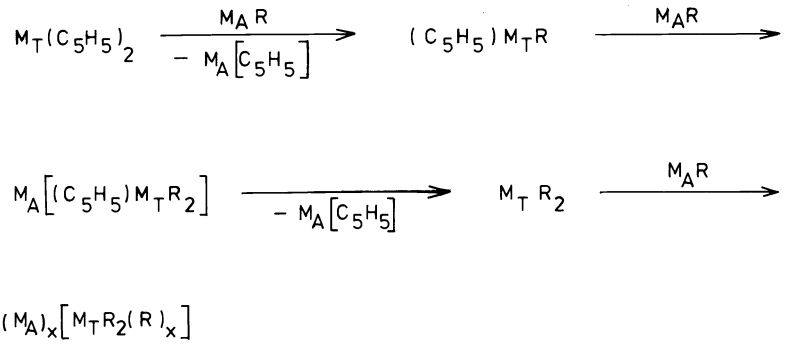


Scheme 1 [M_T = transition metal; M_A = alkali metal; L = olefin, arene, phosphine, CO, N_2, etc.; x = 1 or 2. The donor ligands (THF, Et_2O, etc.) bonded to M_A in the compounds of type A, C, and E, have been omitted.]

Metallocenes of the first row transition metals can be reduced by alkali metals in the presence, or with subsequent addition, of L to give either alkali metal-free (B, D) or alkali metal-containing (C, E) transition metal complexes. Moreover, depending upon the transition metal, it is possible to remove selectively one or both of the C_5H_5-ligands from the transition metal by choice of appropriate reaction conditions and stoichiometry.

A.2. Metathetical reactions of metallocenes with main group metal hydrides or organyls

Certain metallocenes readily undergo metathetical reactions (9b, 11-14). Of relevance here are their reactions with main group metal (Li, Mg, Al, etc.) hydrides or organyls. For example, alkali metal organyls (M_AR) react with metallocenes, giving alkali metal cyclopentadienides as in A.1. However, in contrast to A.1., the removal of a C_5H_5-ring now requires the transfer of an organyl residue (R) to the transition metal, which thus retains its oxidation state.

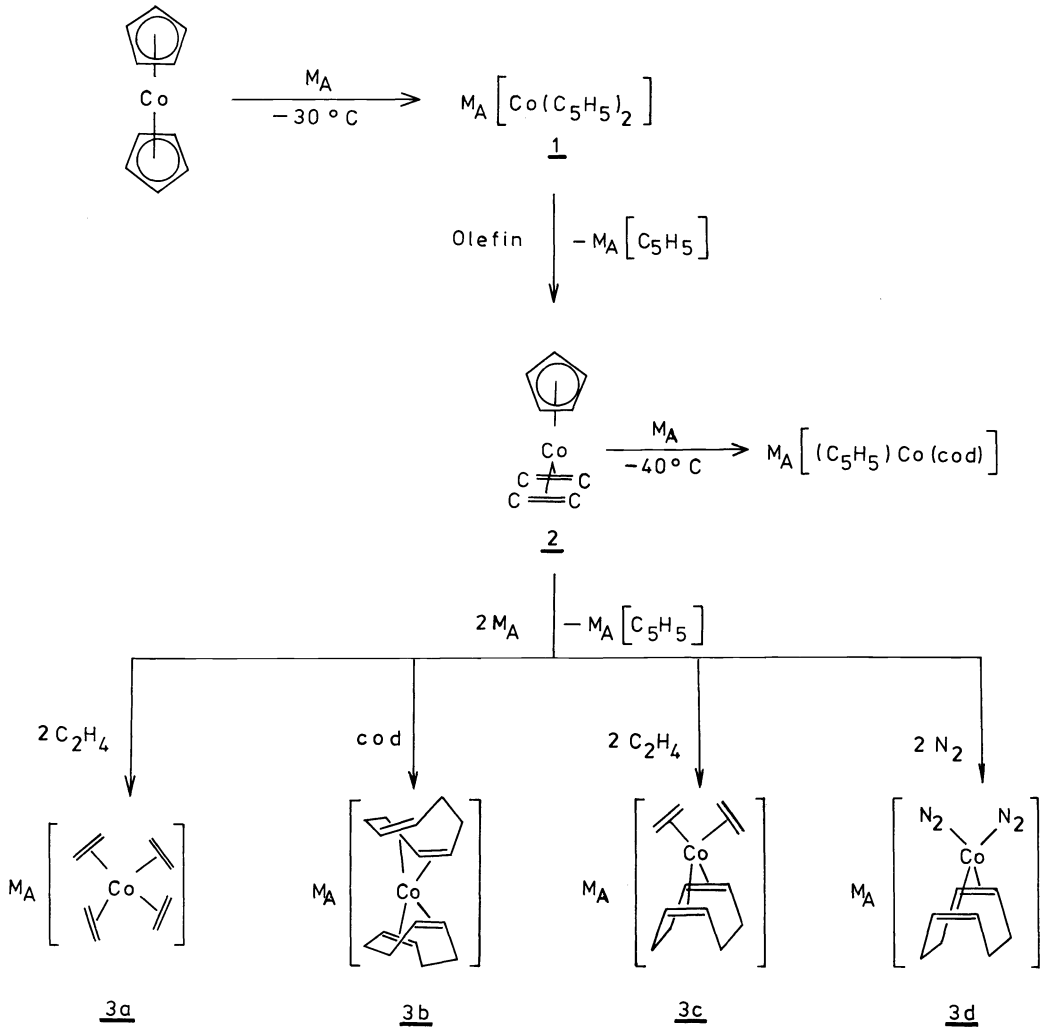


Scheme 2

A.3. Syntheses based on the combination of A.1. and A.2.

Scheme 1 and Scheme 2 indicate that it is possible to remove just one C_5H_5-ring from the metallocene. This creates further possibilities for synthetic applications since the two procedures can be combined so that the first ring may be removed by one method and the second by the other (11).

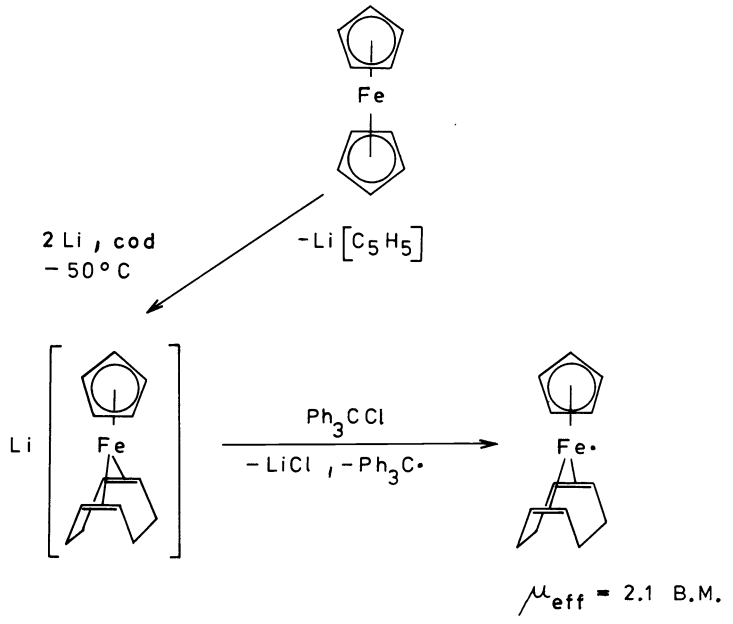
A.1.1. Olefin and dinitrogen complexes of cobalt from cobaltocene. Cobaltocene reacts with lithium or potassium in tetrahydrofuran to give 1:1 adducts 1 which can be isolated at low temperature and in which both C_5H_5-ligands remain bonded to the transition metal. Loss of a cyclopentadienyl ring occurs at low temperature only when olefins are added. Butadiene, 1,3-cyclohexadiene or 1,5-cyclooctadiene react with 1 to afford $(C_5H_5)Co(C_4H_6)$, $(C_5H_5)Co(C_6H_8)$ or $(C_5H_5)Co(cod)$, respectively. With ethylene we achieved the first synthesis of $(C_5H_5)Co(C_2H_4)_2$ (2a), the parent compound of these cobalt(I)-olefin complexes 2 (Scheme 3).



