OLEFIN, ACETYLENE, AND π-ALLYLIC COMPLEXES OF TRANSITION METALS

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I. Introduction

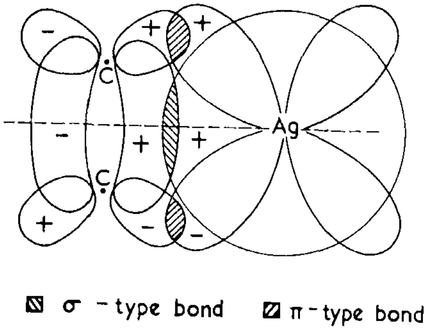
The ability of olefins and acetylenes to function as ligands towards transition metals has aroused considerable interest in the last ten years from both the theoretical and practical viewpoints. Elucidation of the nature of the bonding between the unsaturated hydrocarbon and the metal atom has made an important contribution to the modern concept of valency, and has led to a better understanding of the role metallic catalysts play in chemical reactions.

The first metal-olefin complex was reported in 1827 by Zeise, but, until a few years ago, only palladium(II), platinum(II), copper(I), silver(I), and mercury(II) were known to form such complexes (*67, 138*) and the nature of the bonding was not satisfactorily explained until 1951. However, recent work has shown that complexes of unsaturated hydrocarbons with metals of the vanadium, chromium, manganese, iron, and cobalt subgroups can be prepared when the metals are stabilized in a low-valent state by ligands such as carbon monoxide and the cyclopentadienyl anion. The wide variety of hydrocarbons which form complexes includes olefins, conjugated and nonconjugated polyolefins, cyclic polyolefins, and acetylenes.

This review deals with metal-hydrocarbon complexes under the following headings: (1) the nature of the metal-olefin and -acetylene bond; (2) olefin complexes; (3) acetylene complexes; (4) π-allylic complexes; and (5) complexes in which the ligand is not the original olefin or acetylene, but a molecule produced from it during complex formation. π-Cyclopentadienyl complexes, formed by reaction of cyclopentadiene or its derivatives with metal salts or carbonyls (*78, 217*), are not discussed in this review, neither are complexes derived from aromatic systems, e.g., benzene, the cyclopentadienyl anion, and the cycloheptatrienyl cation (*74, 78, 217*), and from acetylides (*169, 170*), which have been reviewed elsewhere.

II. The Nature of the Metal-Olefin and -Acetylene Bond

None of the theories proposed before 1951 to explain the nature of the bonding in metal-olefin complexes was entirely satisfactory (*35*). Chatt (*33*) suggested that, in addition to the ordinary coordinate bond, some sort of bond involving the filled *d*-orbitals of the metal atom was essential for coordination of the olefin, but such a bond was difficult to formulate until Dewar (*64*) described it in terms of molecular orbitals. The structure which he proposed for the silver-olefin complexes, and that subsequently proposed for the platinum-olefin complexes by Chatt and Duncanson (*35*) are shown schematically in structures (I) and (II). The σ-type bond, which has also been called a μ-bond (*64, 174*), is formed by the overlap of the filled bonding $\pi_z 2p$ molecular orbital of the olefin with the vacant $5s$-orbital of the silver atom or a vacant $5d6s6p^2$ orbital of the platinum atom. The π-type bond is formed by overlap of the vacant antibonding $\pi_z{}^*2p$ molecular orbital of the olefin with a filled $4d$-orbital of the silver atom or a $5d6p$-hybrid orbital of the platinum atom. The spatial arrangement of atoms in the ion $[PtCl_3(C_2H_4)]^-$ shown in structure (III) has been confirmed by X-ray



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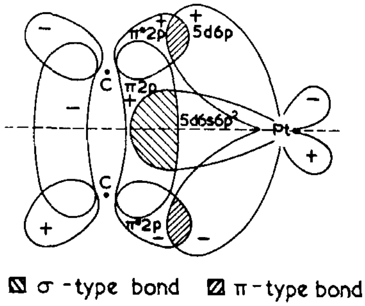

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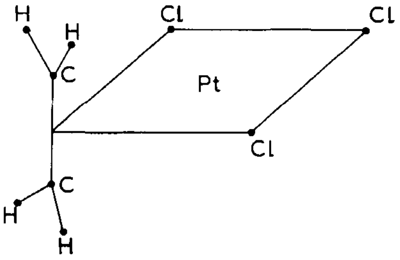
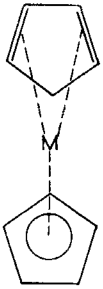


(III)

studies (*221*, *222*) and a similar arrangement has been found for other platinum(II)-olefin complexes (*5*, *14*). The X-ray structures of the complexes [$PdCl_2$(ethylene)$]_2$ (*62*) and [$PdCl_2$(styrene)$]_2$ (*115*) also show that the olefin is orientated perpendicularly to the plane of the complex.

This back-donation of electrons from the metal atom through the π-type bond leaves the olefin much less charged than if it were acting purely as a two-electron donor, as shown by the low platinum-ethylene bond moment (about 2 D) (*38*). In the olefin R·CH:CH_2 electron-donating groups (R = alkyl) will make the π-electrons more available for σ-type bond formation, and electronegative substituents (R = phenyl, fluoro) will facilitate back-donation of electrons from the metal atom by lowering the energy levels of the antibonding π^*-molecular orbitals of the olefin. The stability of a metal-olefin complex will thus depend on the balance of the σ-donor and the π-acceptor powers of the olefin, and on the nature and oxidation state of the metal atom (*34a*). To emphasize the donor and acceptor character of this metal-olefin bond the term $\sigma\pi$-bond will be used in this review.

The above type of bonding is assumed to occur in other metal-olefin and metal-acetylene complexes (*172*). Acetylenes have two mutually perpendicular sets of π-orbitals and are therefore capable of being bonded to one or to two metal atoms; both types of complexes are known. When the hydrocarbon is a nonconjugated polyolefin; e.g., cyclo-octa-1,5-diene, each C:C bond interacts independently with the metal atom. In complexes of conjugated polyolefins, e.g., cyclopentadiene, infrared and nuclear magnetic resonance studies (*99*) indicate that it is not yet possible to distinguish between structure (IV), in which each C:C bond independently contributes two π-electrons to the metal-olefin bonding, and structure (V), in which the π-electrons of the polyolefin are delocalized and the bonding is more closely related to that in ferrocene or dibenzenechromium. Conjugation in the polyolefin favors, but is not essential for, stable metal-olefin bonding;



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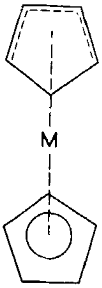


(V)

the essential factor appears to be a suitable spatial arrangement of the C:C bonds for effective overlap with the metal hybrid orbitals (*1*, *175*). It seems possible that conjugation of the C:C bonds confers additional stability on the complex in the same way that it confers additional stability on the olefin itself.

Mathematical treatments of metal-olefin bonding have been given, mainly in terms of molecular-orbital theory (*22*, *54*, *73*).

III. Olefin Complexes

A. GENERAL REMARKS

Olefins form a great variety of complexes with transition metals. In all these complexes the olefin is bonded to the metal atom by both σ-donor and π-acceptor bonds and this is favored by a low valence state of the metal atom.

There is often a striking similarity between olefins and carbon monoxide as ligands, and one of the most common ways of preparing olefin complexes is by replacement of one or more carbon monoxide ligands in a metal carbonyl by olefins. Both olefin and carbonyl complexes frequently obey the simple E.A.N. rule, each CO ligand and C:C bond contributing two π-electrons to the metal atom, to enable it to attain the electronic configuration of the next inert gas in the Periodic Table.

With a few exceptions stable mono-olefin complexes are formed only with the metals towards the end of the transition series, in particular, platinum(II) and silver(I). Most transition metals, however, form stable complexes with diolefins. Iron(0) forms more stable complexes with conjugated diolefins, e.g., butadiene, than with chelating diolefins, e.g., cyclo-octa-1:5-diene, whereas the reverse is usually true of diolefin complexes of rhodium(I) and palladium(II). These differences are nicely illustrated by cyclo-octatetraene which acts as a chelating diolefin in the rhodium(I) complex $[Rh_2Cl_2(C_8H_8)_2]$ but as two conjugated diene systems in the complex $[(CO_3Fe{\cdot}C_8H_8{\cdot}Fe(CO)_3]$. The nature and symmetry of the metal orbitals available for bonding largely determine whether more stable complexes are formed with chelating or with conjugated diolefins.

Modern physical methods, e.g., X-ray, infrared, ultraviolet and Raman spectra, dipole moment and magnetic susceptibility measurements, and, more recently, nmr spectra have played a very important part in elucidating the structure and the bonding in these complexes.

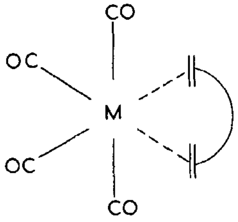
B. VANADIUM

Ultraviolet irradiation of $[VC_5H_5(CO)_4]$ in the presence of certain diolefins gives red complexes of the composition $[V(C_5H_5)(CO)_2(\text{diolefin})]$. The diolefins used were butadiene, 2,3-dimethylbutadiene and cyclohexa-1,3-diene (*81*).

C. CHROMIUM

Chelating polyolefins displace carbon monoxide from chromium hexacarbonyl to form stable olefin complexes. Thus cyclo-octa-1,5-diene gives the yellow complex $[Cr(CO)_4(C_8H_{12})]$ for which the *cis*-structure (VI; M = Cr) is proposed (*79*).

Cycloheptatriene likewise gives the complex $[Cr(CO)_3(C_7H_8)]$ (VII; R = H), in which all six π-electrons of the triene are used in the metal-hydrocarbon bond (*2*). In the complex of 1-phenylcycloheptatriene the metal atom is bound to the seven- and not the six-membered ring (VII; R = Ph). A mixture of cyclo-octa-1,3,5- and 1,3,6-triene reacts with chromium hexacarbonyl to give the analogous complex $[Cr(CO)_3(C_8H_{10})]$, in which the triene is the 1,3,5-isomer (*85*).



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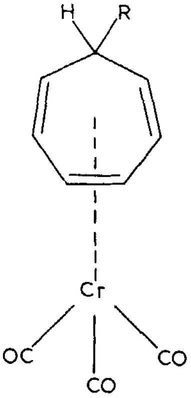


(VII)

Treatment of di-π-cyclopentadienylchromium $[Cr(C_5H_5)_2]$ with hydrogen and carbon monoxide under pressure gives the hydride $[Cr(C_5H_5)H(CO)_3]$ and a second compound which was formulated as the biscyclopentadiene complex $[Cr(CO)_2(C_5H_6)_2]$ (*86*); an alternative structure π-cyclopentadienyl-π-cyclopentenyldicarbonylchromium(II), $[Cr(C_5H_5)(C_5H_7)(CO)_2]$ is possible. Irradiation with ultraviolet light of the binuclear cyclopentadienylchromium complex $[Cr(C_5H_5)(CO)_3]_2$ in the presence of butadiene gives a complex which was formulated as dicarbonyl(butadiene)-cyclopentadienechromium(0), $[Cr(CO)_2(C_4H_6)(C_5H_6)]$ (*81*); again an alternative structure π-crotyl-π-cyclopentadienyldicarbonylchromium(II),$[Cr(C_4H_7)(C_5H_5)(CO)_2]$ is possible.

Tetracyclone reacts with chromium hexacarbonyl to give black, air-sensitive products which contain no carbon monoxide groups, and are probably analogous to the cobalt complex (XXV) (*215*).

Thiophen, however, gives the complex [Cr(C_4H_4S)(CO)$_3$] in which the thiophen molecule contributes four π-electrons from the double bonds and two electrons from the sulfur atom (*83*).

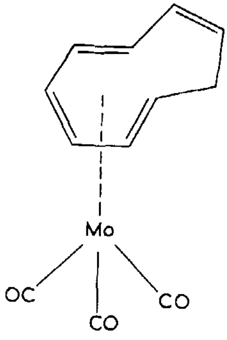
D. MOLYBDENUM

Dienes react with molybdenum hexacarbonyl to give complexes of the type [Mo(CO)$_4$(diene)] and [Mo(CO)$_2$(diene)$_2$], which are generally yellow, soluble in organic solvents, and readily sublimed. Cyclo-octa-1,5-diene (*12*, *79*, *151*), bicyclo[2,2,1]hepta-2,5-diene (*175*), a dimer of cyclo-octatetraene (*12*) and dimethyldivinylsilane (*153*) give the former type of complex with the structure (VI; M = Mo), while butadiene (*81*) and cyclohexa-1,3-diene form the latter type (*80*). Tetracyclone gives the complex [Mo(CO)$_2$(tetracyclone)$_2$] (*215*).

Cycloheptatriene displaces three carbonyl groups from molybdenum hexacarbonyl to form the orange-red complex [Mo(CO)$_3$(C_7H_8)] (*2*, *60*). The X-ray structure of this complex (*72*) shows that the carbon atom of the CH_2 group deviates markedly from the plane of the other six atoms in the ring, these being roughly equidistant from the central metal atom. The pattern of alternate single and double bonds is clearly established from the observed C—C distances. Dicycloheptatrienyl and dicycloheptatrienyl ether give complexes in which a [Mo(CO)$_3$] residue is attached to each of the seven-membered rings (*2*). A mixture of cyclo-octa-1,3,5- and -1,3,6-triene likewise gives two complexes of the composition [Mo(CO)$_3$(triene)] and [Mo(CO)$_2$(triene)$_2$] (*85*). It is suggested that in the complex [Mo(CO)$_3$-(triene)] the triene is the 1,3,5-isomer, and that the complex is analogous to the cycloheptatriene one; the complex [Mo(CO)$_2$(triene)$_2$] is considered to contain the 1,3,6-triene, acting as a diene, and bonded through its 1,3-double bonds. However, from the investigations of Manuel and Stone on the corresponding iron carbonyl complexes (see Section III,H) it is possible that the ligand is bicyclo[4,2,0]octa-2,4-diene (XV). Hydrogenation or nmr studies are required to settle this question.

Bicyclo[4,3,0]nona-2,4,8-triene(C_9H_{10}) gives a brick-red, diamagnetic complex [Mo(CO)$_3$(C_9H_{10})] which absorbs one molecule of hydrogen (*141*, *142*). The complex is thus given structure (VIII), in which the ligand is the monocyclic tautomer cyclonona-1,3,5,7-tetraene, rather than structure (IX).

Molybdenum hexacarbonyl reacts with azulenes to give complexes of the type [Mo$_2$(CO)$_6$(azulene)], of unknown structure (*29*).



