REACTIVE ORGANOMETALLIC COMPOUNDS FROM METALLOCENES

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Abstract - Metalloccenes can be converted into reactive organometallic compounds having readily accessible coordination sites by removing one or both of the C₅H₅-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 (C₅H₅)Co(C₂H₄)₂ and its application as a catalyst precursor for the cobalt-catalysed alkyne cyclooligomerization and the co polymerization of alkynes and nitriles. Also reported are the alkali metal cobaltates M₆[Co(C₂H₄)₄] and M₆[Co(cod)₂] (M₆ = 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 7₆-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)₆Ni₂N₂(Et₂O)₂]₂ (4) and [Ph[Na(Et₂O)₂]₂(Ph₂Ni)₂NaLi₆(OEt)₄-(Et₂O)]₂ (5), respectively. These two compounds, for which the crystal structures have been determined (5, 6), are the first examples of transition metal N₂ complexes in which dinitrogen molecules are bonded side-on. A third example, that of a Ti₄ dinitrogen complex, has recently been reported (7).

![Fig. 1. Side-on coordination of dinitrogen to two nickel centres in [(LiPh)₆Ni₂N₂(Et₂O)₂]₂ (6).](image)
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., \([\text{Li}(\text{TMDA})]_2^{-}[\text{Ni}(\text{adt})]\) and \([\text{Li}(\text{THF})]_2^-\text{[Ni(cod)}]_2\) \((2, 3, 8)\). 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 metalloccenes 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 \([\text{Li}(\text{THF})]_2^-\text{[Co(cod)}]_2\) \((10)\).

\[
\text{Co(C}_{5}\text{H}_{5})_2 \xrightarrow{\text{Li, cod}} \text{Li[Co(cod)}]_2
\]

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

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

The metalloccenes can be converted into reactive organometallic compounds having readily accessible coordination sites by removing one or both of the \(\text{C}_{5}\text{H}_{5}\)-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 \(\text{C}_{5}\text{H}_{5}\)-ligands by alkali metals

\[
\begin{align*}
\text{M}_\text{T}\{\text{C}_{5}\text{H}_{5}\}_2 & \xrightarrow{\text{M}_\text{A}} \text{M}_\text{A}\{\text{M}_\text{T}\{\text{C}_{5}\text{H}_{5}\}_2\} \\
\text{L} & \xrightarrow{-\text{M}_\text{A}} \text{C}_{5}\text{H}_{5} \\
(\text{C}_{5}\text{H}_{5})\text{M}_\text{T}\{\text{L}\}_n & \xrightarrow{\text{M}_\text{A}} \text{M}_\text{A}\{\text{(C}_{5}\text{H}_{5})\text{M}_\text{T}\{\text{L}\}_n\} \\
\text{L} & \xrightarrow{-\text{M}_\text{A}} \text{C}_{5}\text{H}_{5} \\
\text{M}_\text{T}\{\text{L}\}_n & \xrightarrow{\text{M}_\text{A}} \text{M}_\text{A}\{\text{M}_\text{T}\{\text{L}\}_n\}
\end{align*}
\]

Scheme 1 \([\text{M}_\text{T} = \text{transition metal; M}_\text{A} = \text{alkali metal; L = olefin, arene, phosphine, CO, \text{N}_2, \text{etc.}; x = 1 \text{ or } 2. \text{ The donor ligands (THF, Et}_2\text{O, etc.) bonded to M}_\text{A} \text{ in the compounds of type A, C, and E, have been omitted.}]\)
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 \( (MA)_x \) 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.

\[
\begin{align*}
&M_T(C_5H_5)_2 \xrightarrow{MA R} [C_5H_5]M_T R \xrightarrow{MA R} \\
&M_A[\{C_5H_5\}]M_T R \xrightarrow{MA R} \\
&M_A[\{C_5H_5\}]M_T R_2 \xrightarrow{MA R} \\
&(MA)_x[M_T R_2(R)_x]
\end{align*}
\]