Scheme 3

At -40°C in tetrahydrofuran $(C_5H_5)Co(cod)$ reacts with alkali metal to give $M_A[(C_5H_5)-Co(cod)]$, in which the diene remains intact and 1,5-coordinated (however, see Ref. 15). Similarly, 1,5-coordination is retained in the alkali metal cobaltates 3b, 3c and 3d. 3c and 3d are prepared in high yield by reduction of $(C_5H_5)Co(cod)$ with 2 mole equivalents of alkali metal under an ethylene or dinitrogen atmosphere, respectively. The syntheses of the "pure" cobaltates 3a and 3b do not, of course, require the isolation of the intermediates 2. These compounds can be prepared directly from cobaltocene by reduction with at least 3 mole equivalents of alkali metal in the presence of ethylene or 1,5-cyclooctadiene [see also Eq. (1)].

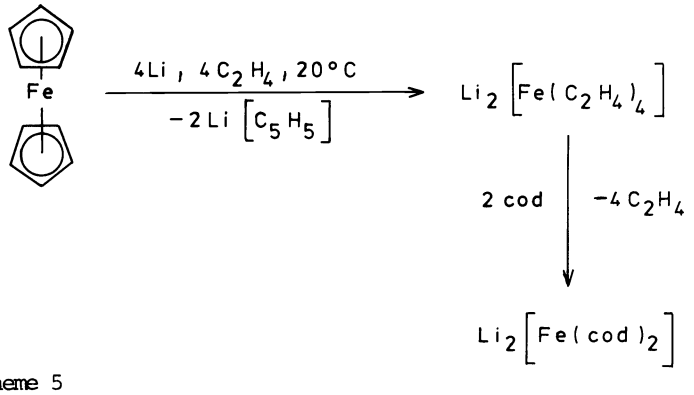
A.1.2. Iron-olefin complexes from ferrocene. Treatment of ferrocene with lithium metal and olefins (ethylene, 1,5-cyclooctadiene) in dimethoxyethane at between -60°C and -40°C results in elimination of only one C_5H_5-ligand. With cyclooctadiene as the olefin, $Li[(C_5H_5)Fe(cod)]$ (4) is obtained, which gives monomeric, alkali metal-free (η^5-cyclopentadienyl)(η^4-1,5-cyclooctadiene)iron (5) when reacted with trityl chloride (2, 3).



4 5

Scheme 4

Both C_5H_5-ligands of ferrocene may be removed by treatment of $Fe(C_5H_5)_2$ with lithium and ethylene at ambient temperature to give $Li_2[Fe(C_2H_4)_4]$, the X-ray structure of which has been determined (2, 3). The ethylene can be displaced by 1,5-cyclooctadiene to afford the corresponding cod complex $Li_2[Fe(cod)_2]$.



Scheme 5

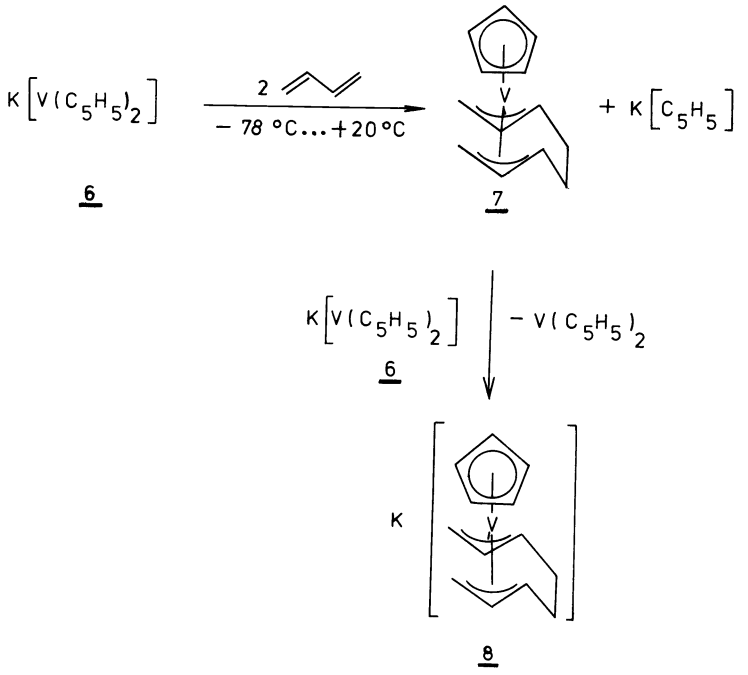
The preparation of this complex completes the series of isoelectronic cyclooctadiene compounds of the Group VIII 3d-elements, namely $Ni(cod)_2$, $M_A[Co(cod)_2]$ and $Li_2[Fe(cod)_2]$.

A.1.3. Olefin and allyl complexes of vanadium from vanadocene. When vanadocene is reduced with potassium in tetrahydrofuran at -78°C, a deep red solution is produced from which $K[V(C_5H_5)_2]$ (6) is precipitated upon addition of cold diethyl ether.

$$V(C_5H_5)_2 + K \xrightarrow[-78^{\circ}C]{THF} \underset{\underline{6}}{K[V(C_5H_5)_2]} \qquad (2)$$

The only other known examples of such 1:1 alkali metal adducts of metallocenes or their derivatives are 1 and $Na[Mn\{C_5(CH_3)_5\}_2]$ (16). As with the alkali metal cobalt complexes 1, this new alkali metal vanadium compound 6 has proved well suited for the preparation of half sandwich complexes (17).

Reaction of 6 with butadiene affords the new potassium vanadate 8, in which two butadiene molecules are coupled to give a C_8H_{12}-chain which is bound to vanadium via two terminal η^3-allyl groups.



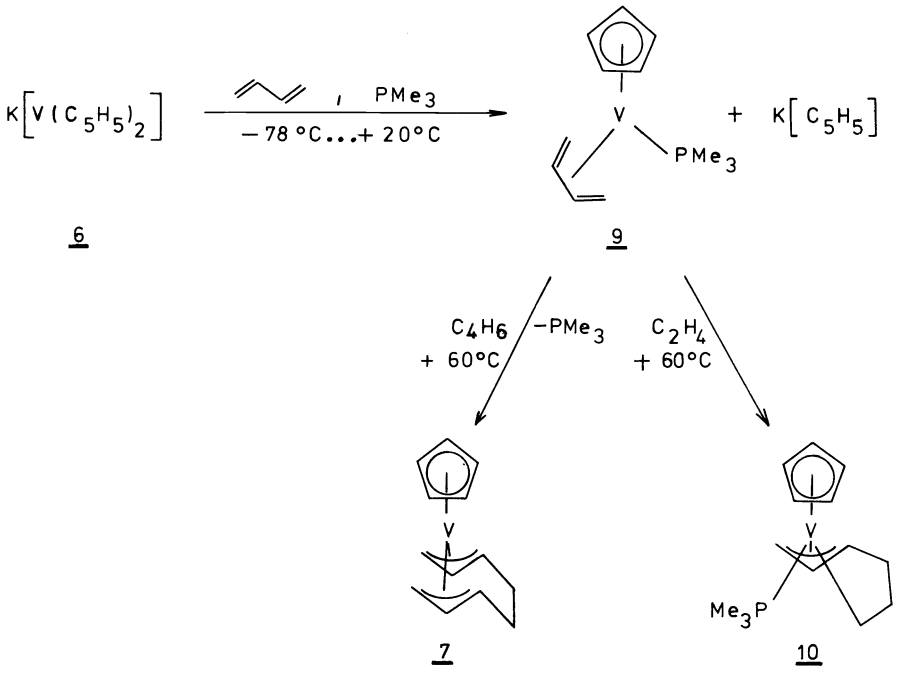
Scheme 6

The formation of 8 probably occurs as shown in Scheme 6. The intermediate potassium-free vanadium(III) complex 7 is formed by reaction of 6 with butadiene and is subsequently reduced to 8 by a second molecule of 6. Thus 6 has a double function - one equivalent provides the $(C_5H_5)V$-units [Eq. (3)] and a second, in undergoing the reverse of the reaction of formation [Eq. (2)], acts as a source of potassium [Eq. (4)].