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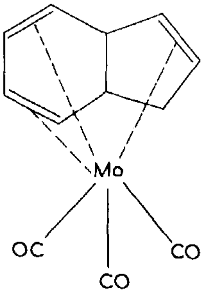

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E. TUNGSTEN

Diene complexes of the type [W(CO)$_4$(diene)] (VI; M = W) are formed by cyclo-octa-1,5-diene (*79, 151*), hexa-1,5-diene (*151*), and dimethyldivinylsilane (*153*) on heating with tungsten hexacarbonyl. Cycloheptatriene (*153*) displaces cyclo-octa-1,5-diene and 1 mol. of carbon monoxide from its tungsten complex:

$$[W(CO)_4(C_8H_{12})] + C_7H_8 \rightarrow [W(CO)_3(C_7H_8)] + C_8H_{12} + CO. \qquad (1)$$

Treatment of tungsten hexacarbonyl with a mixture of cyclo-octa-1,3,5- and -1,3,6-triene gives the complex [W(CO)$_2$(C$_8$H$_{10}$)$_2$] (*85*). The hydrocarbon is believed to be the 1,3,6-triene, acting as a diene, but for the reasons mentioned (see Section III,H) it is possible that the ligand is bicyclo[4,2,0]-octa-2,4-diene (XV).

Tungsten hexacarbonyl on treatment with bicyclo-[4,3,0]nona-2,4,8-triene(C$_9$H$_{10}$) gives a brick red complex [W(CO)$_3$(C$_9$H$_{10}$)] which appears to be completely analogous to the molybdenum complex [Mo(CO)$_3$(C$_9$H$_{10}$)] of structure (VIII) (*142*).

The hydrocarbon complexes of tungsten have been arranged in the following order of stability (*153*): hexamethylbenzene > *p*-cymene > cyclo-octa-1,5-diene > hexa-1,5-diene; *p*-cymene > dipentene; and cyclo-heptatriene > cyclo-octa-1,5-diene.

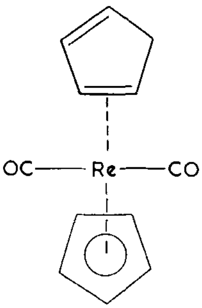
F. MANGANESE

Irradiation of cyclopentadienyltricarbonylmanganese with ultraviolet light in an atmosphere of ethylene gives cyclopentadienyldicarbonylethylenemanganese [Mn(C$_5$H$_5$)(C$_2$H$_4$)(CO)$_2$] as orange-red crystals (*143*), while irradiation in the presence of butadiene gives the red butadiene complex [$Mn(C_5H_5)(CO)(C_4H_6)$], mp, decomp., 134–136° (*81*).

Prolonged treatment of manganese carbonyl with azulenes gives unstable complexes of the type [$Mn_2(CO)_6(azulene)_2$], the structures of which are uncertain (*29*).

G. Rhenium

The reaction of di-π-cyclopentadienylrhenium hydride, [$Re(C_5H_5)_2H$], with carbon monoxide under pressure gives a yellow, diamagnetic complex of the composition [$Re(CO)_2C_{10}H_{11}$] (*90, 101*). Infrared and nmr studies (*99, 101*) have shown that the complex has the structure (X), in which a cyclopentadiene molecule is bonded to the metal by only one olefin-metal link, thus giving the rhenium(I) atom a formal inert gas configuration. The complex absorbs one mol. of hydrogen to give the analogous cyclopentene derivative (XI).



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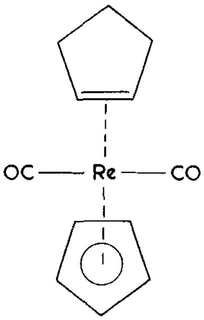

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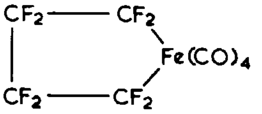
Dicyclopentadiene reacts with rhenium(III) chloride to give the polymeric complex [$ReCl_2(C_{10}H_{12})_2$]$_n$, and with triphenylphosphinerhenium(III) chloride to give the complex [$ReCl(C_{10}H_{12})_2(PPh_3)$] (*49*). The structures of these complexes are unknown.

H. Iron

Olefins readily displace CO groups from the iron carbonyls, $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$, to form complexes in which a C:C bond of the olefin takes the place of each displaced CO group, and by donating its π-electrons preserves the formal inert gas electron configuration of the iron atom in the complex. Acrylonitrile is the only reported example of a monoolefin complexing with iron in this way, but many complexes of iron with polyolefins are known.

Acrylonitrile reacts with iron pentacarbonyl to give $[Fe(CO)_4(CH_2\!:\!CH\cdot CN)]$ (*139*), the infrared spectrum of which suggests that the acrylonitrile is bonded to the iron atoms through its olefinic double bond and not through the nitrile group.

Perfluoroethylene was first thought to react with iron carbonyl to give the iron(0) olefin complex $[Fe(CO)_3(C_2F_4)_2]$ (*213*). It has since been shown that the product is a heterocyclic derivative of iron(II) (structure XII) (*150*, *214*) and not a true olefin complex.



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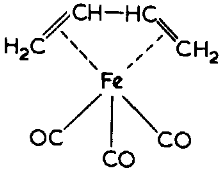


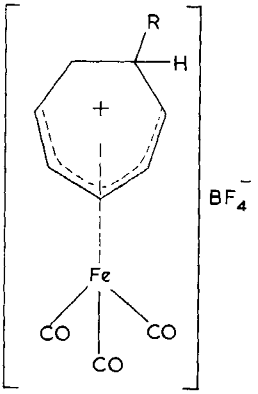
(XIII)

Although the very stable complex $[Fe(CO)_3(C_4H_6)]$, formed by prolonged heating of butadiene with iron pentacarbonyl, was first prepared in 1930 (*181*), it was not until 1958 (*106*, *107*) that the chemical and physical properties of the complex (e.g., its failure to react with hydrogen or maleic anhydride, its diamagnetism, and its ultraviolet and infrared spectra) were satisfactorily explained in terms of the structure (XIII), since confirmed by X-ray methods (*161*). In this structure, the butadiene residue is planar and is bonded to the iron atom by interaction of its π-electrons with d-orbitals of the metal. High resolution nmr measurements suggest that the protons of the terminal methylene groups are not equivalent (*99*), in contrast with π-allylic complexes (Section V,C). Complexes of the formula $[Fe(CO)_3$-(diene)] are also formed by isoprene and piperylene (*140*), cyclohexa-1,3-diene (*106*, *107*), cyclohepta-1,3-diene (*30*, *59*), cyclo-octa-1,5-diene (*140*, *152*), dipentene (*153*), bicyclo[2,2,1]hepta-2,5-diene (*28*), perfluorocyclohexa-1,3-diene (*213*), 1,2,3,4-tetraphenylbutadiene (*187*), and with a number of dienes with the structures $CH_3\cdot CH\!:\!CH\cdot CH\!:\!CH\cdot R$; where R = $COOC_2H_5$, COOH, CN, $CONH_2$, $CO\cdot CH_3$, and CHO (*140*). Nonconjugated 1,4-dienes when treated with iron carbonyls give complexes in which the diene system has become conjugated. Thus penta-1,4-diene with $Fe_3(CO)_{12}$ gives $[Fe(CO)_3$(piperylene)] and 1,3,5-trimethylcyclohexa-1,4-diene gives $[Fe(CO)_3$(1,3,5-trimethylcyclohexa-1,3-diene)] (*140*).

In general, conjugated dienes bonded to an iron tricarbonyl residue give a much more stable system than do nonconjugated dienes. For example, the complex [Fe(CO)$_3$(cyclo-octa-1,5-diene)] decomposes in a few hours at room temperature, whereas the complex [Fe(CO)$_3$(butadiene)] can be recovered unchanged from its solution in concentrated sulfuric acid (*106*).

Cycloheptatriene (C_7H_8) was thought originally to displace three carbonyl groups from iron pentacarbonyl to give the dicarbonyl complex [Fe(CO)$_2$(cycloheptatriene)] (*28*). It has been shown (*30*, *59*) that heating cycloheptatriene (1 mol.) with iron pentacarbonyl (1 mol.) at 135° gives iron tricarbonyl complexes, mainly [Fe(CO)$_3$(cycloheptatriene)], but some [Fe(CO)$_3$(cycloheptadiene)] is also formed. The ratio of these two products is 19:1 after 1 day's heating, but falls to 2:1 after 5 days. The cycloheptatriene complex [Fe(CO)$_3$(cycloheptatriene)] is reduced to the corresponding cycloheptadiene complex by hydrogen using a Raney nickel catalyst (*30*), thus showing that only two of the three double bonds in the cycloheptatriene ligand are used in bonding to the iron atom.

It was originally reported (*92*, *174*) that the cycloheptatriene complex [Fe(CO)$_3$(C_7H_8)] with triphenylmethyl fluoroborate gave a tropylium complex [Fe(CO)$_3$(C_7H_7)] BF$_4$ but subsequent work (*59*) has shown that an adduct [Fe(CO)$_3$($C_7H_8CPh_3$)] BF$_4$ (XIV; R = CPh$_3$) is formed in 96% yield. The cycloheptadiene complex [Fe(CO)$_3$(C_7H_{10})] with triphenylmethyl fluoroborate undergoes hydride ion abstraction to give the bright yellow cycloheptadienium fluoroborate [Fe(CO)$_3$(C_7H_9)] BF$_4$ (XIV; R = H) and triphenylmethane in 93% yield. Treatment of the cycloheptatriene complex [Fe(CO)$_3$(C_7H_8)] with fluoroboric acid also gives this salt, [Fe(CO)$_3$-(C_7H_9)] BF$_4$ which reacts with potassium iodide in acetone to give the tropylium complex [FeI(CO)$_2$(C_7H_7)] as stable maroon crystals. These



(XIV)

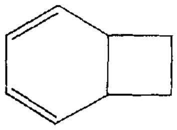
reactions of the cycloheptatriene-substituted iron carbonyls and related compounds are summarized below.

$$\begin{tikzcd}
\mathrm{Fe(CO)_5 + C_7H_8} \arrow[r] & \mathrm{[Fe(CO)_3(C_7H_8)]} \arrow[d, "\mathrm{Ph_3C\ BF_4}"'] \arrow[drr, "\mathrm{HBF_4}"] & + & \mathrm{[Fe(CO)_3(C_7H_{10})]} \arrow[d, "\mathrm{Ph_3C\ BF_4}"] \\
 & \mathrm{[Fe(CO)_3(C_7H_8CPh_3)]\ BF_4} & & \mathrm{[Fe(CO)_3(C_7H_9)]\ BF_4} \arrow[d, "\mathrm{KI}"] \\
 & & & \mathrm{[FeI(CO)_2(C_7H_7)]}
\end{tikzcd}$$

C_7H_7 = tropylium
C_7H_8 = cycloheptatriene
C_7H_9 = cycloheptadienium
C_7H_{10} = cycloheptadiene

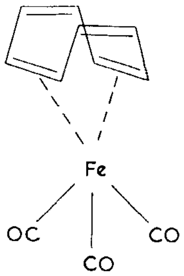
Triphenylmethyl fluoroborate will also abstract a hydride ion from tricarbonylcyclohexa-1,3-dieneiron to give the cyclohexadienyl complex $[Fe(CO)_3(C_6H_7)]\ BF_4$ (*59, 76*), analogous to the cycloheptadienyl complex $[Fe(CO)_3(C_7H_9)]\ BF_4$ described above.

A mixture of cyclo-octa-1,3,5- and 1,3,6-triene, when heated with iron pentacarbonyl in an inert solvent, gives a diamagnetic, orange-yellow oil of the composition $[Fe(CO)_3(C_8H_{10})]$ (*89, 154*), which was formulated (*85*) as $[Fe(CO)_3$(cyclo-octa-1,3,6-triene)], in which the four π-electrons of the conjugated double bonds of the triene are involved in bonding to the metal atom, thus leaving one "free" double bond. However, Manuel and Stone (*152*) point out that this complex does not absorb hydrogen or bromine, and as the 1,3,5-isomer exists in equilibrium with bicyclo-[4,2,0]-octa-2,4-diene(XV), they formulate the complex as tricarbonyl-bicyclo-[4,2,0]octa-2,4-dieneiron(0), in which the bonding is analogous to that in tricarbonylbutadieneiron. The nmr spectrum of this compound has confirmed this proposed structure (*30*). A red crystalline complex of the composition $C_{15}H_{12}Fe_2O_6$ is also formed in this reaction, but its structure is unknown (*85*). On heating $Fe_3(CO)_{12}$ with cyclo-octa-1,3,5-triene in benzene two products with the composition $[Fe(CO)_3(C_8H_{10})]$ are obtained (*154*). One is tricarbonylbicyclo[4,2,0]octa-2,4-dieneiron and the other is probably tricarbonylcyclo-octa-1,3,5-trieneiron. This triene complex is the less stable isomer and on heating with $Fe(CO)_5$ it isomerizes to tricarbonylbicyclo-[4,2,0]octa-2,4-dieneiron.

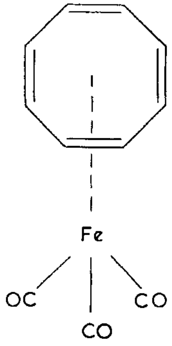


(XV)

Cyclo-octatetraene reacts with iron carbonyls to form complexes with the compositions [$Fe(CO)_3(C_8H_8)$], [$Fe_2(CO)_6(C_8H_8)$], and [$Fe_2(CO)_7(C_8H_8)$] (*152, 168, 180*). Nakamura and Hagihara (*166*) report that the complex [$Fe(CO)_3(C_8H_8)$] decolorizes bromine in carbon tetrachloride and shows absorption bands in its infrared spectrum at 699, 716, and 720 cm^{-1} due to *cis*-double bonds. They suggest structure (XVI) for this complex, i.e., the hydrocarbon retains its "tub" form in the complex. These results are contrary to those of other workers (*152, 180*) who have shown that this complex does not absorb hydrogen or form a Diels-Alder adduct with maleic anhydride. The infrared and nuclear magnetic resonance spectra of [$Fe(CO)_3(C_8H_8)$] also indicate that all eight hydrogens of the C_8 ring are equivalent (*152, 180*). These results suggest that all four double bonds of the cyclo-octatetraene ligand in the complex are involved in complex formation, and that the bonding involves overlap of suitable *d*-orbitals of the iron atom with a symmetrical π-orbital extending over all eight carbon atoms, although only four of the eight π-electrons are used. In this way the cyclo-octatetraene molecule acquires an essentially planar configuration (XVII). Some molecular-orbital calculations by Cotton (*54*) support these conclusions. This planarity, however, does not confer aromatic character on the ring, as shown by the failure of the complex to form an acyl derivative under Friedel-Crafts conditions (*152*).