Scheme 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 \( (C_5H_5)Co(ox) \), respectively. With ethylene we achieved the first synthesis of \( (C_5H_5)Co(C_2H_4)_2 \) (2a), the parent compound of these cobalt(1)-olefin complexes 2 (Scheme 3).
At -40°C in tetrahydrofuran \((\text{C}_5\text{H}_5)\text{Co(cod)}\) reacts with alkali metal to give \(\text{MA}\left[(\text{C}_5\text{H}_5)\text{Co(cod)}\right]\), 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 \(3\text{b}, 3\text{c}\) and \(3\text{d}\). \(3\text{c}\) and \(3\text{d}\) are prepared in high yield by reduction of \((\text{C}_5\text{H}_5)\text{Co(cod)}\) with 2 mole equivalents of alkali metal under an ethylene or dinitrogen atmosphere, respectively. The syntheses of the "pure" cobaltates \(3\text{a}\) and \(3\text{b}\) 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 \(\text{C}_5\text{H}_5\)-ligand. With cyclooctadiene as the olefin, \(\text{Li}\left[(\text{C}_5\text{H}_5)\text{Fe(cod)}\right]\) (4) is obtained, which gives nonmeric, alkali metal-free (\(\eta^5\)-cyclopentadienyl) (\(\eta^4\)-1,5-cyclooctadiene)iron (5) when reacted with trityl chloride (2, 3).
Both C₅H₅-ligands of ferrocene may be removed by treatment of Fe(C₅H₅)₂ with lithium and ethylene at ambient temperature to give Li₂[Fe(C₂H₄)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 Li₂[Fe(cod)₂].

The preparation of this complex completes the series of isoelectronic cyclooctadiene compounds of the Group VIII 3d-elements, namely Ni(cod)₂, M₃[Co(cod)₂], and Li₂[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(C₅H₅)₂] (6) is precipitated upon addition of cold diethyl ether.
The only other known examples of such 1:1 alkali metal adducts of metalloccenes or their derivatives are 1 and Na[Mn(C5(CH3)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 C8H12-chain which is bound to vanadium via two terminal η3-allyl groups.

\[ V(C_5H_5)_2 + K \xrightarrow{-78^\circ C} K[V(C_5H_5)_2] \]

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)].

\[ K[V(C_5H_5)_2] \rightarrow \frac{[V(C_5H_5)_2]}{[C_5H_5]} + K[C_5H_5] \]  

(3)

\[ K[V(C_5H_5)_2] \rightarrow V[C_5H_5]_2 + K \]  

(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.
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 PMe₃, ethylene reacts with formation of a C₆H₁₀-chain to give 10, in which trimethylphosphine is retained. X-ray structures have been determined for 9 and 10 (18).

A.2.1. Li[(C₅H₅)V(C₃H₅)₂] and (C₅H₅)V(C₃H₅)₂ from vanadocene. After the vanadium-allyl complexes 7 and 8 had been synthesised, the preparation of the parent compounds (C₅H₅)V(C₃H₅)₂ (11) and Li[(C₅H₅)V(C₃H₅)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 C₅H₅-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).
B. REACTIVE METAL COMPLEXES PREPARED FROM METALLOCENES AS PRECURSORS
FOR ORGANOMETALLIC SYNTHESSES

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 tem-
peratures below 0°C when diethylether is used as solvent, just one C$_5$H$_5$-ligand is removed
even when excess potassium is present (19).

\[
\text{Co}(C_5H_5)_2 + K + 2 C_2H_4 \xrightarrow{\text{Et}_2O} \text{Et}_2O \xrightarrow{-20^\circ C \ldots 0^\circ C} (C_5H_5)_2\text{Co}(C_2H_4)_2 + K[C_5H_5] \quad (5)
\]

The simple preparation of 2a and the ease of replacement of the ethylene ligands make this
compound a particularly useful starting material in organo-cobalt 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$_5$H$_5$)Co(CO)$_2$
or (C$_5$H$_5$)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.

\[
\text{Co} + 3 \text{CH}_3-\text{C}≡\text{C}—\text{CH}_3 \xrightarrow{\text{hexane, -15 }^\circ \text{C}} -2 \text{C}_2\text{H}_4
\]

\[\mu_{\text{eff}} = 2.85 \text{ B.M.}\]