$$\underset{\underline{6}}{K[V(C_5H_5)_2]} \longrightarrow [(C_5H_5)V] + K[C_5H_5] \qquad (3)$$

$$\underset{\underline{6}}{K[V(C_5H_5)_2]} \longrightarrow V(C_5H_5)_2 + K \qquad (4)$$

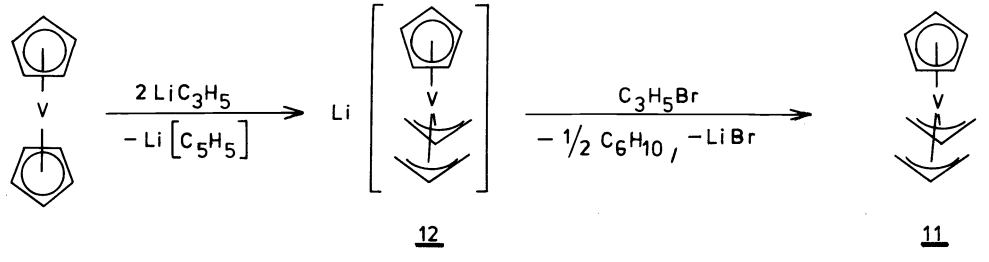
On the other hand when 6 reacts with a mixture of butadiene and trimethylphosphine, it functions exclusively as a source of $(C_5H_5)V$-fragments in forming the alkali metal-free olefin complex 9.



Scheme 7

The reactions of 9 with olefins at elevated temperature are particularly interesting. While butadiene undergoes C-C coupling to give 7 with the liberation of PMe_3, ethylene reacts with formation of a C_6H_{10}-chain to give 10, in which trimethylphosphine is retained. X-ray structures have been determined for 9 and 10 (18).

A.2.1. $Li[(C_5H_5)V(C_3H_5)_2]$ and $(C_5H_5)V(C_3H_5)_2$ from vanadocene. After the vanadium-allyl complexes 7 and 8 had been synthesised, the preparation of the parent compounds $(C_5H_5)V(C_3H_5)_2$ (11) and $M_A[(C_5H_5)V(C_3H_5)_2]$ (12) was attempted. It was found that 12 can be readily synthesised following Scheme 2 (Section A.2.) by reacting vanadocene with two moles of allyllithium. As with other LiR-reagents (13), not only is a C_5H_5-ligand replaced by R, but a second LiR-molecule is added to the vanadium to yield the ate complex 12. Treatment of 12 with allylbromide leads to delithiation with the formation of 11 (17) (see Scheme 8).



Scheme 8

B. REACTIVE METAL COMPLEXES PREPARED FROM METALLOCENES AS PRECURSORS FOR ORGANOMETALLIC SYNTHESES

B.1. Cyclopentadienylbis(ethylene)cobalt as a catalyst precursor for the cobalt-catalysed alkyne cyclooligomerization and the cocyclization of alkynes and nitriles

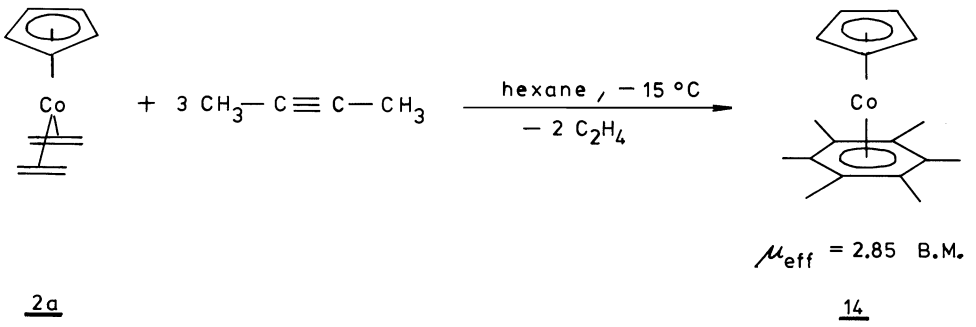
Although we had originally synthesised cyclopentadienylbis(ethylene)cobalt (2a) from 1 and ethylene (see Scheme 3), later experiments showed that the reaction of cobaltocene with potassium and ethylene provides a simpler and equally effective synthesis of 2a. At temperatures below 0°C when diethylether is used as solvent, just one C_5H_5-ligand is removed even when excess potassium is present (19).

$$Co(C_5H_5)_2 + K + 2\,C_2H_4 \xrightarrow[-20^{\circ}C\ldots0^{\circ}C]{Et_2O} \underset{\underline{2a}}{(C_5H_5)Co(C_2H_4)_2} + K[C_5H_5] \qquad (5)$$

The simple preparation of 2a and the ease of replacement of the ethylene ligands make this compound a particularly useful starting material in organocobalt chemistry. Some of this potential has been reported elsewhere (19); here just one example must suffice.

Alkynes and mixtures of alkynes and nitriles undergo cobalt-catalysed cyclotrimerization (20) or cocyclization to pyridines (21), respectively. Typical catalysts are $(C_5H_5)Co(CO)_2$ or $(C_5H_5)Co(cod)$ and temperatures in excess of 100°C are necessary.

At -15°C cyclopentadienylbis(ethylene)cobalt (2a) reacts with 2-butyne to afford the deep red solid 14, which can be recrystallized from refluxing hexane.



2a 14

Scheme 9

While attempts to determine the structure of 14 by X-ray structure analysis were unsuccessful because of disorder in the crystals, it could be confirmed that cobalt is sandwiched between the C_5H_5- and hexamethylbenzene ligands (18). The magnetic moment μ_{eff} = 2.85 B.M. of solid 14 is almost exactly that expected for two unpaired electrons according to the spin-only formula. We thus assign 14 as $(\eta^5\text{-}C_5H_5)Co[\eta^6\text{-}C_6(CH_3)_6]$, which is isoelectronic with the cation of $\left[\{C_6(CH_3)_6\}_2Co\right]PF_6$ (22), and in which the krypton electronic configuration is exceeded by two electrons. This probably accounts for the ease of displacement of the hexamethylbenzene ligand, e.g., with CO [Eq. (6)], and why 14 is the first reported $(C_5H_5)Co$-compound that can catalyse the cyclotrimerization of alkynes and cocyclization of alkynes and nitriles at room temperature (Scheme 10).

$$(C_5H_5)Co[C_6(CH_3)_6] \xrightarrow[20^oC]{CO\ (1\ atm)} (C_5H_5)Co(CO)_2 + C_6(CH_3)_6 \qquad (6)$$

14

3 $H-C\equiv C-H$ $\xrightarrow[20-40\,^oC]{14}$

3 $CH_3-C\equiv C-CH_3$ $\xrightarrow[20\,^oC]{14}$

2 $H-C\equiv C-H + C_2H_5CN$ $\xrightarrow[20-40\,^oC]{14}$ C_2H_5

Scheme 10

B.2. Chemistry of $\left[(C_6H_{11})_2PC_2H_4P(C_6H_{11})_2\right]$CoH-fragments: the hydrocobaltation and cobalt-catalysed hydrogenation of arenes

Catalysts containing transition metals such as cobalt (23), rhodium (24) or ruthenium (25) have been reported for the homogeneous hydrogenation of arenes, but relatively little is known about the mechanisms of the reactions involved.