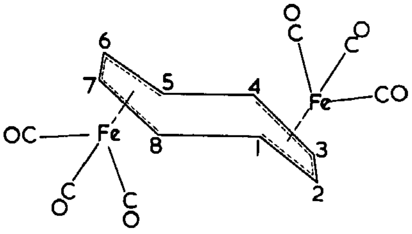


(XVI)



(XVII)

A single crystal X-ray structural determination of the binuclear complex [$Fe_2(CO)_6(C_8H_8)$] (*64a*) shows it to have the structure (XVIII) and not one of the previously suggested structures (*22, 54, 152, 166, 174*) including "tub" and planar forms of the cyclo-octatetraene ring. The cyclo-octatetraene ring in the complex approximates to a "chair" form in which the four carbon atoms associated with each iron atom are planar or very nearly so. The observed Fe—C and C—C distances in this complex are compared



(XVIII)

below (Table I) with those observed for tricarbonylbutadieneiron (*161*). The carbon atoms of the cyclo-octatetraene residue are numbered as shown in (XVIII).

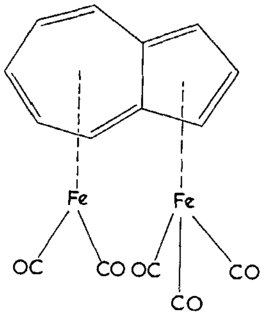
TABLE I
COMPARISON OF THE BOND LENGTHS IN $[(CO)_3Fe(C_8H_8)Fe(CO)_3]$ WITH THOSE OF $[Fe(CO)_3C_4H_6]$

$[(CO)_3Fe(C_8H_8)Fe(CO)_3]$	$[Fe(CO)_3(C_4H_6)]$
Bond lengths ± 0.03Å C—C	Bond lengths ± 0.04Å C—C
1.39Å C_2—C_3, C_6—C_7 1.44Å C_1—C_2, C_3—C_4, C_5—C_6, C_7—C_8 1.49Å C_4—C_5, C_8—C_1	1.45–1.46Å and all equal within experimental error.
Fe—C_8H_8	Fe—C_4H_6
2.06Å Fe—C_2, —C_3, —C_6, —C_7 2.15Å Fe—C_1, —C_4, —C_5, —C_8	2.1Å and roughly all of equal distance.

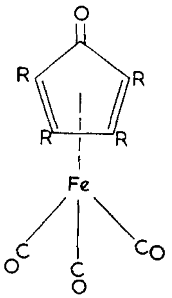
The second binuclear complex $[Fe_2(CO)_7(C_8H_8)]$ is a black solid, and appears to be a derivative of $Fe_2(CO)_9$, as it shows bands due to bridging carbonyl groups in its infrared spectrum (*152*).

These iron-olefin complexes undergo interesting reactions with other ligands capable of bonding to the metal atom (*152*). Triphenylphosphine displaces cyclo-octatetraene from the complex $[Fe(CO)_3(C_8H_8)]$ to give the complex $[Fe(CO)_3(PPh_3)_2]$, but triphenylarsine and triphenylstibine give the complexes $[Fe(CO)_2(C_8H_8)(AsPh_3)]$ and $[Fe(CO)_2(C_8H_8)(SbPh_3)]$ respectively. Tricarbonylcycloheptatrieneiron gives the complexes $[Fe(CO)_3(PPh_3)_2]$ and $[Fe(CO)_2(PPh_3)_3]$ on treatment with triphenylphosphine, and $[Fe(CO)_3(C_8H_8)]$ on treatment with cyclo-octatetraene.

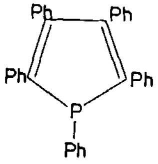
Interaction of azulenes (= az) with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ gives reddish-brown complexes of the type $[Fe_2(CO)_5(az)]$ (*29*); with azulene itself a compound [$Fe_5(CO)_{13}$(azulene)] was also obtained. Complexes of azulene, 1,3-dideuteroazulene, 4,6,8-trimethylazulene, 4-methylazulene and guaiazulene (5-isopropyl-3,8-dimethylazulene) have been prepared. The dipole moment ($\mu = 3.97$ D) of the azulene complex [$Fe_2(CO)_5(C_{10}H_8)$] favors a *cis*-structure (XIX), although similar structures involving iron-iron bonds are also possible (*29*). The complex [$Fe_2(CO)_5$(guaiazulene)] exists in two geometric isomers which were separated by chromatography.



(XIX)



(XX)



(XXI)

Substituted cyclopentadienones react with iron carbonyls to form stable, diamagnetic π-complexes of the type [$Fe(CO)_3$(cyclopentadienone)] (*215*). The proposed structure is shown in (XX). These complexes undergo reactions typical of metal carbonyls, e.g., displacement of carbon monoxide by tertiary phosphines, but the carbonyl group of the ligand does not show reactions characteristic of a keto-group. These complexes are also formed by interaction of acetylenes with iron carbonyls (see Section VI,C). Interaction of tetracyclone and $Fe_3(CO)_{12}$ gives unstable complexes which contain the sandwich anion [Fe(tetracyclone)$_2$]$^{2-}$ analogous to the anion (XXV) (*215*).

Heterocyclic dienes (un) also form iron carbonyl complexes, e.g., thiophen dioxides (*215*) give complexes of the type [$Fe(CO)_3$(un)] and pentaphenylphosphole (XXI) (*20*) gives the complexes [$Fe(CO)_3$(un)], in which the heterocyclic molecule is attached through its two double bonds, and [$Fe(CO)_4$(un)], in which it is attached through the phosphorus atom. Iron pentacarbonyl desulfurizes thiophen to give the complex [$Fe_2(CO)_6$-(C_4H_4)] (*134*), for which structure (LX) has been suggested. This complex is also formed by treating acetylene with iron pentacarbonyl (see Section VI,C). The report (*28*) that thiophen reacts with iron carbonyl to give a thiophen complex [$Fe(CO)_2$(thiophen)] is erroneous; the properties of the supposed thiophen complex correspond very closely with those of the complex $[Fe_2(CO)_6(C_4H_4)]$, and there can be little doubt that the two are identical.

Reduction of arene-π-cyclopentadienyliron(II) cations, which are isoelectronic with the di-π-cyclopentadienylcobalt cation, with lithium aluminium hydride yields the neutral arenecyclopentadiene-iron complexes (*100*):

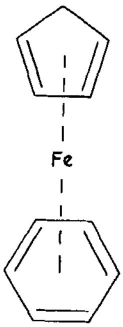
$$[Fe(C_5H_5)(C_6H_6)]^+ + H^- \rightarrow [Fe(C_5H_6)(C_6H_6)]. \qquad (2)$$

The chemical properties of these complexes, together with their infrared and high resolution nuclear magnetic resonance spectra, show that the cyclopentadiene group is bound to the iron atom as shown in (XXII). By sharing the six π-electrons of the benzene molecule and the four π-electrons of the cyclopentadiene molecule, the iron(0) atom acquires the electronic configuration of krypton.

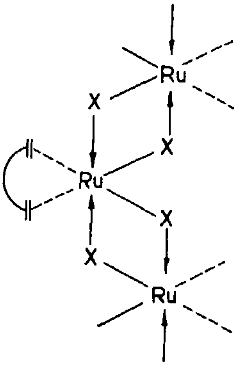
*Winkhaus *et al.* (*217a*) have re-examined the nmr spectrum of their compound $C_{11}H_{12}Fe$ and have reformulated the structure as π-cyclopentadienyl-π-cyclohexadienyliron(II), $[(\pi\text{-}C_5H_5)(\pi C_6H_7)Fe]$.

I. RUTHENIUM

Reduction of ammonium chlororuthenate with titanous chloride gives a solution containing divalent ruthenium which will absorb ethylene or propylene to give a 1:1 ruthenium-olefin complex which was not isolated (*108*). Ethylene was previously reported not to form stable complexes on treatment with ruthenium halides (*97*).



(XXII)



(XXIII)

The strongly chelating dienes bicyclo[2,2,1]hepta-2,5-diene (*1*) and cyclo-octa-1,5-diene (*12*) react with ruthenium halides to give stable, diamagnetic complexes of the composition $[RuX_2(diene)]$ (X = Cl, Br, I).

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* Note added in proof.

The complexes are insoluble in all solvents, which suggests that they are polymers, $[RuX_2(diene)]_n$, in which the metal atom attains its usual co-ordination number of six by the formation of the halogen-bridged structure (XXIII). *p*-Toluidine (*p*-tol) causes fission of the halogen bridge and gives complexes of the type $[RuX_2(diene)(p\text{-tol})_2]$. Cyclo-octa-1,5-diene forms the unstable complex $[RuCl_2(PEt_2Ph)_2(C_8H_{12})]$ on treatment with the halogen-bridged complex $[Ru_2Cl_3(PEt_2Ph)_6]$ (*40*).

J. OSMIUM

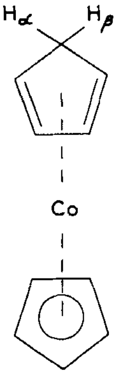
Osmium(IV) does not react with ethylene under pressure (*97*), or with cyclo-octa-1,5-diene (*45*), but the osmium(II) complex $[Os_2Cl_3(PEtPh_2)_6]Cl$ gives the stable, 6-coordinated complex $[OsCl_2(PEtPh_2)_2(C_8H_{12})]$ on treatment with cyclo-octa-1,5-diene, which acts as a chelating ligand in the complex (*40a*).

K. COBALT

Reduction of cobalticenium halides by sodium borohydride in aqueous ethanol or by lithium aluminium hydride in tetrahydrofuran gives the neutral diamagnetic complex $[Co(C_5H_5)(C_5H_6)]$(XXIV) in which one π-cyclopentadienyl anion has been converted into cyclopentadiene (*99*):

$$[Co(C_5H_5)_2]^+ + H^- \rightarrow [Co(C_5H_5)(C_5H_6)]. \quad (3)$$

By sharing the four π-electrons of the diene and the six π-electrons of the cyclopentadienyl anion, the cobalt(I) atom acquires the electronic configuration of krypton. The formulation of the complex as (XXIV) is supported by nuclear magnetic resonance studies, and by its infrared spectrum, which shows bands characteristic of a π-cyclopentadienyl-metal grouping, and



(XXIV)

bands due to olefinic C—H stretching modes. The complex is unaffected by catalytic hydrogenation, and its chemical properties indicate that the endo-hydrogen atom H_α of the methylene groups is usually reactive, due to its close proximity to the metal atom, e.g., it is readily removed to form the cobalticenium ion:

$$[Co(C_5H_5)(C_5H_6)] + H^+ \rightarrow [Co(C_5H_5)_2]^+ + H_2 \tag{4}$$

$$[Co(C_5H_5)(C_5H_6)] + CCl_4 \rightarrow [Co(C_5H_5)_2]Cl + CHCl_3. \tag{5}$$

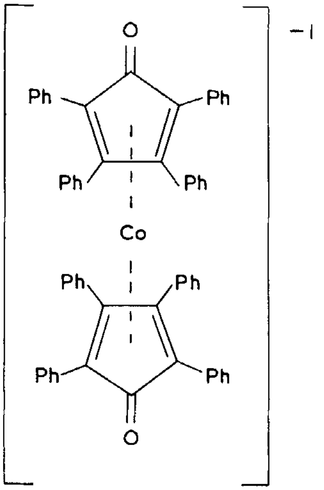
The corresponding derivatives $[Co(C_5H_5)(1\text{-}\mathit{endo}\text{-}Me{\cdot}C_5H_5)]$ and $[Co(C_5H_5)(1\text{-}\mathit{endo}\text{-}CF_3{\cdot}C_5H_5)]$ are prepared by the action of the appropriate alkyl halide on cobaltocene, e.g.,

$$2[Co(C_5H_5)_2] + MeI \rightarrow [Co(C_5H_5)(1\text{-}Me{\cdot}C_5H_5)] + [Co(C_5H_5)_2]I. \tag{6}$$

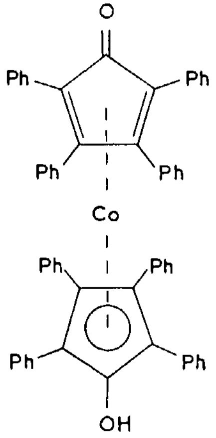
It is interesting to note that the complex of the composition $[C_{10}H_{10}(CCl_3)Co]$ obtained previously (*137*) by reaction of carbon tetrachloride with cobaltocene is the 1-*endo*-trichloromethyl analogue of complex (XXIV): this complex can be reduced by lithium aluminium hydride to the 1-*endo*-dichloromethyl derivative (*99*).

The compound cyclopentadienylcyclo-octatetraenecobalt is probably analogous to the compound cyclopentadienylcyclopentadienecobalt (XXIV). The cyclo-octatetraene residue shows two proton resonance lines in the nmr spectrum (*167*) in contrast to that in the iron complex $[Fe(CO)_3$(cyclo-octatetraene)] which shows only one proton resonance line (*152*, *180*).

Diolefins such as butadiene, cyclohexa-1,3-diene, 2,3-dimethylbuta-1,3-diene and bicyclo[2,2,1]hepta-1,5-diene react with dicobalt octacarbonyl to



(XXV)



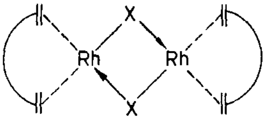
(XXVI)

give complexes of the types $[Co_2(CO)_6(\text{diolefin})]$ and $[Co_2(CO)_4(\text{diolefin})_2]$ (*82*, *218*, *219*). With the triolefins cyclo-octa-1,3,5- and -1,3,6-triene in *n*-heptane at 130° dicobalt octacarbonyl reacts to give the complex $[Co_2(CO)_4(C_8H_{10})_2]$ (*84*). This complex might be a derivative of bicyclo-[4,2,0]octa-2,4-diene like the corresponding iron complex $[Fe(CO)_3(C_8H_{10})]$ (*30*, *152*). Dicobalt octacarbonyl reacts with perfluoroethylene to give the binuclear cobalt(I) complex $[(CO)_4CoCF_2{\cdot}CF_2Co(CO)_4]$ (*214*).

Tetracyclone reacts with dicobaltoctacarbonylmercury, $[Co(CO)_4]_2Hg$, to give the complex $[Co(CO)_2(\text{tetracyclone})]_2Hg$, and with dicobaltoctacarbonyl to give the violet complex $[Co(\text{tetracyclone})_2]_2Co$, which contains the sandwich anion (XXV) (*215*). Treatment of this complex salt with hydrochloric acid gives the π-cyclopentadienyl derivative (XXVI).

L. Rhodium

Halogen-bridged rhodium(I) complexes of the type $[Rh_2X_2(\text{diene})_2]$ ($X = Cl, Br, I$) have been prepared from chelating cyclic dienes, e.g., cyclo-octa-1,5-diene (*45*), dicyclopentadiene (*45*), bicyclo[2,2,1]hepta-1,5-diene (*1*) and cyclo-octatetraene (*1*, *45*) (functioning as a diene). Dipentene, hexa-1,5-diene, and styrene do not form stable complexes. The cyclo-octa-1,5-diene complex may be prepared by (a) heating the diene with rhodium trichloride; (b) reducing the trichloride with sodium borohydride in the presence of the diene; and (c) displacement of the carbonyl groups in rhodium carbonyl chloride, $[Rh_2Cl_2(CO)_4]$, with the diene. The physical and chemical properties of the complexes accord with the structure (XXVII;



(XXVII)

X = halogen) in which the rhodium atoms, isoelectronic with palladium(II), have a planar (*dsp*^{2}) stereochemistry. The nmr spectra of several of these complexes are likewise consistent with structure (XXVII) (*99*).