Scheme 9

While attempts to determine the structure of 14 by X-ray structure analysis were un-
successful because of disorder in the crystals, it could be confirmed that cobalt is sand-
wiched between the C$_5$H$_5$- and hexamethylbenzene ligands (18). The magnetic moment $\mu_{\text{eff}} = 2.85$ B.M. of solid 14 is almost exactly that expected for two unpaired electrons accord-
ing to the spin-only formula. We thus assign 14 as ($\eta^5$-C$_5$H$_5$)Co[$\eta^6$-C$_6$(CH$_3$)$_6$], which is
isoelectronic with the cation of [C$_6$(CH$_3$)$_6$Co][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$_5$H$_5$)Co-compound that can catalyse the cyclotrimerization of
alkynes and cocyclization of alkynes and nitriles at room temperature (Scheme 10).
Reactive organometallic compounds from metallocenes

\[
\frac{(C_5H_5)_2Co[C_6(CH_3)_6]}{14} + \text{CO (1 atm)} \xrightarrow{20^\circ C} \frac{(C_5H_5)Co(O)_{2} + C_6(CH_3)_6}{14} \quad \text{(6)}
\]

\[
\frac{3}{14} \quad 
\begin{align*}
\text{H--C}&\equiv&\text{C--H} \\
\text{CH}_3&\equiv&\text{C--CH}_3
\end{align*}
\quad \xrightarrow{14} \quad \begin{array}{c}
\text{20--40}^\circ \text{C}
\end{array}
\]

\[
\begin{align*}
2 \text{H--C}&\equiv&\text{C--H} + \text{C}_2\text{H}_5\text{CN} & \xrightarrow{14} & \quad \begin{array}{c}
\text{20--40}^\circ \text{C}
\end{array}
\end{align*}
\]

Scheme 10

B.2. Chemistry of \( [(C_6H_{11})_2Pc_2H_4P(C_6H_{11})_2]CoH \)-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.

\[
M_A \left[ \begin{array}{c}
\text{Co}
\end{array} \right] \xrightarrow{P, P, -2\text{C}_2\text{H}_4} M_A \left[ \begin{array}{c}
\text{Co}
\end{array} \right] \xrightarrow{\text{Br, } -2\text{C}_2\text{H}_4, -M_A\text{Br}} C_2\text{H}_4 \xrightarrow{\text{P, P}} \text{Co}
\]

\[
\frac{3a}{15a}
\]

\[
M_A \left[ \text{Co(cod)}_2 \right] \xrightarrow{\text{ROH, } -M_A\text{OR}} \left( \text{C}_8\text{H}_{13} \right)^2\text{Co(cod)} \xrightarrow{\text{P, P, } -\text{C}_8\text{H}_{12}} C_2\text{H}_4 \xrightarrow{\text{P, P}} \text{Co}
\]

\[
\frac{3b}{15b}
\]
The hydrocobaltation of benzene or deuterobenzene proceeds via cis addition of the \( \left( \text{Cy}_2 \text{P}_2 \text{H}_4 \text{PO}_{2} \right) \text{CoH} \)-species to the arene, as indicated by the infrared spectra of 17 and 18. Complex 17 shows a strong band at 2735 cm\(^{-1}\) \( \nu(\text{C-H}_{\text{exo}}) \), characteristic of cyclohexadienyl transition metal complexes \( \nu(\text{C-H}_{\text{exo}}) < 2800 \text{ cm}^{-1} \) (27, 28). This absorption is absent in the spectrum of 18, but a band is found at 2010 cm\(^{-1}\) which is assigned to \( \nu(\text{C-D}_{\text{exo}}) \). 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 \( (19a, 19b, 19c, \text{ in the approximate ratio } 1:1:1) \). Correspondingly, hydrocobaltation of p-xylene yields only one of the two possible isomers, i.e., 20.
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 \((\mathrm{Cy_2PC_2H_4PCy_2})\mathrm{CoH}\)-fragments suitable for the further study of their chemistry.

At room temperature the complexes 17-20 react with \(\mathrm{CO}\) to yield \((\mathrm{Cy_2PC_2H_4PCy_2})\mathrm{CoH(CO)}_2\), while treatment of 20 with phosphines gives the new hydrido-cobalt phosphine complexes 21 together with the liberated p-xylene.
Of these hydrido-cobalt complexes 21, the 16-electron complex 21c is particularly noteworthy. It combines with hydrogen or dinitrogen to yield \((\text{Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)\text{(PCy}_3\text{)}\text{CoH}_3\text{)}\) or \((\text{Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)\text{(PCy}_3\text{)}\text{Co—H(N}_2\text{)}\), respectively. 21c, which is dark blue, reacts slowly in benzene solution to produce the red coloured hydrocobaltated benzene calex 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.