Starting from the alkali metal cobaltates 3a and 3b we have prepared a series of new organocobalt complexes containing the chelating phosphine $(C_6H_{11})_2PC_2H_4P(C_6H_{11})_2$, which provide new insights into the processes involved in metal-catalysed arene hydrogenation (26).

Fundamental to these investigations are the 16-electron allyl cobalt complexes 15a and 15b prepared according to Scheme 11.

M_A [Co] $\xrightarrow[-2C_2H_4]{P\ P}$ M_A [P P Co] $\xrightarrow[-2C_2H_4,\,-M_ABr]{Br}$ P P Co

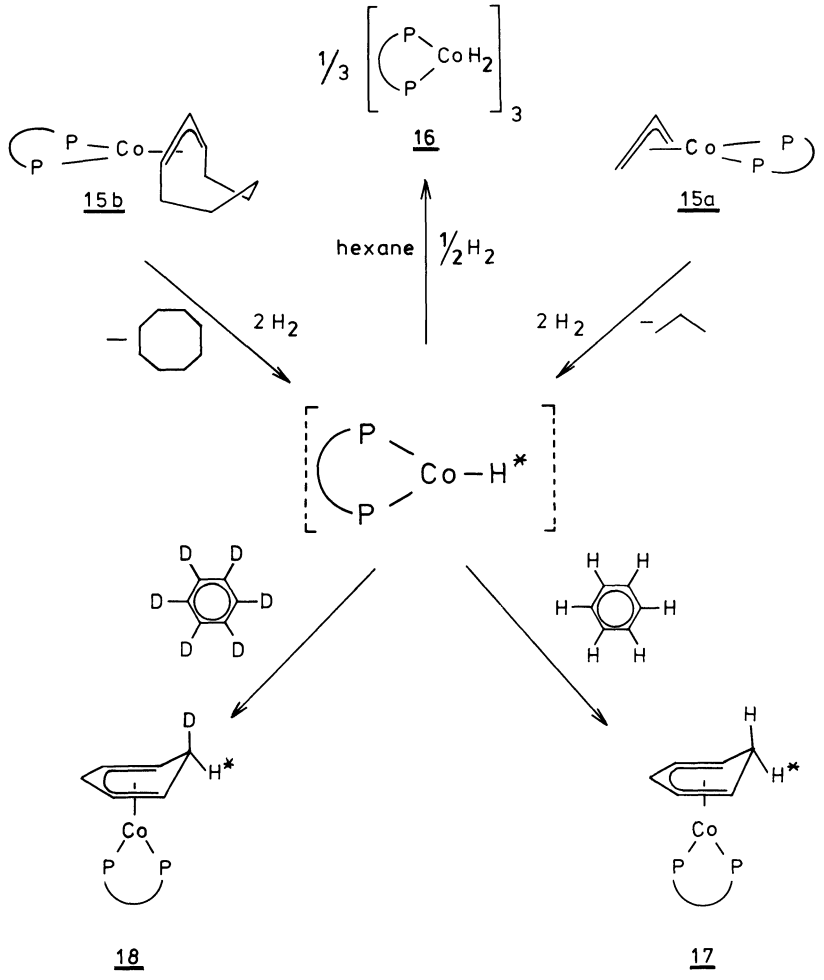
3a 15a

$M_A[Co(cod)_2] \xrightarrow[-M_AOR]{ROH} (\eta^3-C_8H_{13})Co(cod) \xrightarrow[-C_8H_{12}]{P\ P}$ P P Co

3b 15b

Scheme 11 [P P = $Cy_2PC_2H_4PCy_2$ (Cy = cyclohexyl)]

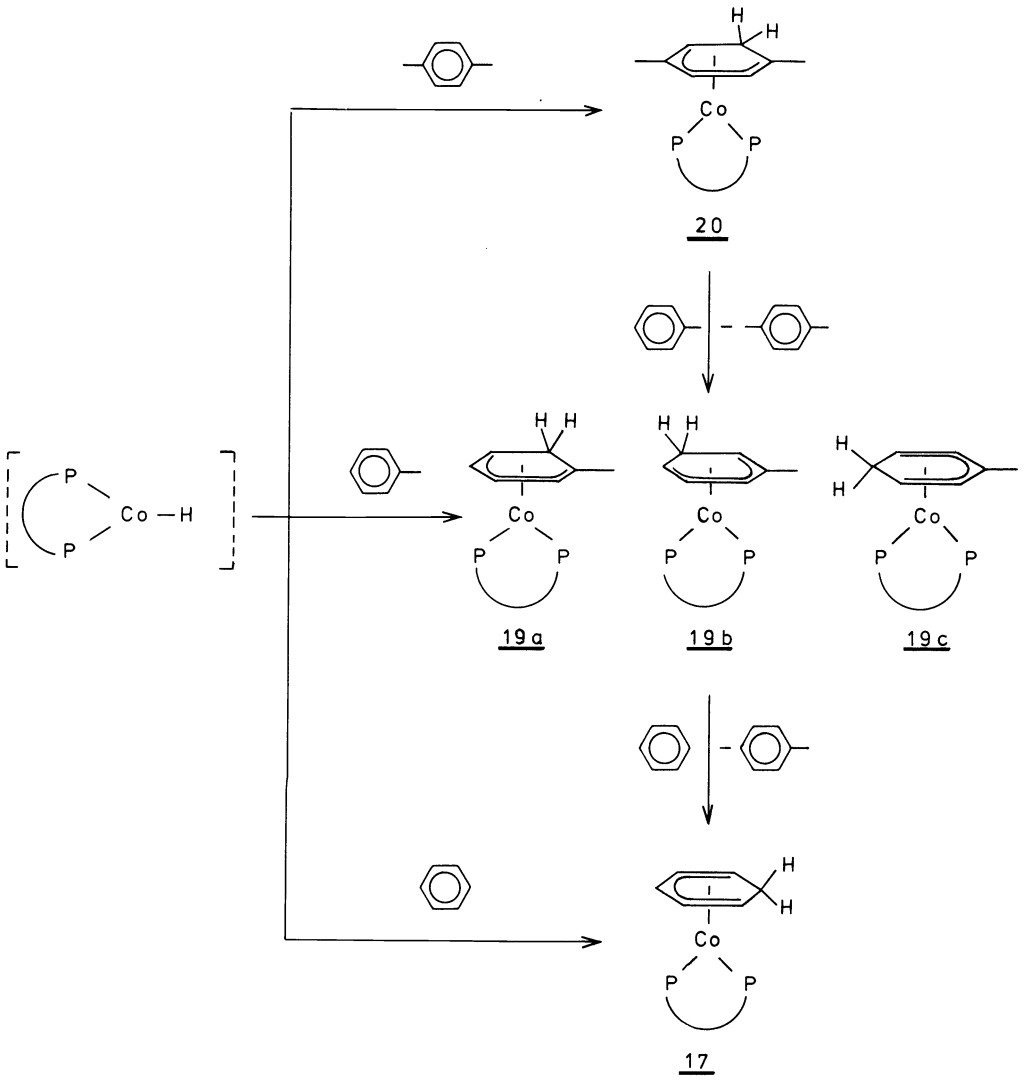
Both 15a and 15b react readily with hydrogen at low temperatures (-30°C...+20°C), e.g., in hexane or THF (H_2:Co = 2.5:1), with elimination of the allylic ligands as propane or cyclooctane, respectively, to give the new dark blue trimeric hydrido-cobalt complex 16. However, when the hydrogenolysis is carried out at 20°C in benzene or deuterobenzene (H_2:Co = 2:1), the red cobalt(I) complex, 17 or 18, is formed.