Amines (am) react with these bridged complexes to give mononuclear complexes of the type $[RhX(\text{am})(\text{diene})]$; a similar complex is formed by triphenylphosphine, but not by triphenylarsine or diphenylsulphide. Cationic and anionic complexes of the type $[Rh(\text{diamine})(\text{diene})]^+$ and $[RhCl_2(\text{diene})]^-$ are readily formed. The stable acetate (XXVII; $X = OAc$) is prepared from the corresponding chloride and potassium acetate; its infrared spectrum indicates that each acetate group is symmetrically bound through both oxygen atoms. A binuclear methanol derivative of the composition $[Rh_2(MeOH)_2(C_8H_{12})_2]$ is formed by the reaction of the diene complex (XXVII) with anhydrous sodium carbonate in methanol. Its infrared spectrum indicates that it contains a hydroxyl group, but its structure is unknown (*45*).

Treatment of the complex (XXVII; X = Cl) with acetylacetone (acacH) in alkali gives the mononuclear α-acetylacetonyl compound $[Rh(acac)(C_8H_{12})]$. The stable, diamagnetic complex cyclo-octa-1,5-diene-cyclopentadienylrhodium(I), $[Rh(C_5H_5)(C_8H_{12})]$, is formed from the dimer (XXVII; X = Cl) and cyclopentadienyl sodium (*44*, *45*). The analogous complex, with cyclopentadiene as the chelating diene, has been prepared in 1–2% yield (*91*) by the reaction:

$$RhCl_3 + C_5H_6 + KC_5H_5 \rightarrow [Rh(C_5H_5)(C_5H_6)] \qquad (7)$$

and in 80% yield by reduction of the di-π-cyclopentadienylrhodium(III) ion in aqueous ethanol by sodium borohydride (*99*). The formulation of these compounds as π-cyclopentadienyl-diene complexes similar to the cobalt complex (XXIV) is supported by their diamagnetism and their nmr (*99*) and infrared spectra (*84*, *99*).

There is evidence that an unstable complex is formed when rhodium(III) chloride is treated with ethylene at high pressure (*97*).

M. IRIDIUM

No complex was obtained on treatment of iridium(III) chloride with ethylene (*67*, *97*, *138*) or cyclo-octa-1,5-diene (*45*), but the ethylene complex $[IrCl_2(C_2H_4)]$ was reported to be formed by the action of ethanol on iridium chloride (*67*, *138*). No further examination of this complex has been reported.

Iridium(I), stabilized by the π-cyclopentadienyl anion, forms a stable, diamagnetic complex $[Ir(C_5H_5)(C_5H_6)]$ with cyclopentadiene (*91*) by the reaction:

$$IrCl_3 + KC_5H_5 + C_5H_6 \rightarrow [Ir(C_5H_5)(C_5H_6)]. \qquad (8)$$

This complex is analogous in all ways to the cobalt complex (XXIV), and the proposed structure is supported by its infrared spectrum which shows bands due to the π-cyclopentadienyl-metal grouping, a methylene group, and conjugated double bonds co-ordinated to the metal atom (at 1451 cm^{-1}).

N. NICKEL

The ability of nickel complexes, e.g., nickel carbonyl and its phosphine derivatives, to catalyze polymerization and other reactions of olefins and acetylenes has been studied extensively (*46*, *53*), particularly by Reppe.

Such reactions probably occur through the formation of nickel-olefin and -acetylene complexes, but until recently no stable complex was known.

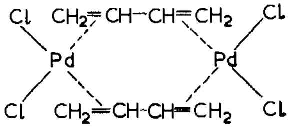
Schrauzer (*186, 188*) has prepared red crystalline complexes of the type $[Ni(un)_2]$ (un = CH_2:CH·CN, NC·CH:CH·CN, Ph·CH:CH·CN, or CH_2:CH·CHO) from nickel carbonyl and the corresponding olefins. These complexes are very insoluble and probably polymeric. Their infrared spectra show that the olefin is bonded to the metal atom through its C:C bond, and not through the ·C:N or ·CHO groups. The complexes have catalytic reactivity, e.g., bis-acrylonitrilenickel(0) catalyzes the polymerization of acetylene to cyclo-octatetraene and the co-polymerization of acetylene and acrylonitrile to 2,4,6-heptatrienenitrile. Bis-acrylonitrilenickel(0) reacts with triphenylphosphine to give the complexes $[Ni(CH_2:CH{\cdot}CN)_2(PPh_3)]$ and $[Ni(CH_2:CH{\cdot}CN)_2(PPh_3)_2]$.

Nickel carbonyl reacts with tetracyclone to give the complex $[Ni(tetracyclone)_2]$ (*215*) and with duroquinone to give the complex $[Ni(duroquinone)_2]$ (*189*).

O. PALLADIUM

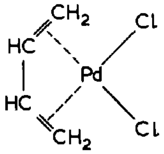
Olefins(un) react readily with dichlorobis-(benzonitrile)-palladium(II), $[PdCl_2(Ph{\cdot}CN)_2]$, to form complexes of the type $[Pd_2Cl_4un_2]$ which are less stable than the corresponding complexes of platinum (*67, 138*). Recently it has been shown that $[Pd_2Cl_4(C_2H_4)_2]$ may be prepared in benzene from palladium chloride and ethylene under pressure (*97, 147*). Many olefins react with palladium(II) chloride in 50% acetic acid at room temperature to give olefin complexes $[Pd_2Cl_4un_2]$ (*123*); at higher temperatures π-allylic complexes are formed (see Section V,E).

Chelate complexes of the type $[PdX_2(diene)]$ (X = Cl, Br) are readily formed by the dienes hexa-1,5-diene (*124*), bicyclo 2,2,1]hepta-2,5-diene (*1, 7*) tricyclo[4,2,2,0]-deca-triene and -diene derivatives (*10*), cyclo-octa-1,5-diene and dicyclopentadiene, but not dipentene (*43*). These may be converted to complexes of the types $[Pd_2X_2(dieneOR)_2]$ and [PdCl(dieneOR)-(amine)] (R = alkyl) (*43*), and their properties indicate that they have similar structures to the platinum complexes (XXXI) and (XXXIII).



(XXVIII)

Generally, the compounds are more deeply colored, more easily formed, more reactive, and less stable than their platinum(II) analogs. Butadiene reacts with $[PdCl_2(PhCN)_2]$ to give an unstable yellow complex which is formulated as the butadiene-bridged compound (XXVIII) as its infrared spectrum shows no absorption due to an isolated C:C double bond (*192*). However, no molecular-weight determinations were reported to distinguish between structure (XXVIII) and the chelate structure (XXIX).



(XXIX)

Palladium chloride or the chloropalladite ion catalyze the oxidation of olefins to aldehydes or ketones, presumably by forming unstable palladium-olefin complex intermediates (*196*). A reaction of great industrial importance is the palladium chloride/cupric chloride catalyzed oxidation of ethylene to acetaldehyde (*195*). The first stage is presumably the oxidative hydrolysis of ethylene,

$$C_2H_4 + PdCl_2 + H_2O \rightarrow CH_3{\cdot}CHO + Pd + 2HCl. \qquad (9)$$

Deposition of palladium is prevented by the cupric chloride

$$Pd + 2CuCl_2 \rightarrow PdCl_2 + Cu_2Cl_2 \qquad (10)$$

and oxygen or air is used to reoxidize the cuprous chloride to cupric chloride.

$$Cu_2Cl_2 + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2CuCl + H_2O \qquad (11)$$

Propylene may similarly be oxidized to acetone.

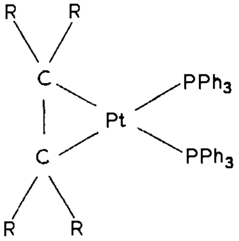
P. PLATINUM

Most of the earlier work on olefin complexes was carried out with this metal, which forms a variety of complexes, e.g., $M[PtX_3un]$, $[Pt_2X_4un_2]$, *trans*-$[PtX_2un_2]$, *cis*- and *trans*-$[PtX_2(am)(un)]$, all three stereoisomers of $[PtClBr(NH_3)(C_2H_4)]$, and $PtX(NH_3)(am)(C_2H_4)]NO_3$ (M = Na, K, NH_4; X = halogen; am = amine; un = olefin). These have been described in detail (*33*, *67*, *95*, *138*), and only recent work will be discussed here.

The gaseous products formed on thermal decomposition of ethylene-platinous chloride are ethylene, hydrogen chloride, vinyl chloride, ethyl chloride, ethylene dichloride and ethylidine dichloride. The half life for the decomposition at 130° is 4.5 days, at 172° it is 1.7 hours (*98*). The hydrolysis of Zeise's salt $K[PtCl_3(C_2H_4)]$ by water and dilute acids has been studied;

ethylene and acetaldehyde are the main organic products with sometimes a trace of ethyl alcohol (*133*).

The properties of platinum-olefin complexes can be explained satisfactorily (*176*) in terms of the structure (II) in which the olefin is bonded to the platinum atom by a $\sigma\pi$-bond. The relative contributions of the σ-bond and the π-bond may vary considerably, depending on the nature of the olefin, without altering the strength of the $\sigma\pi$-bond, e.g., in complexes of substituted styrenes $R\cdot C_6H_4\cdot CH:CH_2$ (R = 4-MeO, 4-Me, 3-MeO, C-31, and 4-NO_2) the σ- and π-bonds are affected approximately equally, but in opposite directions, by the substituent R, and a strong $\sigma\pi$-bond results in each case (*131*). It is possible that in the stable complexes of the type $[Pt(PPh_3)_2(un)]$, formed by reduction of an alcoholic suspension of *cis*-$[PtCl_2(PPh_3)_2]$ in the presence of an electronegatively substituted olefin (un) (*42*), the olefin is bonded to the metal by an essentially pure π-bond, although it is equally possible that rehybridization at the carbon atoms occurs, leading to two Pt-C σ-bonds as shown in structure (XXX). The unstable complexes formed by perfluoro-olefins e.g., $CF_2:CF\cdot CF:CF_2$ and $CF_2:CF_2$ (*39*, *213*) may also have this type of bonding.



(XXX)

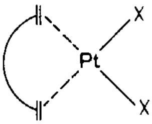
The infrared spectra of several of these complexes confirm that the olefin exists, with its double bond, in the complex (*35*, *177*, *178*), but that the double bond is weakened by complex formation, as shown by the decrease of some 140 cm^{-1} in the C:C stretching frequency (*35*). The total platinum-olefin bond order is approximately 4/3 (*35*), and the C:C bond order approximately 5/3 (*126*).

This formulation has been criticized by Gelman and co-workers (*11*) on the grounds that the bands at 1490–1510 cm^{-1} in the spectra of these complexes should be assigned to the deformational vibration of $:CH_2$ units, and not to a weakened C:C stretching vibration. However, it has been pointed out that olefins which do not contain a $:CH_2$ group, e.g., *cis*- and *trans*-4-methylpent-2-ene, show similar bands in this region on complex formation (*3*, *179*).

Infrared spectral studies have shown that *cis*- and *trans*-olefins are not isomerized by coordination to, or displacement from, platinum salts (*127*). *cis*-4-Methylpent-2-ene forms a more stable complex than do *trans*-4-methylpent-2-ene or *cis*-pent-2-ene; it is suggested (*132*) that the electron-donating nature of the methyl group is responsible for the latter result by strengthening the σ-component of the metal-olefin bond.

When polyolefins react with platinum(II) three types of reaction may occur: (i) platinum or some other decomposition products may be produced as with hexa-2,4-diene or divinyl ether (*124*); (ii) the diene may act as a bridging group joining two platinum atoms to give binuclear complex salts, as do butadiene (*67*, *138*) and hexa-1,5-diene (*124*); or (iii) the olefin may chelate to one platinum atom.

The dienes bicyclo[2,2,1]hepta-2,5-diene (*1*, *7*), cyclo-octa-1,5-diene (*43*), dicyclopentadiene (*43*, *68*), dipentene (*43*), hexa-1,5-diene (*43*, *124*) and diallyl ether (*124*) form complexes of the type [PtX_2(diene)] (X = halogen). These complexes are monomeric and nonconducting, and are formulated as chelate complexes of type (XXXI) in which the diene, represented by the symbol (XXXII) functions as a bidentate ligand and occupies two coordination positions. The dipole moments (6–7 D) of these complexes are consistent with the *cis*-structure shown (*124*). Cyclic dienes, in which the double bonds are more suitably placed for chelation, form complexes which are much more stable than those formed by dienes in which the double bonds are not fixed rigidly (*43*). The stabilities of the dihalides decrease in the order Cl > Br > I, in accord with the increasing *trans*-effect of the halogens Cl < Br < I.



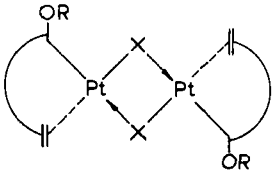
(XXXI)

(XXXII)

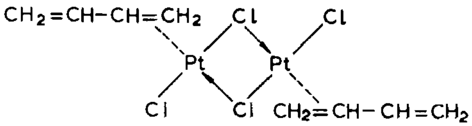
Cyclo-octatetraene forms similar complexes (*125*) in which only two of its four double bonds (probably the 1,5-bonds) are involved in bonding, as shown by the uptake of two molecules of hydrogen by the complex [$PtI_2(C_8H_8)$] (*152*). Cycloheptatriene gives the complex [$PtCl_2(C_7H_8)$] in which two of the three double bonds are involved in bonding to the metal (*7*); Fischer and Fritz (*77*) report that platinum(IV) bromide reacts with cycloheptatriene to give the tropylium complex [$Pt_2Br_4(C_7H_7)_2$].

The infrared spectra of these diene complexes show absorption bands in the 1430–1512 cm^{-1} region which are attributed to C:C stretching vibrations lowered by coordination to the metal (*7, 43, 68*).

With anhydrous sodium carbonate in alcohol (ROH) these complexes give stable alkoxy-halides [Pt_2X_2(dieneOR)$_2$] (XXXIII) (*43*) in which one double bond has been opened by Pt(OR)X and the other is coordinated to the metal. *p*-Toluidine splits the halogen bridge to give the monomeric complex [PtCl(*p*-toluidine)(dieneOR)], and the alkoxy group can be removed by concentrated hydrochloric acid with the formation of [$PtCl_2$(diene)]. These complexes are thus analogous to the alkoxy mercuric compounds formed from olefins and mercuric salts (see Section III,T).



(XXXIII)



(XXXIV)

Slade and Jonassen (*192*) treated ethyleneplatinous chloride, [Pt_2Cl_4-(C_2H_4)$_2$], with butadiene, and obtained an unstable complex to which they ascribed the chlorine-bridged structure (XXXIV), on the evidence that its infrared spectrum showed a weak absorption at 1608 cm^{-1} due to the free double bond of each butadiene molecule.