\[\text{(Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)\text{(PCy}_3\text{)}\text{Co—H} \xrightarrow{\text{C}_6\text{H}_6, 50^\circ\text{C}} \text{(Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)\text{Co}(^7\text{C}_6\text{H}_7)\]  

(7)
The \((\text{Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)\text{CoH-fragrrent}\) 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 ctrans-decalin is formed), cyclohexane and ethane, respectively. When heptane or THF is used as solvent, then the cobalt residue forms \([(\text{Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)\text{CoH}_2]_3\) (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.

\[
\begin{align*}
\text{22} & \quad \text{Co(H)}_4 \quad \text{C}_10\text{H}_8 + 2\text{H}_2 \quad \text{C}_6\text{H}_6 \quad 20^\circ\text{C} \quad \text{17} + \text{tetralin} \quad (8) \\
\text{23} & \quad \text{Co(C}_6\text{H}_9) + 2\text{H}_2 \quad \text{C}_6\text{H}_6 \quad 20^\circ\text{C} \quad \text{17} + \text{cyclohexane} \quad (9) \\
\text{24} & \quad \text{Co(C}_2\text{H}_4\text{C}_2\text{H}_5) + 2\text{H}_2 \quad \text{C}_6\text{H}_6 \quad 20^\circ\text{C} \quad \text{17} + 2\text{ethane} \quad (10)
\end{align*}
\]

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.
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 \([(\text{Cy}_2\text{PC}_2\text{H}_4\text{Py}_2)\text{CoH}_2]_3\) (16) from \((\text{Cy}_2\text{PC}_2\text{H}_4\text{Py}_2)\text{CoH}\)-fragments and hydrogen.

\[ \text{H}_2 \quad \text{rapid} \quad \text{H}_2 \quad \text{rapid} \]

\[ \text{H}_2 \quad \text{very slow} \]

\[ \quad \text{60°C} \]

Scheme 17

**B.3. \(\eta^6\)-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 \(\text{Pd}_2(\text{C}_6\text{H}_6)_2(\text{AlCl}_4)_2\) and \(\text{Pd}_2(\text{C}_6\text{H}_6)_2(\text{AlCl}_7)_2\) reported by Allegra et al. in 1965 (31). In both these complexes the benzene ligands appear to be bound as conjugated dienes (\(\eta^4\)-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 \(\eta^6\)-arene ligands are bonded to two metal centres (32–34).

Starting material for the preparation of the new binuclear cobalt complex \([\text{(Cy}_2\text{PC}_2\text{H}_4\text{Py}_2)\text{-CO}]_2\text{C}_6\text{H}_4(\text{CH}_3)_2\) (25) is the mononuclear cobalt complex \((\text{Cy}_2\text{PC}_2\text{H}_4\text{Py}_2)\text{Co}[\text{\(\eta^5\)-C}_6\text{H}_5(\text{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 \(\text{C}_6\text{H}_4(\text{CH}_3)_2\) functions as two allyl groups, each of which has geometrical data similar to those of typical \(\eta^3\)-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°.
Parallel to investigations into the reactivity of the 18-electron cobalt complex \( \left( C_5H_5 \right) Co\left( C_2H_4 \right)_2 \) (2a) (Section B.1.), the behaviour of the 17-electron iron complex \( \left( C_5H_5 \right) Fe\left( cod \right) \) (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 \( \left( C_5H_5 \right) Fe\left( C_6R_6 \right) \) (26). These compounds are fluxional and display antiferromagnetic behaviour (29, 34).

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 \( \left( C_5H_5 \right) VH\left( C_6H_6 \right) \) (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, \( 2KV\left( C_5H_5 \right) \) (6) with 1,3-cyclohexadiene (32).

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 \( \left[ P_3, As_3 \right] \) (38) or \( As_5 \) (39) as the bridging ligands.
The novel vanadium complexes [(C₅H₅)V]₂C₆H₆ (28a), [(C₅H₅)V]₂C₆H₅CH₃ (28b), [(C₅H₅)V]₂C₆H₅C₃H₇ and [(C₅H₅)V]₂C₆H₅(CH₃)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 (C₅H₅)V(C₃H₅)₂ (11) (17) with an excess of 1,3-cyclohexadiene in refluxing heptane (33).

![Scheme 21](image)

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](image)
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 C5H5-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 π-arene bridging ligands are capable of bonding two metal centres in at least four different ways.

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