Scheme 12

The hydrocobaltation of benzene or deuterobenzene proceeds via cis addition of the $(Cy_2PC_2H_4PCy_2)$CoH-species to the arene, as indicated by the infrared spectra of 17 and 18. Complex 17 shows a strong band at 2735 cm^{-1} [ν(C-H_{exo})], characteristic of cyclohexadienyl transition metal complexes [ν(C-H_{exo}) < 2800 cm^{-1} (27, 28)]. This absorption is absent in the spectrum of 18, but a band is found at 2010 cm^{-1} which is assigned to ν(C-D_{exo}). The structure of 17 has been elucidated by X-ray crystallography (18).

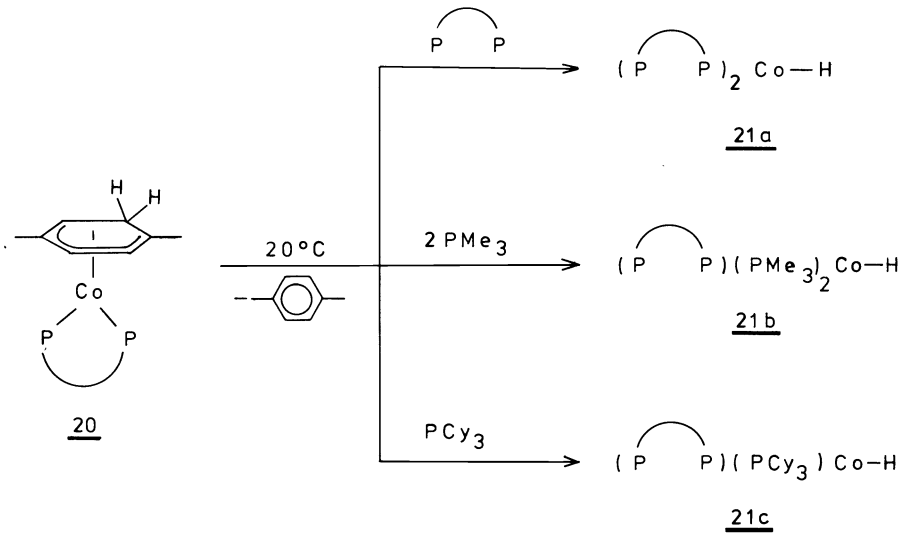
Similarly, 15 with hydrogen and toluene or p-xylene affords the products of cis addition (Scheme 13). Four isomers are possible with toluene, differing in the position of the methyl group, but only three of these are observed (19a, 19b, 19c, in the approximate ratio 1:1:1). Correspondingly, hydrocobaltation of p-xylene yields only one of the two possible isomers, i.e., 20.



Scheme 13

The cyclohexadienyl groups in the cobalt complexes 17-20 (Schemes 12 and 13) are relatively weakly bound and can be easily displaced as the corresponding arene. These compounds, especially the hydrocobaltated p-xylene complex 20, thus represent a ready source of $(Cy_2PC_2H_4PCy_2)CoH$-fragments suitable for the further study of their chemistry.

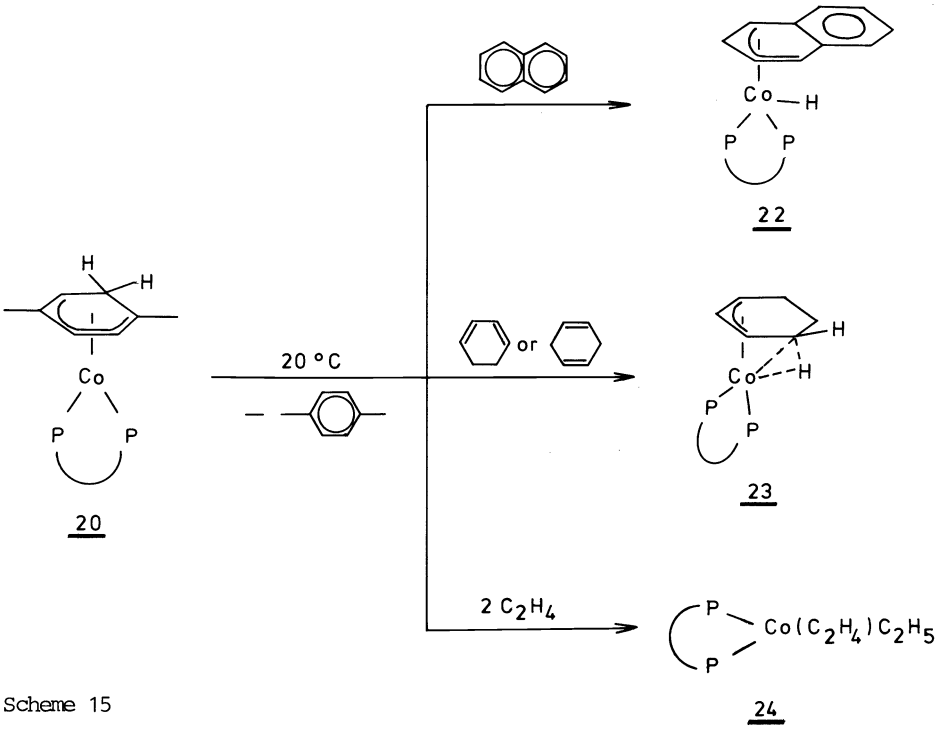
At room temperature the complexes 17-20 react with CO to yield $(Cy_2PC_2H_4PCy_2)CoH(CO)_2$, while treatment of 20 with phosphines gives the new hydrido-cobalt phosphine complexes 21 together with the liberated p-xylene.



Scheme 14

Of these hydrido-cobalt complexes 21, the 16-electron complex 21c is particularly noteworthy. It combines with hydrogen or dinitrogen to yield $(Cy_2PC_2H_4PCy_2)(PCy_3)CoH_3$ or $(Cy_2PC_2H_4PCy_2)(PCy_3)Co-H(N_2)$, respectively. 21c, which is dark blue, reacts slowly in benzene solution to produce the red coloured hydrocobaltated benzene complex 17 [Eq. (7)]. To our knowledge, this is the first example of an arene hydrometallation where the hydrido-metal compound that undergoes reaction is isolable.

$$\underset{\text{21c}}{(Cy_2PC_2H_4PCy_2)(PCy_3)Co-H} \xrightarrow[-PCy_3]{C_6H_6,\ 50^{\circ}C} \underset{\text{17}}{(Cy_2PC_2H_4PCy_2)Co(\eta^5\text{-}C_6H_7)} \qquad (7)$$



Scheme 15

The $(Cy_2PC_2H_4PCy_2)CoH$-fragment can also be transferred from 20 to condensed arenes such as naphthalene or anthracene, yielding complexes of type 22. Reaction of 20 with cyclohexadiene leads to the formation of 23 which has been shown by NMR (29) and X-ray (18) studies to be fluxional with an agostic enyl ligand. Complexes bearing such two electron three centre C-H→M interactions have recently been reviewed (30). Whether 24, prepared by treatment of 20 with ethylene, also belongs to this class of organometallic compounds and has an agostic ethyl group, is currently under investigation.