Q. COPPER

Mono-olefins (un) react with solid copper(I) halides to form unstable complexes of the type [CuX(un)] (X = Cl, Br), which dissociate into their constituents above 0° (*67, 138*). Dienes (e.g., butadiene, isoprene, piperylene, bicyclo[2,2,1]hepta-2,5-diene, and cyclopolyolefins) form more stable complexes of the type [Cu_2X_2(diene)] (*1, 53, 67, 138, 192*), in which a copper atom is attached to each C:C bond; industrial processes to separate dienes from mono-olefins and paraffins are based on this difference in stability (*8*). Complexes of the type [Cu(un)]$^+$, [CuCl(un)], and [$CuCl_2$(un)]$^-$ have been shown to exist in dilute acid solution (*15, 67, 138*).

R. SILVER

Silver-olefin complexes have been extensively investigated, and have been reviewed in some detail (*67, 138, 176, 183*). Distribution studies have shown the existence in solution of complexes of the types [Ag(olefin)]$^+$,

$[Ag(diene)]^+$, and $[Ag_2(diene)]^{++}$; equilibrium constants and thermodynamic functions have been evaluated for the reactions (*21, 67, 138, 207, 208*):

$$\text{olefin}(CCl_4) + Ag^+(H_2O) \rightleftharpoons [Ag(\text{olefin})]^+(H_2O) \tag{12}$$

$$\text{diene}(CCl_4) + Ag^+(H_2O) \rightleftharpoons [Ag(\text{diene})]^+(H_2O) \tag{13}$$

$$[Ag(\text{diene})]^+(H_2O) + Ag^+(H_2O) \rightleftharpoons [Ag_2(\text{diene})]^{++}(H_2O). \tag{14}$$

Evidence for the existence of a $\sigma\pi$-bond in these complexes (*64*) comes from the lowering of some 65 cm^{-1} in the C:C stretching frequency (Raman) of the olefin on complex formation (*202*); a similar lowering has been found in the infrared spectra of complexes of natural rubber and silver salts (*184*). As with platinum, *cis*-olefins form more stable silver complexes than do *trans*-olefins, and geometrically isomeric olefins are not isomerized by coordination to, or displacement from, silver salts. In contrast, however, each substitution of a hydrogen atom of the olefin by a methyl group lowers the stability of the complex (*67, 138, 220*). It is suggested that in these complexes the electron-donating alkyl group lessens the stability of the complex by weakening the π-component of the $\sigma\pi$-bond (*176*).

The ability of cyclic olefins to form silver complexes decreases in the order cyclopentene > cycloheptene > cyclohexene and bicyclo[2,2,1]hept-2-ene > bicyclo[2,2,2]oct-2-ene, which is also the estimated order of relative strain in the olefins. It is suggested that ring strain facilitates complex formation by deforming the π-orbital and thus increasing the availability of electrons (*207, 208*). The effect of the relative spatial distribution of the π-orbital and the *d*-orbitals of the metal has also been discussed (*208*). Similarly it is postulated that the linear relationship between the heat of hydrogenation of olefins and the logarithms of their argentation constants is due to the relief of steric strain in the olefin, by hydrogenation in the first case and complex formation in the second (*94*).

Anhydrous silver-olefin complexes are readily dissociable, low-melting, and variable in composition (*92a, 176, 183*). Cyclic olefins and polyolefins form stable complexes with silver nitrate or perchlorate, but again the Stoichiometry of the complexes varies considerably, sometimes depending on the conditions of preparation. The following types have been isolated: $[Ag(un)_2]X$ (un = e.g., cyclohexene, α- and β-pinene) (*130*), $[Ag(diene)]X$ diene = e.g., dicyclopentadiene (*220*), cyclo-octa-1,5-diene (*50, 130*), bicyclo[2,2,1]hepta-2,5-diene (*207*), and cyclo-octa-1,3,5-triene (*52*), and $[Ag_2(diene)]X_2$ (diene = e.g., cyclo-octa-1,3- and -1,4-diene (*130*), bicyclo[2,2,1]hepta-2,5-diene (*1*) and tricyclo[4,2,2,0]-decatriene (*10*)). Cyclo-octatetraene (cot) forms three adducts with silver nitrate (*52*), viz., $[Ag(cot)]NO_3$, $[Ag(cot)_2]NO_3$, and $[Ag_3(cot)_2](NO_3)_3$. On heating, the first two lose cyclo-octatetraene and all three decompose at the same temperature. From the stoichiometry of the above complexes it appears that the silver atom may be bonded to either one or two C:C bonds of the ligand; the latter structure has been verified by X-ray studies in the case of the complexes [Ag(un)]NO_3 {un = cyclo-octatetraene (*157*, *158*) or its dimer (*171*)}.

S. GOLD

There is evidence for the formation of an unstable gold(III)-styrene complex during the reduction of gold(III) bromide by styrene (*18*).

T. MERCURY

Mercury(II) forms either coordination complexes or organometallic complexes with olefins, depending on the reaction conditions (*19*, *34*). In solutions of suitable pH and purity of reagents the following equilibria are established:

$$C_2H_4 + [Hg(H_2O)_2]^{++} \rightleftharpoons [Hg(H_2O)(C_2H_4)]^{++} + H_2O \rightleftharpoons$$
$$[Hg(OH)(C_2H_4)]^{+} + H_3O^{+} \rightleftharpoons [Hg(CH_2CH_2{\cdot}OH)]^{+} + H_3O^{+}. \qquad (15)$$

The coordination complexes $[Hg(H_2O)(C_2H_4)]^{++}$ and $[Hg(OH)(C_2H_4)]^{+}$ are formulated as π-complexes, analogous to the Cu(I), Ag(I), and Pt(II) complexes. The products isolated from these reactions are, however, the organometallic complexes of type $[HgX(CH_2CH_2Y)]$ (where X = anionic ligand such as Cl or acetate and Y = anionic ligand such as OH, OR or acetate), in which the mercury(II) salt has added across the double bond of the olefin, and from which the olefin is regenerated by treatment with hydrochloric acid.

IV. Acetylene Complexes

A. GENERAL REMARKS

The ease with which olefins form complexes with metals naturally led to investigation of acetylenes as ligands but until recent years only a few ill-defined, unstable acetylene complexes of copper and silver were known. Now complexes of acetylenes with metals of the chromium, manganese, iron, cobalt, nickel, and copper subgroups are known. These complexes fall naturally into two classes—those in which the structure of the acetylene is essentially retained and those in which the acetylene is changed into another ligand during complex formation. Complexes of the first class are discussed here and the second class is discussed in Section VI.

The first class of complexes are often analogous to olefin complexes (see Section III). Thus the acetylene is intact in the complex, it can be recovered unchanged in many cases, and it is π-bonded to the metal through its C⁝C bond, as shown by X-ray structural determinations and changes in its C⋮C stretching frequency on complex formation. Examples of analogous acetylene and olefin complexes are [Pt_2Cl_4(di-*tert*-butylacetylene)$_2$] and [Pt_2Cl_4(ethylene)$_2$]. Acetylenes, however, have two sets of π-orbitals and can also act as a bridging group between two metal atoms, e.g., in the complex [$Co_2(CO)_6$(acetylene)].

As was mentioned in Section III,A a very useful method of synthesis of olefin complexes involves the displacement of carbon monoxide from metal carbonyls by olefins. Under similar conditions acetylenes usually react to give new ligands, e.g., cyclobutadienes, cyclopentadienones, and quinones (see Sections V,E and VI,C), and it is not surprising, therefore, that the range of known acetylene complexes is smaller than the range of olefin complexes.

Acetylene complexes, like olefin complexes, are admirably suitable for study by physical techniques (see Section III,A).

B. CHROMIUM

Acetylenes do not react with chromium hexacarbonyl on exposure to sunlight (*155*) but react readily with trialkyl- and triarylchromium tritetrahydrofuranates, e.g., [$CrPh_3{\cdot}3THF$], to give substituted benzenes, styrenes, stilbenes, and polynuclear hydrocarbons in amounts which depend on the reaction stoichiometry (*113, 159, 209, 223*). It is suggested that these products are formed from intermediate π-complexes of the type $CrR_3(THF)_n(ac)_m$] (R = alkyl, aryl; ac = acetylene; $n + m = 3$). The group R can also be incorporated in the product, as shown by the formation of 1,2,3,4-tetramethylnaphthalene from dimethylacetylene and triphenylchromium. This provides a new synthesis of aromatic ring systems by choosing the appropriate organochromium derivative and acetylene.

C. MOLYBDENUM

Molybdenum hexacarbonyl and dimethylacetylene give no complex on exposure to sunlight (*155*).

D. TUNGSTEN

Tungsten hexacarbonyl is reported to form a number of stable complexes with acetylenes (*116, 118*), but no details have been published.

E. MANGANESE

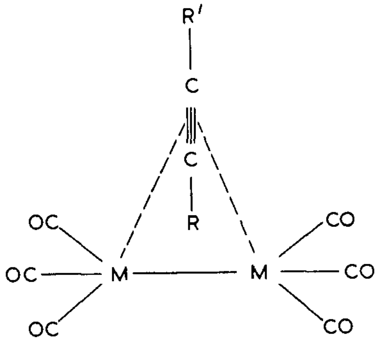
It is stated (*116, 118*) that manganese carbonyl gives a series of very stable complexes on treatment with acetylenes, but no details have been published.

F. RHENIUM

Very stable, monomeric, and diamagnetic complexes of the types [ReCl(ac)$_2$] and [ReCl(ac)$_2$(PPh$_3$)] have been obtained by the reaction of acetylenes (ac), e.g., Ph·C⋮C·Me or Me$_2$C(OH)·C⋮C·H, with rhenium(III) chloride and triphenylphosphinerhenium(III) chloride, respectively (*49*). The bonding is analogous to that in the corresponding platinum complexes (see Section IV,J), as shown by the similar lowering in the C⋮C and O—H stretching frequencies of the acetylenes on complex formation.

G. IRON

One of the complexes formed in the reaction of diphenylacetylene and iron dodecacarbonyl is a red, crystalline compound of the composition [Fe$_2$(CO)$_6$(PhC$_2$Ph)], which, on reduction with sodium in liquid ammonia, gives dibenzyl (*117*). By analogy with the cobalt carbonyl complex, structure (XXXV; M = Fe) is proposed, in which the π-electrons of the triple bond interact with the *d*-orbitals of both iron atoms. In this structure the iron atoms would not obey the E.A.N. rule unless some sort of iron-iron double bond is present. The structure of the complex [Fe$_3$(CO)$_{10}$(PhC$_2$Me)] is not known, but a similar bonding of the acetylene to the metal is envisaged (*118*).



(XXXV)

H. COBALT

The two bridging carbonyl groups in dicobalt octacarbonyl are readily replaced by acetylenes (ac) to give deeply colored, stable complexes of the type [Co$_2$(CO)$_6$(ac)] (*102, 197*):

$$Co_2(CO)_8 + ac \rightarrow [Co_2(CO)_6(ac)] + 2CO. \qquad (16)$$

This reaction is general and proceeds smoothly and quantitatively in light petroleum at room temperature; each triple bond of a diyne reacts independently. The complexes are diamagnetic, and show bands in their infrared spectra characteristic of terminal carbonyl groups, but no bands due to bridging carbonyl groups or a $\mathrm{C{\vdots}C}$ stretching vibration.

X-ray studies (*193*) on the complex derived from diphenylacetylene show that it has the structure (XXXV; M = Co), in which the C—C bond of the acetylene is normal to the Co—Co bond. Although at a preliminary stage of refinement, the results also show that the configuration of the acetylene has changed considerably on complex formation, e.g., the $\mathrm{C{\vdots}C}$ bond has increased in length to 1.46Å, and the Ph—C—C angle is no longer 180°, but 137°.

There is kinetic evidence for a reactive form of dicobalt octacarbonyl, $[\mathrm{Co_2(CO)_8}]^*$, and an acetylenic dicobalt heptacarbonyl intermediate in these reactions, and the following mechanism has been proposed (*205*, *206*):

$$[\mathrm{Co_2(CO)_8}] \rightleftharpoons [\mathrm{Co_2(CO)_8}]^* \tag{17}$$

$$[\mathrm{Co_2(CO)_8}]^* + \mathrm{ac} \rightarrow [\mathrm{Co_2(CO)_7(ac)}] + \mathrm{CO} \tag{18}$$

$$[\mathrm{Co_2(CO)_7(ac)}] \rightarrow [\mathrm{Co_2(CO)_6(ac)}] + \mathrm{CO}. \tag{19}$$

A perfluorobut-2-yne complex $[\mathrm{Co_2(CO)_6(CF_3{\cdot}C{\vdots}C{\cdot}CF_3)}]$ has also been prepared (*17*).

A tetrameric cobalt tricarbonyl substituted with diphenylacetylene has been obtained, but no details have been published (*118*).

I. Nickel

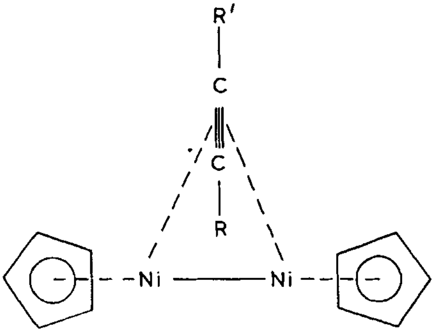
When di-π-cyclopentadienyldicarbonyldinickel is treated with an acetylene, $\mathrm{R{\cdot}C{\vdots}C{\cdot}R'}$, both carbonyl groups are smoothly replaced by one molecule of the acetylene (*17*, *203*, *204*):

$$[\mathrm{Ni_2(C_5H_5)_2(CO)_2}] + \mathrm{R{\cdot}C{\vdots}C{\cdot}R'} \rightarrow [\mathrm{Ni_2(C_5H_5)_2(R{\cdot}C{\vdots}C{\cdot}R')}] + 2\mathrm{CO}. \tag{20}$$

Dicyclopentadienyldinickeldiphenylbutadiyne-dicobalt hexacarbonyl has been prepared from diphenyldiacetylene in which one triple bond acts as a bridging group between two nickel atoms and the other between two cobalt atoms (*203*). Reduction of the diphenylacetylene complex (R = R′ = Ph) with sodium and alcohol in liquid ammonia yields dibenzyl, showing that the diphenylacetylene grouping is bonded only to the nickel atoms. The corresponding complex of acetylene (R = R′ = H) has also been prepared from nickelocene and acetylene (*69*):

$$[\mathrm{Ni(C_5H_5)_2}] + \mathrm{HC{\vdots}CH} \rightarrow [\mathrm{Ni_2(C_5H_5)_2(HC{\vdots}CH)}]. \tag{21}$$

This complex is diamagnetic, indicating that the nickel atoms have attained the electronic configuration of krypton, and the infrared spectrum shows absorption bands characteristic of a π-bonded cyclopentadienyl-metal grouping. A structure (XXXVI), analogous to that of the cobalt carbonyl complexes, is proposed, in which the acetylene is bonded via its four π-electrons to a binuclear π-cyclopentadienylnickel system.



(XXXVI)

The formation of 1,2,3,4-tetraphenyldihydrobenzene from diethylnickel and diphenylacetylene probably proceeds through an intermediate π-complex, e.g., $[NiEt_2(Ph{\cdot}C{\vdots}C{\cdot}Ph)_2]$ (*209*) (cf. the reactions of acetylenes with triethylchromium in Section IV,B).

J. Platinum

The acetylenic diol $Me_2C(OH){\cdot}C{\vdots}C{\cdot}C(OH)Me_2$ (ac) forms complexes of the types $K[PtCl_3ac]$ and *cis*- and *trans*-$[PtCl_2(ac)(am)]$ (am = amine), by reactions commonly used in the preparation of olefin complexes (*23*, *25*, *26*, *96*, *164*), i.e.,

$$K_2PtCl_4 + ac \rightarrow K[PtCl_3ac] + KCl \tag{22}$$

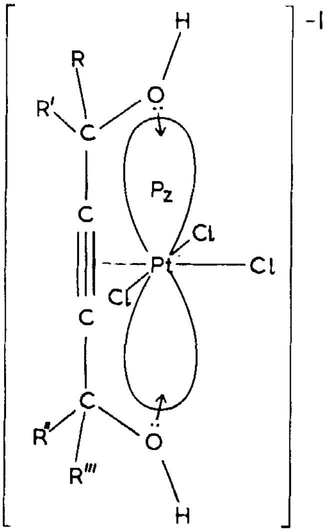
$$K[PtCl_3(C_2H_4)] + ac \rightarrow K[PtCl_3ac] + C_2H_4 \tag{23}$$

$$K[PtCl_3ac] + am \rightarrow \textit{trans}\text{-}[PtCl_2(ac)(am)] + KCl \tag{24}$$

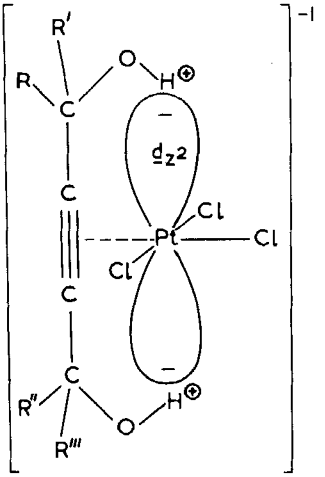
$$K[PtCl_3(NH_3)] + ac \rightarrow \textit{cis}\text{-}[PtCl_2(ac)(NH_3)] + KCl. \tag{25}$$

Olefins, e.g., ethylene or styrene, do not displace the hydroxyacetylene from these complexes. The stability of the complexes depends on the group R of the acetylene $RMeC(OH){\cdot}C{\vdots}C{\cdot}C(OH)Me_2$; it decreases in the order R = methyl > phenyl > hydrogen. Methylation of the hydroxyl groups also lowers the stability of the complexes (*36*).

The proposed structures for these complexes are shown in (XXXVII) and (XXXVIII). The acetylene is bonded to the metal atom through its triple bond, as shown by the lowering of some 200 cm^{-1} in the $C{\vdots}C$ stretching frequency on complex formation. In addition, the hydroxyl groups interact with the $6p_z$- or $5d_{z^2}$-orbitals of the metal atom, as shown by the



(XXXVII)



(XXXVIII)

lowering of 110–140 cm^{-1} in the O—H stretching frequency on complex formation (*36*).

Alkynes of the type $Bu^{t}\cdot C\vdots C\cdot R$ (R = Me, Et, Pr^{i}, Bu^{t}, CMe_2Ph) (ac′) give complexes of the types $K[PtCl_3ac']$, $[Pt_2Cl_4ac'_2]$, and *trans*-$[PtCl_2(ac')(am)]$ (*37*, *38*).

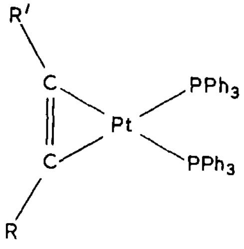
$$2Na_2PtCl_4 + 2ac' \rightarrow [Pt_2Cl_4ac'_2] + 4NaCl \qquad (26)$$

$$[Pt_2Cl_4(C_2H_4)_2] + 2ac' \rightarrow [Pt_2Cl_4ac'_2] + 2C_2H_4 \qquad (27)$$

$$[Pt_2Cl_4ac'_2] + 2am \rightarrow 2\ trans\text{-}[PtCl_2(ac')(am)] \qquad (28)$$

Normal, secondary, or conjugated alkynes (e.g., $Bu^{n}\cdot C\vdots C\cdot Bu^{n}$, $Pr^{i}C\vdots C\cdot Et$, $Ph\cdot C\vdots C\cdot Ph$, $Bu^{t}C\vdots C\cdot C\vdots C\cdot Bu^{t}$) do not form stable complexes under these conditions. Prolonged interaction of $[Et_3NH]_2[PtCl_4]$ and diphenylacetylene at 50–60°, however, gives the complex $[Et_3NH][PtCl_3(Ph\cdot C\vdots C\cdot Ph)]$; it is possible that the large organic cation helps to stabilize the complex (*27*). Complexes of the type $[Pt_2Cl_4ac_2]$, in which ac = $Ph\cdot C\vdots C\cdot C\vdots C\cdot Ph$, $Ph\cdot C\vdots C\cdot CH_2\cdot C\vdots C\cdot Ph$, or $Me_2C(OH)\cdot C\vdots C\cdot C\vdots C\cdot C(OH)Me_2$, have been reported but no method of preparation is recorded (*24*).

Reduction of an alcoholic suspension of *cis*-$[PtCl_2(PPh_3)_2]$ with hydrazine hydrate in the presence of an acetylene (ac) gives stable complexes of the type $[Pt(PPh_3)_2(ac)]$ (*41*). The infrared spectra of the complexes indicate that the $C\vdots C$ bond of the acetylene has been reduced almost to a C∶C bond, and preliminary X-ray studies (*173*) support the planar structure (XXXIX) in which the bonding is similar to that in the corresponding olefin complexes (see Section III,P). Acetylenes will displace one another from these complexes. The following is the approximate order of affinities of acetylenes for platinum in complexes of this type: $C_2H_2 < AlkC\vdots CH < C_2Alk_2 \sim Ph{\cdot}C\vdots CH \sim C_2Ph_2 < C_2(p\text{-}C_6H_4{\cdot}NO_2)_2$.

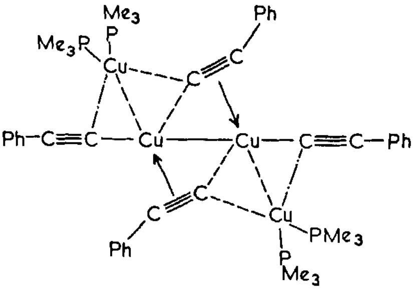


(XXXIX)

K. Copper

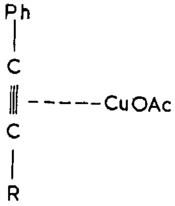
Acetylene reacts with copper(I) chloride in dilute acid solution to give colorless, crystalline compounds of the types $[(CuCl)_3(C_2H_2)]$ and $[(CuCl)_2(C_2H_2)]$ (*210, 211*). The complexes $[Cu(C_2H_2)]^+$, $[CuCl(C_2H_2)]$, and $[CuCl_2(C_2H_2)]^-$ have also been shown to exist in solution (*212*). X-ray studies on the but-2-yne complex of copper(I) chloride, $[CuCl(C_4H_6)]$, have shown that the copper atom is on the perpendicular bisector of the $C\vdots C$ bond of the alkyne (*31*), as required by Dewar's theory (*64*).

It has been suggested that the copper acetylides are coordination polymers, with intermolecular interaction between the $C\vdots C$ bonds of the acetylides and copper atoms as shown in (XL) (*13*). The chains may be broken with tertiary phosphines (PR'_3) to give complexes of the type $[CuC\vdots CR(PR'_3)]_4$. The X-ray structure of the complex $[CuC\vdots CPh(PMe_3)]_4$ has some very interesting and unexpected features (*46a*); see structure (XL).



(XL)

Thus only two of the copper atoms are bonded to the trimethylphosphines and each phenylethynyl group appears to be associated with three copper atoms. The four copper atoms of the tetramer lie approximately in the same plane. When the acetylide Cu·C⋮C·Ph is heated with acetic acid the complex $Cu_2C_{10}H_8O_2$ is obtained (*201*). This is probably an acetylenic complex (XLI; R = Cu), since an analogous complex (XLI; R = Ph) is obtained by reaction of diphenylacetylene with cuprous oxide in acetic acid (*16*). The bands at 1985 and 1971 cm^{-1} in the infrared spectrum of the diphenylacetylene complex are attributed to the C⋮C stretching frequency, which is lowered by coordination to the copper atom.



(XLI)

L. SILVER

Distribution (*66*) and solubility (*112*) studies have shown that substituted hexynes (ac) form complexes of the type $[Ag(ac)]^+$, and, to a lesser extent, $[Ag_2(ac)]^{++}$ with silver(I) in aqueous solution:

$$\mathrm{ac} + \mathrm{Ag}^+ \rightleftharpoons [\mathrm{Ag(ac)}]^+ \qquad (29)$$

$$\mathrm{Ag}^+ + [\mathrm{Ag(ac)}]^+ \rightleftharpoons [\mathrm{Ag_2(ac)}]^{++}. \qquad (30)$$

The alkynes are bonded in essentially the same way as, but less firmly than, the olefins (see Section III,R). In the hex-3-yne series, substitution of an α-hydrogen atom by a methyl group reduces the argentation constant (a measure of the silver-alkyne bond strength) by a factor of roughly 1/3; this influence of methyl substitution on complex formation is opposite to that observed in the platinum(II) complexes (see Section IV,J).

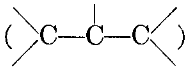
In the absence of solvent, disubstituted alkynes react with silver nitrate and silver perchlorate to form colorless complexes of variable stoichiometry which readily lose the alkyne on exposure to air (*51*).

It has been suggested that silver acetylides have a structure similar to that (XL) proposed for copper acetylides (*13*).

V. π-Allylic Complexes

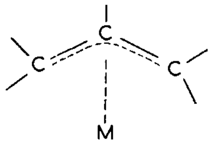
A. General Remarks

The discovery of π-allylic complexes is an exciting recent development in coordination chemistry. In these complexes the bonding of the allylic radical



to the metal atom is believed to be similar to that of an olefin to a metal atom in an olefin complex; in other words, the allylic radical donates its π-electrons to the metal atom in a σ-type bond and accepts electrons from the metal into its antibonding π* molecular orbitals in a π-type bond. It is convenient to refer to these complexes as π-allylic complexes to distinguish them from compounds such as allylmagnesium bromide in which the allyl radical is bonded to the magnesium atom by what is essentially a σ-bond.

The nuclear (proton) magnetic resonance spectra of allylic complexes strongly favor a structure in which all three carbon atoms of the allylic radical are symmetrically bonded to the transition metal M as shown in (XLII). The value of nmr spectroscopy in confirming the presence of a π-allylic system cannot be overemphasized, and most of the papers published in this field contain nmr data. To illustrate the value of nmr spectroscopy in this field, one example of its use is discussed, and the data reproduced in some detail (see Section V,C), but generally we do not quote nmr data.

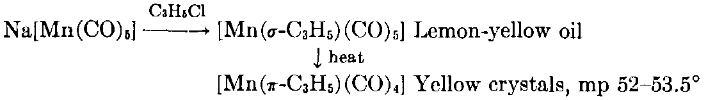


(XLII)

π-Allylic complexes of manganese, cobalt, nickel, palladium, and platinum have so far been described.

B. Manganese

Treatment of $Na[Mn(CO)_5]$ with allyl chloride gives the complex $[Mn(\sigma\text{-}C_3H_5)(CO)_5]$ in which the allyl group is σ-bonded to the manganese atom (*136*). This complex, on being heated at 80° for 12 hours loses one mol. of carbon monoxide, and the π-allyl complex $[\mathrm{Mn}(\pi\text{-}\mathrm{C_3H_5})(\mathrm{CO})_4]$ is formed in 89% yield.

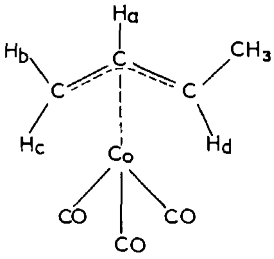


$$\begin{array}{lll} \mathrm{Na[Mn(CO)_5]} \xrightarrow{\mathrm{C_3H_5Cl}} & [\mathrm{Mn}(\sigma\text{-}\mathrm{C_3H_5})(\mathrm{CO})_5] & \text{Lemon-yellow oil} \\ & \big\downarrow \text{heat} & \\ & [\mathrm{Mn}(\pi\text{-}\mathrm{C_3H_5})(\mathrm{CO})_4] & \text{Yellow crystals, mp } 52\text{–}53.5^\circ \end{array} \qquad (31)$$

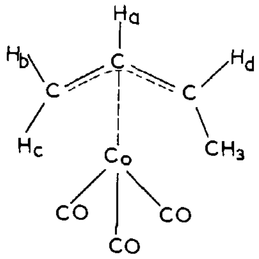
$\mathrm{Na[Mn(CO)_5]}$ on treatment with perfluorallyl chloride gives a compound $[\mathrm{Mn(C_3F_5)(CO)_5}]$ which was shown by its nmr spectrum to be the σ-bonded perfluoropropenyl complex, $[\mathrm{Mn(CF{:}CF{\cdot}CF_3)(CO)_5}]$ (*135*).

C. COBALT

Cobalt carbonyl hydride, $[\mathrm{Co(CO)_4H}]$, when treated with butadiene gives a mixture of two isomeric compounds $[\mathrm{Co(C_4H_7)(CO)_3}]$ (*6, 128, 165*). The same mixture of isomers is formed when $\mathrm{Na[Co(CO)_4]}$ is treated with "crotyl bromide," i.e., a 1-bromobut-2-ene/3-bromobut-1-ene mixture (*109*). These two compounds, $[\mathrm{Co(C_4H_7)(CO)_3}]$, have been shown by their nmr spectra to be the two geometrical isomers (XLIII) and (XLIV) of π-crotyltricarbonylcobalt (*165*).