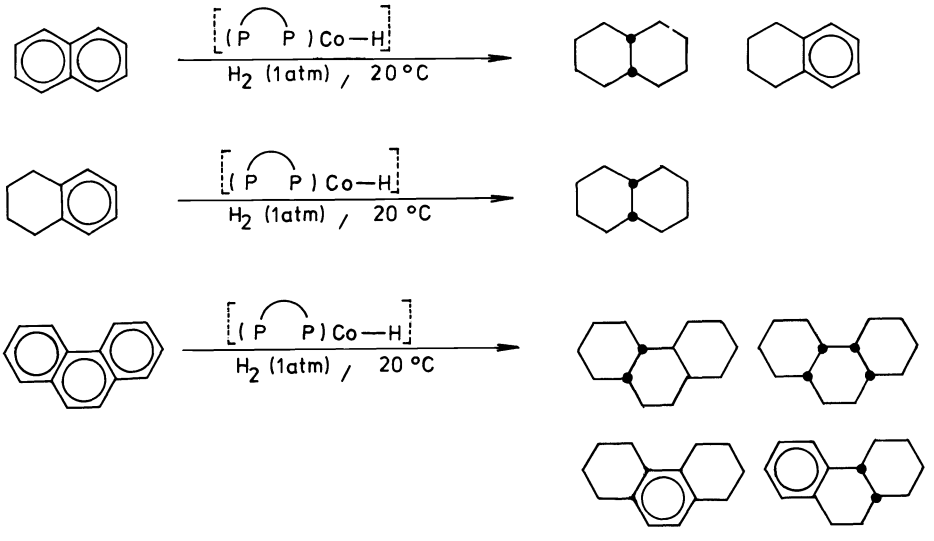
Solutions of the three cobalt complexes 22-24 take up hydrogen (1 atm) at room temperature just as rapidly as the allyl cobalt complexes 15 (Scheme 12) leading to conversion of the organic ligands to tetralin (a very small amount of cis-decalin is formed), cyclohexane and ethane, respectively. When heptane or THF is used as solvent, then the cobalt residue forms $[(Cy_2PC_2H_4PCy_2)CoH_2]_3$ (16). While the organic ligands are hydrogenated as above when the hydrogenolysis of 22-24 is carried out in benzene, the other product is the hydrocobaltated benzene complex 17.

$$\underset{\underline{22}}{(Cy_2PC_2H_4PCy_2)CoH(\eta^4\text{-}C_{10}H_8)} + 2\,H_2 \xrightarrow[20^oC]{C_6H_6} \underline{17} + \text{tetralin} \qquad (8)$$

$$\underset{\underline{23}}{(Cy_2PC_2H_4PCy_2)Co(C_6H_9)} + 2\,H_2 \xrightarrow[20^oC]{C_6H_6} \underline{17} + \text{cyclohexane} \qquad (9)$$

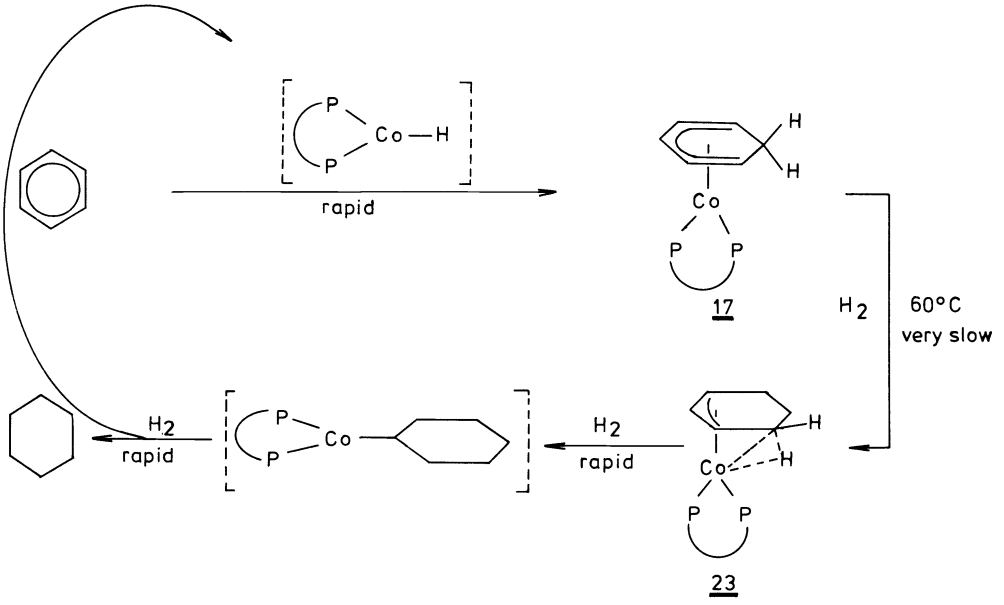
$$\underset{\underline{24}}{(Cy_2PC_2H_4PCy_2)Co(C_2H_4)C_2H_5} + 2\,H_2 \xrightarrow[20^oC]{C_6H_6} \underline{17} + 2\ \text{ethane} \qquad (10)$$

Equations (8) - (10) show very convincingly why the cobalt compounds 15, 17-20 and 22-24 can be used as catalyst precursors for the hydrogenation of olefins (26) and condensed arenes such as naphthalene and phenanthrene, but the catalysis does not proceed with benzene at room temperature.



Scheme 16

Even at 60°C the hydrogenolysis of the hydrocobaltated benzene complex 17 to form 23 proceeds much too slowly for the efficient conversion of benzene to cyclohexane. Furthermore, increasing the hydrogen pressure produces no improvement since this favours the formation of the catalytically inactive $[(Cy_2PC_2H_4PCy_2)CoH_2]_3$ (16) from $(Cy_2PC_2H_4PCy_2)CoH$-fragments and hydrogen.



Scheme 17

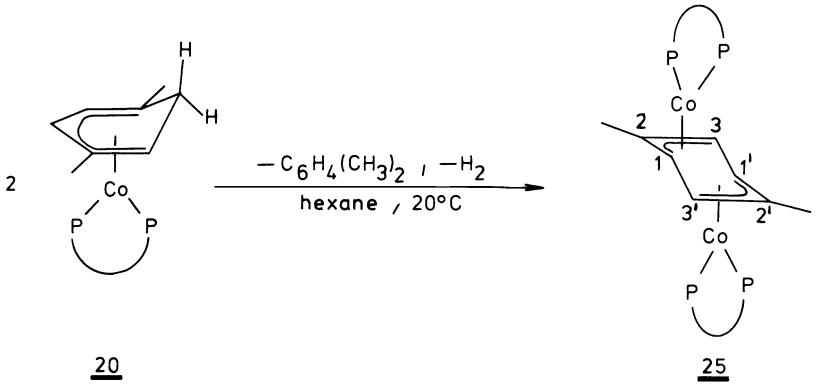
B.3. η^6-Bonded arenes as novel bridging ligands in binuclear complexes of cobalt, iron and vanadium

Until recently the only complexes known to have bridging arene ligands were the palladium complexes $Pd_2(C_6H_6)_2(AlCl_4)_2$ and $Pd_2(C_6H_6)_2(Al_2Cl_7)_2$ reported by Allegra et al. in 1965 (31). In both these complexes the benzene ligands appear to be bound as conjugated dienes (η^4-benzene).

We have been able to synthesise a series of novel binuclear complexes of Co, Fe and V that are the first examples in which η^6-arene ligands are bonded to two metal centres (32-34).

Starting material for the preparation of the new binuclear cobalt complex $[(Cy_2PC_2H_4PCy_2)Co]_2C_6H_4(CH_3)_2$ (25) is the mononuclear cobalt complex $(Cy_2PC_2H_4PCy_2)Co[\eta^5\text{-}C_6H_5(CH_3)_2]$ (20), prepared by hydrocobaltation of p-xylene according to Scheme 13. When a solution of 20 in p-xylene is diluted with hexane and then allowed to stand at room temperature, 25 precipitates as dark red crystals (Scheme 18).