(XLIII)



(XLIV)

Isomer 1 is more stable than Isomer 2 and can be produced from it by thermal isomerization. The structures (XLIII) and (XLIV) were assigned to the two isomers on the basis of their nmr spectra. It is to be expected by analogy with other organometallic compounds, e.g., $[(\pi\text{-}\mathrm{C_5H_5})(\mathrm{C_5H_6})\mathrm{Co}]$ (*99*), that the methyl protons in structure (XLIV), being nearer to the cobalt atom than in structure (XLIII), would show the greater chemical shift, while for the proton $\mathrm{H_d}$, the greater chemical shift would be expected for the structure (XLIII). The chemical shift of the methyl protons is greater in Isomer 2 than in Isomer 1, while the chemical shift of the proton $\mathrm{H_d}$ is less: hence Isomer 1 has structure (XLIII) and Isomer 2 structure

(XLIV). The chemical shift and spin-coupling data for these two isomers is given in Table II. Of special interest is the almost zero value of the coupling constant for the *gem*-protons, viz., J_{bc}. This phenomenon is general for π-allylic complexes, and has usually been explained in terms of the theory of Gutowsky *et al.* (*104*), in which the coupling between *gem*-protons passes through zero with an H—C—H bond angle of 125°, i.e., when the hybridization is close to sp^2. It is not unreasonable to assume that in π-allylic complexes the H—C—H bond angle for *gem*-protons is in the region of 125°.

TABLE II

CHEMICAL SHIFT AND SPIN-COUPLING DATA FOR THE TWO ISOMERS OF π-CROTYLTRICARBONYLCOBALT

Proton	Chemical Shifts (ppm, relative to benzene) Isomer 1	 Isomer 2
H_a	1.89	1.65
H_b	3.73	3.35
H_c	4.65	3.80
H_d	3.49	2.38
CH_3	5.03	5.45
	Coupling Values (cps)	
J_{ab}	6.3	7.1
J_{ac}	10.5	12.3
J_{ad}	10.5	6.8
J_{bc}	<0.2	0.6
J_{bd}	<0.2	1.6
J_{d-CH}	6.5	7.0

The compound π-allyltricarbonylcobalt has also been made by treating allyl bromide with $Na[Co(CO)_4]$ (*109*, *111*). If this reaction is carried out in an atmosphere of carbon monoxide then about one-half mol. of carbon monoxide is absorbed, and the infrared absorption spectrum of the product shows a band at about 1720 cm^{-1}. This band is believed to be due to the presence of but-2-enoyltetracarbonylcobalt. On standing, carbon monoxide is evolved and the π-allyl complex $[Co(\pi\text{-}C_3H_5)(CO)_3]$ is formed. These reactions may be summarized as follows:

$$C_3H_5Br + Na[Co(CO)_4] + CO \rightarrow [Co(CO{\cdot}CH_2{\cdot}CH{:}CH_2)(CO)_4] \qquad (32)$$
$$\downarrow -2CO$$
$$[Co(\pi\text{-}C_3H_5)(CO)_3] \text{ Yellow liquid mp } -33 \text{ to } -32°.$$

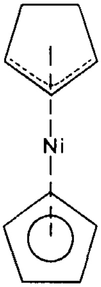
Derivatives of these and other similar complexes, in which one carbon monoxide ligand is replaced by triphenylphosphine, are often remarkably stable and are more readily characterized (*110*, *123*). Thus, $[Co(\pi\text{-}C_3H_5)$-

$(CO)_3]$ reacts with triphenylphosphine to give $[Co(\pi\text{-}C_3H_5)(CO)_2(PPh_3)]$, mp 132° (decomp.). Also, the reaction between $Na[Co(CO)_4]$, allyl bromide, carbon monoxide and triphenylphosphine gives $[Co(3\text{-butenoyl})(CO)_3(PPh_3)]$; the same product is formed from $Na[Co(CO)_4]$, but-3-enoyl chloride and triphenylphosphine.

D. Nickel

Allyl bromide reacts with nickel carbonyl in benzene to give the volatile π-allyl complex $[NiBr(\pi\text{-}C_3H_5)]_2$ as a violet-red solid (*75*).

The deep-red, crystalline compound $C_{10}H_{14}Ni$, prepared by treating nickel carbonyl with cyclopentadiene, was first thought to have the structure dicyclopentadienenickel(0) $[Ni(C_5H_6)_2]$ (*87*). This compound has now been shown by nmr spectroscopy to have the structure π-cyclopentadienyl-π-cyclopentenylnickel(II) (XLV), $[Ni(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_7)]$ (*70, 89, 129*). This structure was also suggested by analogy with similar palladium and platinum complexes (*191*). $[Ni(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_7)]$ is also formed by reducing dicyclopentadienylnickel with sodium amalgam in ethyl alcohol, or by treating nickel bromide with cyclopentadienylsodium followed by cyclopentenylmagnesium chloride (*70*).



(XLV)

E. Palladium

Palladium forms the largest series of π-allylic complexes of any metal, and many of these complexes are readily prepared. The majority are chloro-bridged complexes of the type $[PdCl(all)]_2$, where "all" = an allylic radical.

The first member of the chloro-bridged series di-μ-chlorodi-π-allyldipalladium, $[PdCl(\pi\text{-}C_3H_5)]_2$ is conveniently prepared by treating allyl alcohol (*162, 163, 194*) or allyl chloride (*121, 122, 123*) with palladium chloride or sodium chloropalladite. A solvent such as 50% acetic acid may be used. Thus, on warming a suspension of palladium chloride in allyl alcohol to 50°, a vigorous evolution of propylene occurs, metallic palladium is deposited, and yellow crystals of $[PdCl(\pi\text{-}C_3H_5)]_2$ separate on cooling. A cyclic alcohol $C_6H_{10}O_2$, of unknown structure, is also formed. The stoichiometry of the reaction has not been elucidated.

$[PdCl(\pi\text{-}C_3H_5)]_2$ is reported to exist in two forms (*163*), i.e., the yellow or α-form described above, and a dark green or β-form prepared by reacting palladium chloride with an acidified aqueous solution of allyl alcohol below 10°; at 15° the product is the yellow α-form (*163*). Isomerization of this type has not been reported for other π-allylicpalladium complexes.

Treatment of crotyl alcohol (*162*, *194*) or methallyl alcohol (or methallyl chloride) (*121*, *122*, *123*) with palladium chloride gives the corresponding π-crotyl- and π-methallyl-palladium complexes $[PdCl(\pi\text{-}C_4H_7)]_2$. Two geometrical isomers of the π-crotyl complex are possible, but careful chromatography of the crude complex has yielded only one isomer, and this in very good yield (~90%) (*61*). It will be remembered that two geometrical isomers of the π-crotylcobalt complex $[Co(\pi\text{-}C_4H_7)(CO)_3]$ have been prepared (see Section V,C).

Several olefins, on heating to 50–100° with solutions of palladium chloride in 50% acetic acid, give π-allylicpalladium complexes as yellow, crystalline solids (*123*). The compositions of these, with the starting olefin shown in parentheses, are $[PdCl(C_4H_7)]_2$ (isobutene); $[PdCl(C_8H_{13})]_2$ (di-isobutene); $[PdCl(C_{12}H_{23})]_2$ (tri-isobutene); $[PdCl(C_6H_9)]_2$ (cyclohexene); $[PdCl(C_7H_{11})]_2$ (1-methylcyclohex-1-ene); and $[PdCl(C_9H_9)]_2$ (α-methylstyrene). These olefins react at room temperature with palladium chloride in 50% acetic acid to give the olefin complexes $[PdCl_2(\text{olefin})]_2$ (see Section III,O), which at the higher temperature lose the elements of hydrogen chloride to give the more stable allylic complex. General equations summarizing these reactions are

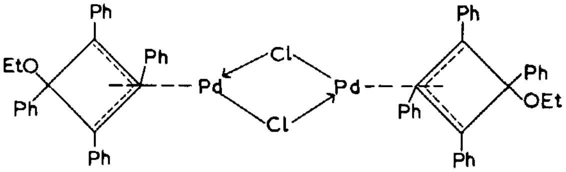
$$2PdCl_2 + 2C_xH_y \xrightarrow{20^\circ} \underset{\substack{\text{Olefin complex}\\ \text{Red-brown or brown}}}{[PdCl_2(C_xH_y)]_2} \xrightarrow{50\text{–}100^\circ} \underset{\substack{\text{Allylic complex}\\ \text{Yellow}}}{[PdCl(C_xH_{y-1})]_2}, \tag{33}$$

where C_xH_y = olefin and C_xH_{y-1} = allylic radical. The relationship between the isobutene complex $[PdCl_2(C_4H_8)]_2$ and the methallyl complex $[PdCl(\pi\text{-}C_4H_7)]_2$ is particularly instructive. Heating the isobutene complex with water gives the π-methallyl complex, which on treatment with dry hydrogen chloride in ether is converted quantitatively into the isobutene complex:

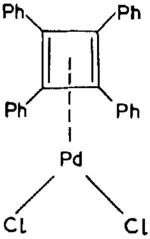
$$[PdCl_2(C_4H_8)]_2 \underset{\text{dry HCl}}{\overset{H_2O}{\rightleftharpoons}} [PdCl(\pi\text{-}C_4H_7)]_2. \tag{34}$$

In the above-mentioned preparation of the π-cyclohexenyl complex, $[PdCl(\pi\text{-}C_6H_9)]_2$, benzene and cyclohexane are formed. This π-cyclohexenyl complex is also formed from cyclohexa-1,3-diene, either by treating it with sodium chloropalladite (*191*) or with palladium chlorocarbonyl, $[PdCl_2(CO)]_2$ (*81, 88*).

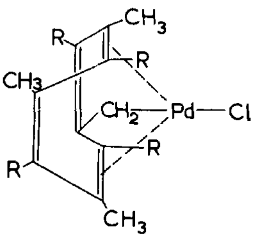
Diphenylacetylene and methylphenylacetylene react with palladium halides to give a very interesting series of compounds some of which are almost certainly π-allylicpalladium complexes. Thus diphenylacetylene ($C_{14}H_{10}$) reacts with palladium(II) chloride in ethanol to give hexaphenylbenzene and a complex of the composition $[PdCl(C_{14}H_{10})_2(OC_2H_5)]$ (*148, 149*) which we formulate as the π-allylic complex (XLVI) (see Section III,O). This complex on treatment with hydrochloric acid, is converted to a complex $[PdCl_2(C_{14}H_{10})_2]$, formulated as the tetraphenylcyclobutadiene derivative (XLVII). Under the same conditions, methylphenylacetylene gives an oxygen-free complex for which we propose the π-allylic structure (XLVIII): a second compound formed in this reaction was formulated as the structure (XLIX) but again π-allylic structures can be written for a compound with this composition. The π-allylic structures (XLVI) and (XLVIII) seem more probable than the structures originally proposed (*148, 149*), but these complexes are very insoluble and difficult to study and there must be some doubt as to their true constitution.



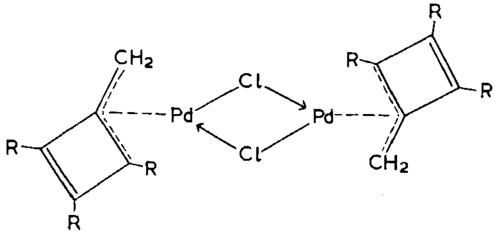
(XLVI)



(XLVII)



(XLIX)



(XLVIII)

On prolonged boiling with water $[PdCl(\pi\text{-}C_3H_5)]_2$ decomposes according to the equation

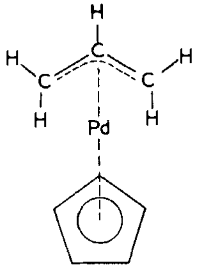
$$[PdCl(C_3H_5)]_2 + H_2O \rightarrow CH_2{=}CH{\cdot}CHO + CH_3{\cdot}CH{=}CH_2 + 2Pd + 2HCl. \quad (35)$$

Similar treatment of the π-methallyl complex $[PdCl(\pi\text{-}C_4H_7)]_2$ gives methacrolein, isobutene and some isobutyraldehyde as the organic products (*123*).

The π-allylpalladium complex $[PdCl(\pi\text{-}C_3H_5)]_2$ on heating decomposes quantitatively into allyl chloride and palladium. The analogous π-methallylpalladium complex gives a 96% yield of methallyl chloride but a little isobutene is also formed (*123*).

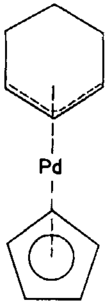
The bridging chlorine atoms in these π-allylicpalladium complexes are readily replaced by bromine, iodine, or the thiocyanate group by treatment with the corresponding alkali metal salt in a suitable solvent such as acetone (*105*, *194*). The chlorine bridge is split by amines: for example, the π-allyl complex $[PdCl(\pi\text{-}C_3H_5)]_2$, with *p*-toluidine, gives $[PdCl(\pi\text{-}C_3H_5)(p\text{-toluidine})]$ as stable, pale yellow crystals (*105*).

Treatment of the chloro-bridged complex $[PdCl(\pi\text{-}C_3H_5)]_2$ with cyclopentadienylsodium gives π-allyl-π-cyclopentadienylpalladium(II) $[Pd(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)]$ as dark red, voltatile crystals, mp 64° (*190*). Its nmr spectrum (*191*) confirms the 'sandwich' structure (L) in which the palladium has the electronic configuration of xenon.



(L)

Similarly, treatment of the π-cyclohexenylpalladium complex [PdCl(π-C_6H_9)]$_2$ with cyclopentadienylsodium gives the red, crystalline complex π-cyclohexenyl-π-cyclopentadienylpalladium(II) (LI), the structure of



(LI)

which has been confirmed by its nmr spectrum (*89*, *129*, *191*). This compound was previously thought to have the constitution cyclohexa-1,3-diene(cyclopentadiene)palladium(0) (*88*).

F. PLATINUM

In contrast to palladium chloride, platinous chloride does not give a π-allylic complex on heating with allyl alcohol: instead, the diallyl ether complex [$PtCl_2(C_3H_5OC_3H_5)$] is formed in good yield (*105*).

Treatment of propyleneplatinous chloride with a mixture of allylmagnesium bromide (1 mol.) and cyclopentadienylsodium (1 mol.) gives π-allyl-π-cyclopentadienylplatinum(II), [Pt(π-C_3H_5)(π-C_5H_5)] as volatile, lemon-yellow crystals. The nmr spectrum of this complex confirms the assigned structure. This spectrum also shows that coupling takes place between the magnetic nucleus of the platinum (Pt^{195} isotope, 33% natural abundance) and the hydrogen nuclei in the organic ligands (*191*).

VI. Miscellaneous Complexes, and Complexes in Which an Olefinic Ligand Has Been Produced during Complex Formation

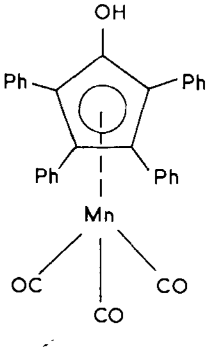
A. GENERAL REMARKS

The complexes described in this Section overlap considerably with those described in Section III and many of the remarks in Sections III,A and IV,A apply equally well to the complexes described here.

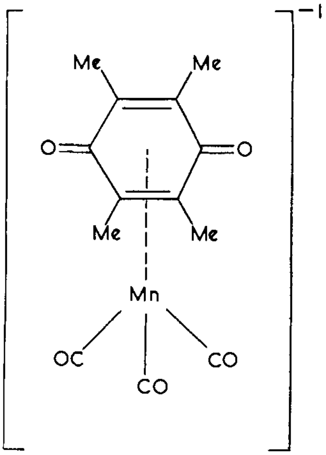
Attention should be drawn to the remarkable structures of many of the compounds formed from acetylenes during complex formation. Acetylenes by self condensation can give complexes of the elusive cyclobutadiene and, by condensation with carbon monoxide, complexes of cyclopentadienones, quinones, and tropones. The structures of many of these complexes have been verified by direct synthesis (see Section III) and by X-ray crystallography.

B. MANGANESE

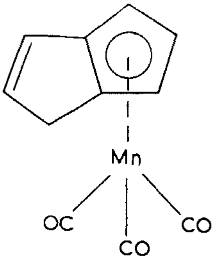
Manganese carbonyl, $Mn_2(CO)_{10}$, when treated with tetracyclone at 140–150°, gives an air-sensitive product which on hydrolysis gives the π-cyclopentadienyl complex (LII) (*215*). Manganese carbonyl does not react with dimethylacetylene in sunlight, but duroquinone was formed in a similar reaction of the alkyne with $[Mn(CO)_5]^{-1}$ (*155*). Mn(−1) is isoelectronic with Fe(0), and it is suggested that the unstable quinone complex (LIII) is an intermediate in the reaction. With acetylene under pressure manganese carbonyl gives π-dihydropentalenylmanganese tricarbonyl (LIV) and with cyclo-octatetraene it gives the dihydro-derivative of (LIV) (*47, 48*).



(LII)



(LIII)



(LIV)

C. IRON

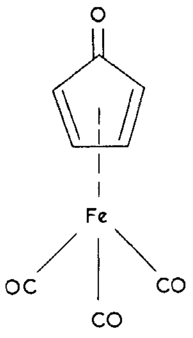
The reaction of acetylenes with the iron carbonyls gives a wide variety of stable complexes, the composition of which depends on the alkyne, the carbonyl, the reaction temperature, and the solvent used in the preparation (Table III) (*116, 117, 118, 120, 182, 187*). Iron dodecacarbonyl yields as many as seven different kinds of complexes, depending on the acetylene studied. The complexes are generally yellow, red, or black, soluble in organic solvents, and are invariably diamagnetic; they show infrared absorption bands characteristic of terminal carbonyl groups, and a few show bands corresponding to bridging carbonyl groups.

A great deal of physical and chemical evidence has been collected to show that these compounds are complexes built from an organic ligand and one or more iron carbonyl residues, e.g., $\{Fe(CO)_3\}$. The organic ligand is usually a conjugated ring system of the cyclopentadienone, quinone, or tropone class, which has been formed from several molecules of the acetylene and carbon monoxide, and is bonded to the iron atom through its π-electrons as shown in the structures (LV) (*118*, *145*, *185*, *215*), (LVI) (*100*, *216*), (LVII) (*120*), and (LVIII) (*198*). The cyclopentadienone ring

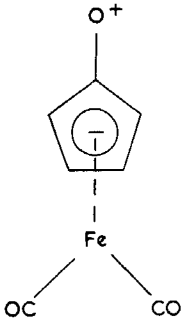
TABLE III

Types of Complexes Made from Iron Carbonyls and Acetylenic Compounds (ac) (*118*)

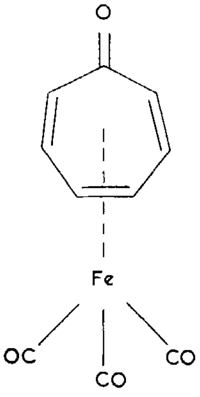
	1 Alkyne	2 Alkynes	3 Alkynes	4 Alkynes	5 Alkynes
1Fe		$[Fe(CO)_3(ac)_2]$	$[Fe(CO)_2(ac)_3]$	$[Fe(CO)_3(ac)_4]$	$[Fe(CO)_4(ac)_5]$
		$[Fe(CO)_4(ac)_2]$	$[Fe(CO)_4(ac)_3]$	—	—
2Fe	$[Fe_2(CO)_6(ac)]$	$[Fe_2(CO)_6(ac)_2]$	$[Fe_2(CO)_6(ac)_3]$	—	—
		$[Fe_2(CO)_7(ac)_2]$	—	—	—
3Fe	$[Fe_3(CO)_{10}(ac)]$	$[Fe_3(CO)_8(ac)_2]$	—	—	—



(LV)

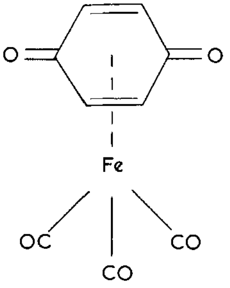


(LVI)

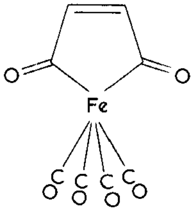


(LVII)

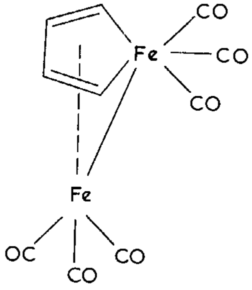
can behave either as a four- or six-electron donor system (*100*), as shown in structures (LV) and (LVI) respectively. Complex formation alters the polarity of the keto-group in the cyclopentadienone complex (LV), enabling it to form salts with halogen acids, and the complex $[\{Fe(CO)_3(cyclopentadienone)\}_2(quinol)]$ with quinol (*216*). Other systems have a conjugated ring σ-bonded to the iron atom as in (LIX) (*32*, *120*), and sometimes the ring is simultaneously π-bonded to another iron atom as shown in (LX)



(LVIII)

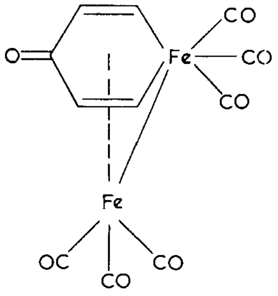


(LIX)

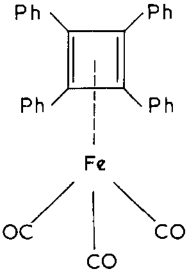


(LX)

(*100*, *114*, *117*, *187*) and (LXI) (*117*, *187*). The complex $[Fe(CO)_3(PhC_2Ph)_2]$ has been shown to be the tetraphenylcyclobutadiene derivative (LXII)



(LXI)



(LXII)

(*65*). Complexes containing three molecules of an acetylene give high yields of substituted benzenes on decomposition (*117*, *119*). Possible structures of the more complicated complexes and intermediates have been discussed (*117*, *172*, *200*).

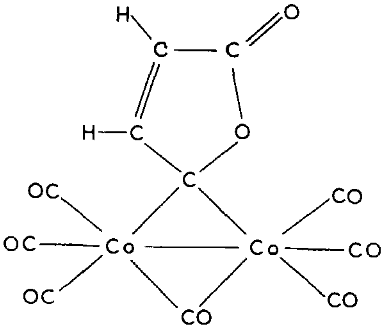
D. Cobalt

When dicobalt octacarbonyl is treated with acetylenes (ac) and carbon monoxide under pressure, stable crystalline complexes of the type $[Co_2(CO)_9(ac)]$ are formed. They can also be prepared from $[Co_2(CO)_6(ac)]$ and carbon monoxide (*199*):

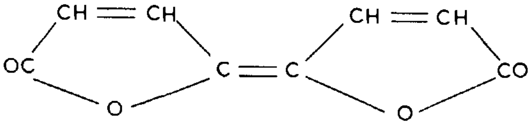
$$Co_2(CO)_8 + ac + CO \rightarrow [Co_2(CO)_9(ac)] \tag{36}$$

$$[Co_2(CO)_6(ac)] + 3CO \rightarrow [Co_2(CO)_9(ac)]. \tag{37}$$

Only seven of the nine carbonyl groups can be liberated as carbon monoxide, indicating that two carbonyl groups have combined with the acetylene to form a new ligand. X-ray studies on the complex derived from acetylene show that the complex contains an unsaturated lactone ring as shown in (LXIII) (*160*). An important structural feature of (LXIII) is that the cobalt atoms and the bridging carbon atoms are not coplanar, but that the molecule is folded about the axis of the bridging carbon atoms. The formation of the dilactone (LXIV) and its *trans*-isomer in the reaction of acetylene and carbon monoxide in the presence of dicobalt octacarbonyl (*4*) is readily explained in terms of a complex of this structure.



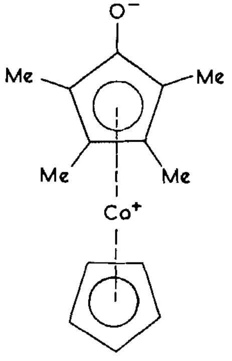
(LXIII)



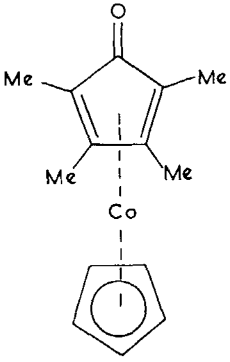
(LXIV)

π-Cyclopentadienyldicarbonylcobalt(I) $[Co(C_5H_5)(CO)_2]$ reacts with dimethylacetylene on exposure to sunlight to form the stable, orange complex $[Co(C_5H_5)(C_9H_{12}O)]$ in which the $C_9H_{12}O$ ligand is a substituted cyclopentadienone formed by condensation of two mols. of the acetylene and one of carbon monoxide (*155*). However, the meso-ionic structure (LXV) is preferred to the structure (LXVI), as the complex is water-soluble, forms a hydrochloride, and has an exceptionally low C=O stretching frequency (1569 cm^{-1}). The X-ray structure of this compound shows several interesting features; thus the carbonyl group is 9° out of the plane of the cyclopentadiene ring away from the cobalt, and the two rings are eclipsed (*58*).

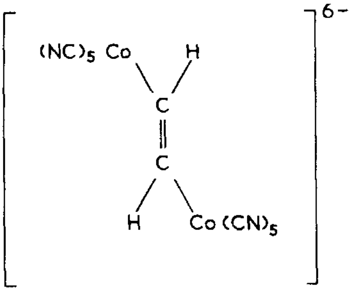
The pentacyanocobalt(II) ion reacts with acetylene to form a yellow crystalline salt $K_6[Co_2(CN)_{10}(C_2H_2)]\cdot 4H_2O$ (*103*). The nuclear magnetic resonance spectrum of the ion shows a single proton resonance line in the olefinic region, and in the infrared spectrum a band at 1615 cm^{-1} is attributed to a C=C stretching vibration. On the basis of these spectra and the observed diamagnetism of the ion, structure (LXVII) is suggested, in which a tervalent cobalt atom in an octahedral configuration is bound to five cyanide groups and to an ethylene group, giving a diamagnetic ion with each cobalt atom having an inert gas configuration.



(LXV)

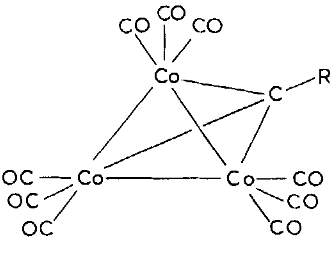


(LXVI)



(LXVII)

Treatment of complexes of the type $[Co_2(CO)_6(RC \vdots CH)]$ with hydrochloric acid in ethanol gives stable complexes of the composition $[Co_3(CO)_9(C_2HR)H]$ (*156*). The acetylene complex (R = H) is neutral, soluble in organic solvents, diamagnetic, and the infrared spectrum shows the absence of bridging carbonyl groups. This acetylenic complex is identical with the product obtained by treating 1,1,1-trichloroethane with dicobalt octacarbonyl (*63*) and the phenylacetylene complex (R = Ph) on bromination gives 2,2,2-tribromoethylbenzene (*144*). The structures originally proposed for these trinuclear complexes (*156*) are incompatible with these results and structure (LXVIII) (*63, 144*) seems a very probable one.



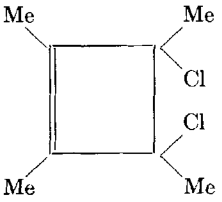
(LXVIII)

The dark red crystalline compound $C_{12}H_5Co_3O_8$ formed by treating dicobalt octacarbonyl with acetylene, carbon monoxide, hydrogen, and isopropyl alcohol (*57*) may have a similar structure, i.e., (LXVIII; R = allyl and one CO ligand replaced by the C=C bond of the allyl group).

E. Nickel

Nickel carbonyl does not react with dimethylacetylene in the presence of sunlight, but an alkaline solution of nickel carbonyl, which contains the ion $[Ni(CO)_3]^{2-}$, yields hexamethylbenzene on similar treatment (*155, 200*). The nature of the intermediate π-complex is not known. Diphenylacetylene reacts with nickel carbonyl to give the dienone complex [Ni-(tetracyclone)$_2$] (*215*) (see Section III,N).

The prediction that cyclobutadiene would be stabilized by complex formation with transition metals (*146*) has been verified by the preparation of dichlorotetramethylcyclobutadienenickel(II) by the following reaction (*56*):

2


$$+ 2Ni(CO)_4 \rightarrow [NiCl_2(C_8H_{12})]_2 + 8CO \qquad (38)$$

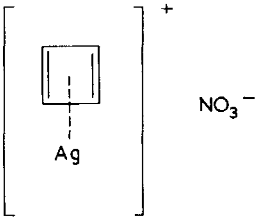
The complex is dimeric and has a chlorine-bridged structure in which each tetramethylcyclobutadiene molecule is bound to a nickel atom by its four π-electrons (*71*). The nuclear magnetic resonance spectrum of the complex indicates that the twelve hydrogen atoms are equivalently bonded. The diene immediately dimerizes on liberation from the complex. It is probable that this type of complex is an intermediate in the polymerization of acetylene to cyclo-octatetraene in the presence of nickel(II) cyanide (*146*).

F. PALLADIUM

The possible formation of a tetraphenylcyclobutadienepalladium complex [$PdCl_2(C_{14}H_{10})_2$] (XLVII), by treating palladium(II) chloride with diphenylacetylene in ethyl alcohol followed by hydrochloric acid (*148*, *149*) has been mentioned in Section V,E.

G. SILVER

A silver-cyclobutadiene complex is obtained when the mercury-containing, bromine-free oil, obtained by treatment of 1,2,3,4-tetrabromocyclobutane with lithium amalgam, is treated with silver nitrate (*9*). The complex forms colorless crystals which, on treatment with steam, evolve a gas with the empirical formula CH; when the gas is bubbled, within a short time of liberation, through aqueous silver nitrate, it regenerates the complex. The suggested structure is shown in (LXIX). Infrared evidence supports this structure (*93*).



(LXIX)

ACKNOWLEDGMENTS

We should like to express our thanks to Drs. J. Chatt, W. Hübel, and H. R. Watson for making valuable comments on this review.

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