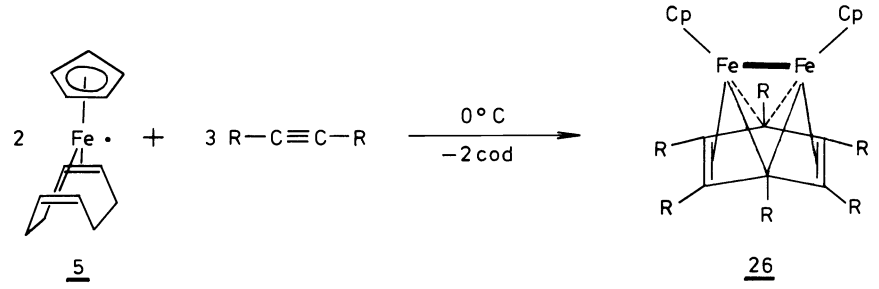
In the centrosymmetric cobalt complex 25, the bridging ligand $C_6H_4(CH_3)_2$ functions as two allyl groups, each of which has geometrical data similar to those of typical η^3-methallyl complexes. (The structure of 25 should be compared with that of the mononuclear compounds 15.) The angle between the planes C-1, C-2, C-3 and C-1, C-3', C-1', C-3, describing the deviation from planarity of the ligand in the direction of the chair form of cyclohexane, is 157.36°.



20 25

Scheme 18

Parallel to investigations into the reactivity of the 18-electron cobalt complex $(C_5H_5)Co(C_2H_4)_2$ (2a) (Section B.1.), the behaviour of the 17-electron iron complex $(C_5H_5)Fe(cod)$ (5) towards alkynes was examined. It was found that 5 reacts with 2-butyne or 3-hexyne in the ratio 2:3 to yield the binuclear complexes $[(C_5H_5)Fe]_2C_6R_6$ (26). These compounds are fluxional and display antiferromagnetic behaviour (29, 34).

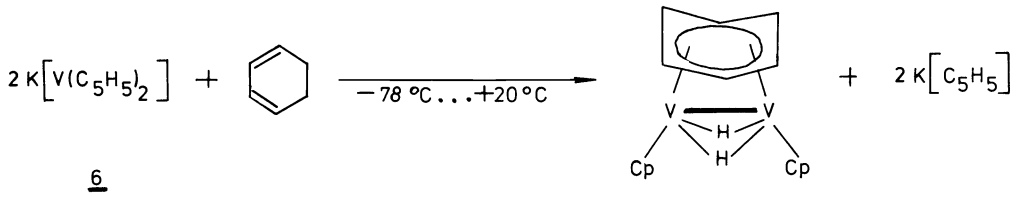


5 26

R = CH_3 , C_2H_5

Scheme 19

In the compounds 26 and in the cobalt complex 25, the six-membered rings are not planar and their C-C bond lengths are unequal. On the other hand, while the bridging benzene in the hydrido-vanadium complex $[(C_5H_5)VH]_2C_6H_6$ (27) is also non-planar, the six C-C bonds are approximately equal in length. This diamagnetic hydrido-vanadium complex 27, which is fluxional in solution, is obtained by treatment of the 1:1 adduct between vanadocene and potassium, $K[V(C_5H_5)_2]$ (6) with 1,3-cyclohexadiene (32).

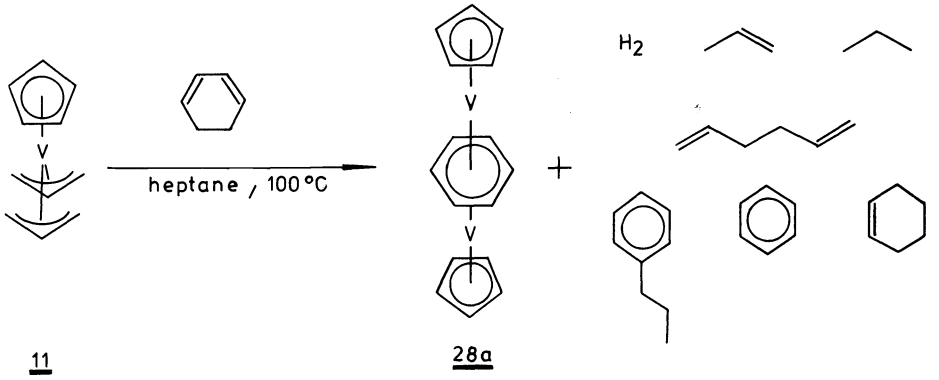


6 27

Scheme 20

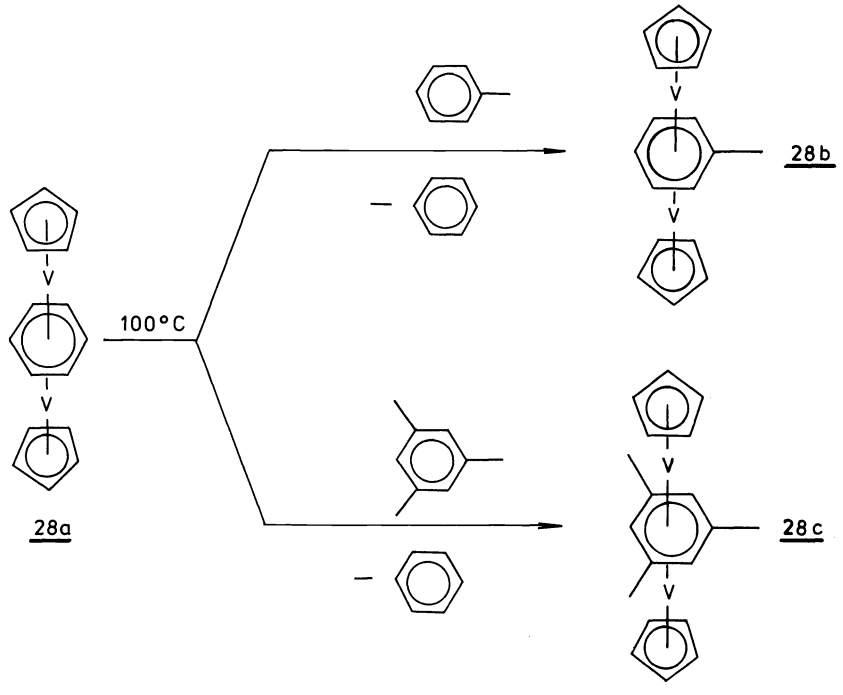
Until recently triple- and tetra-decker sandwich complexes have only been prepared with five- (35) or eight-membered (36) carbocyclic or heterocyclic (37) groups or group 5 element rings [P_3, As_3 (38) or As_5 (39)] as the bridging ligands.

The novel vanadium complexes $[(C_5H_5)V]_2C_6H_6$ (28a), $[(C_5H_5)V]_2C_6H_5CH_3$ (28b), $[(C_5H_5)V]_2$-$C_6H_5C_3H_7$ and $[(C_5H_5)V]_2C_6H_3(CH_3)_3$ (28c) are the first examples of arene-bridged, binuclear transition metal compounds with triple-decker sandwich structures. The parent complex 28a, with benzene as the central fragment, was prepared by reaction of $(C_5H_5)V(C_3H_5)_2$ (11) (17) with an excess of 1,3-cyclohexadiene in refluxing heptane (33).



Scheme 21

It is interesting to note that 28a undergoes arene exchange reactions with retention of the triple-decker sandwich structure. Thus 28a may be converted to the toluene or mesitylene analogues, 28b or 28c, respectively, according to Scheme 22.



Scheme 22

Compounds 28a and 28c have been investigated by X-ray crystallographic methods. Figure 2 shows the structure of the parent compound 28a. As in 28c, all cyclic fragments in 28a are planar and essentially parallel to each other. The two C_5H_5-rings are in staggered conformation.

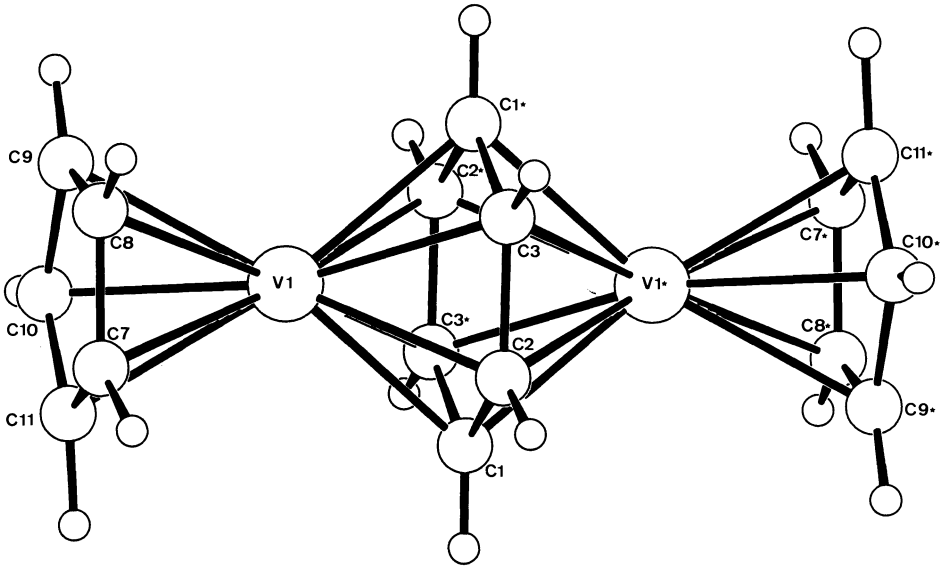


Fig. 2. Molecular structure of 28a in the crystal (33).

The synthesis and structures of these binuclear complexes of cobalt, iron and vanadium (25, 26, and 27 and 28, respectively), demonstrate that η^6-arene bridging ligands are capable of bonding two metal centres in at least four different ways.

Acknowledgements - The author gratefully acknowledges the enthusiastic collabaration of his coworkers in the research reported here. He also wishes to thank his colleagues Prof. C. Krüger for the X-ray diffraction studies, Dr. R. Benn for ^{1}H-NMR investigations, Dr. R. Mynott for ^{13}C- and ^{31}P-NMR studies and his assistance in translating this account, and Dr. K. Seevogel for carrying out the infrared spectroscopic investigations. The author also expresses his gratitude to Prof. G. Wilke, the director of the Max-Planck-Institut für Kohlenforschung, for his continuous support and interest in this work.

REFERENCES

1. K. Fischer, K. Jonas, P. Misbach, R. Stabba and G. Wilke, Angew. Chem. 85, 1002 (1973); Angew. Chem. Int. Ed. Engl. 12, 943 (1973).
2. K. Jonas and C. Krüger, Angew. Chem. 92, 513 (1980); Angew. Chem. Int. Ed. Engl. 19, 520 (1980), and references cited therein.
3. K. Jonas, Adv. Organomet. Chem. 19, 97 (1981), and references cited therein.
4. K. Jonas, Angew. Chem. 85, 1050 (1973); Angew. Chem. Int. Ed. Engl. 12, 997 (1973).
5. K. Jonas, D.J. Brauer, C. Krüger, P.J. Roberts and Y.-H. Tsay, J. Am. Chem. Soc. 98, 74 (1976).

6. C. Krüger and Y.-H. Tsay, Angew. Chem. 85, 1051 (1973); Angew. Chem. Int. Ed. Engl. 12, 998 (1973).
7. G.P. Pez, P. Apgar and R.K. Crissey, J. Am. Chem. Soc. 104, 482 (1982).
8. K. Jonas, Angew. Chem. 87, 809 (1975); Angew. Chem. Int. Ed. Engl. 14, 752 (1975).
9. a) D.S. Trifan and L. Nicholas, J. Am. Chem. Soc. 79, 2746 (1957). b) G.W. Watt and L.J. Baye, J. Inorg. Nucl. Chem. 26, 2099 (1964).
10. K. Jonas, R. Mynott, C. Krüger, J.C. Sekutowski and Y.-H. Tsay, Angew. Chem. 88, 808 (1976); Angew. Chem. Int. Ed. Engl. 15, 767 (1976).
11. K. Jonas, G. Burkart, J. Klocke and V. Wiskamp, unpublished results.
12. E.L. Muetterties and B.W. Howk, J. Am. Chem. Soc. 83, 1601 (1961).
13. W. Seidel and P. Scholz, Z. Chem. 18, 106 (1978).
14. H. Lehmkuhl, Ch. Naydowski and M. Bellenbaum, J. Organometal. Chem. 246, C5-C8 (1983), and references cited therein.
15. J. Moraczewski and W.E. Geiger, Jr., J. Am. Chem. Soc. 103, 4779 (1981).
16. J.C. Robbins, N.M. Edelstein, St.R. Cooper and J.C. Smart, J. Am. Chem. Soc. 101, 3853 (1979).
17. K. Jonas and V. Wiskamp, Z. Naturforsch. 38b (1983).
18. C. Krüger et al., unpublished results.
19. K. Jonas, E. Deffense and D. Habermann, Angew. Chem. 95 (1983).
20. K.P.C. Vollhardt, Acc. Chem. Res. 10, 1 (1977).
21. H. Bönnemann, Angew. Chem. 90, 517 (1978); Angew. Chem. Int. Ed. Engl. 17, 505 (1978).
22. a) E.O. Fischer and H.H. Lindner, J. Organometal. Chem. 1, 307 (1964). b) M.R. Thompson, C.S. Day, V.W. Day, R.I. Mink and E.L. Muetterties, J. Am. Chem. Soc. 102, 2979 (1980).
23. a) E.L. Muetterties and J.R. Bleeke, Acc. Chem. Res. 12, 324 (1979). b) J.R. Bleeke and E.L. Muetterties, J. Am. Chem. Soc. 103, 556 (1981), and references cited therein.
24. M.J. Russell, C. White and P.M. Maitlis, J. Chem. Soc., Chem. Commun. 427 (1977).
25. M.A. Bennett, T.N. Huang and T.W. Turneg, J. Chem. Soc., Chem. Commun. 312 (1979).
26. K. Jonas and G. Koepe, unpublished results.
27. I.U. Khand, P.L. Pausen and W.E. Watts, J. Chem. Soc. (C), 2257 (1968); ibid, 2024 (1969).
28. M.R. Churchill and F.R. Scholer, Inorg. Chem. 8, 1950 (1969).
29. R. Mynott, unpublished results.
30. M. Brookhart and M.L.H. Green, J. Organometal. Chem. 250, 395 (1983).
31. a) G. Allegra, A. Immirzi and L. Porri, J. Am. Chem. Soc. 87 (1965). b) G. Allegra, G. Tettamanti Casagrande, A. Immirzi, L. Porri and G. Vitulli, J. Am. Chem. Soc. 92, 289 (1970).
32. K. Jonas, V. Wiskamp, Y.-H. Tsay and C. Krüger, J. Am. Chem. Soc. 105 (1983).
33. A.W. Duff, K. Jonas, R. Goddard, H.-J. Kraus and C. Krüger, J. Am. Chem. Soc. 105 (1983).
34. K. Jonas, G. Koepe, L. Schieferstein, R. Mynott, C. Krüger and Y.-H. Tsay, Angew. Chem. 95 (1983).
35. a) A. Salzer and H. Werner, Inorg. Metal.-Org. Chem. 2, 239 (1972). b) H. Werner, Angew. Chem. 89, 1 (1977).
36. a) W.E. Geiger and I. Moraczewski, J. Am. Chem. Soc. 100, 7429 (1978). b) J.E. Dobson, S.P. Kolesnikov and P.S. Skell, ibid 100, 999 (1978).
37. W. Siebert, Adv. Organomet. Chem. 18, 301 (1980).
38. L. Sacconi and M. Di Vaira, Angew. Chem. 94, 338 (1982).
39. A.L. Reingold, M.I. Folly and P.J. Sullivan, J. Am. Chem. Soc. 104, 4727 (1982).