OLEFIN COMPLEXES OF THE TRANSITION METALS

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I. Introduction

The investigation of the interaction of olefins with the transition metals has proceeded at a rapid pace over the past decade. During this period a number of reviews, covering various aspects of the field have appeared (*11*, *47*, *47a*, *113*, *219*, *220*, *226*, *384*, *469*, *470*, *590*). This summary, which covers the literature to mid-1968, is intended to supplement that of Guy and Shaw (*268*) which appeared in Volume 4 of this series. It consequently incorporates some of the material covered by more recent reviews.

Primarily because of the quantity of material involved, this survey covers only the transition metal complexes of olefins and is confined almost exclusively to discussion of those which have been isolated and characterized. Only occasional brief mention has been made of the participation of the complexes in catalytic reactions, a very fascinating and important subject in itself which has been summarized by Halpern (*270*, *271*) and others (*4*, *65*, *98*, *314a*, *555*). Furthermore, it ignores almost completely such closely related but recently reviewed topics as allyl (*113*, *256*, *609*), acetylene (*76*), and cyclobutadiene complexes (*388*). The complexes of the azulenes (*67*, and references therein) and of those π-cyclopentadienyl compounds which do not contain other olefinic ligands are also beyond the scope of this review.

It has not been the intention of the authors to make this review a truly critical assessment of the topic. However, where appropriate, an attempt has been made to correlate the complexing tendencies of the various transition metals and to comment on the factors affecting the metal–olefin bonding. In some instances, all the metals of a group in the periodic table has been simultaneously discussed, while, in others, they have been individually reviewed.

II. Group IVB: Titanium

Titanium is the only element of group IVB for which olefin complexes have been reported. When an excess of cyclooctatetraene is heated with $Ti(OC_4H_9)_4$ and $Al(C_2H_5)_3$, deep violet-red crystals of bis(cyclooctatetraene)titanium, $(C_8H_8)_2Ti$, are obtained (*84*). If a significantly lower ratio of olefin-to-titanium is employed, the product is the yellow tris(cyclooctatetraene)dititanium, $(C_8H_8)_3Ti_2$ (*84*). Both compounds are extremely sensitive to air and sparingly soluble in aromatic hydrocarbons. The chemical behavior of the complexes indicates that the olefin molecules are bonded to the titanium at least in part as quasi-aromatic, planar ten π-electron systems, i.e., as dianions.

Although the structure of $(C_8H_8)_2Ti$ is unknown, that of $(C_8H_8)_3Ti_2$ has been found (*174*, *176*) (Fig. 1) to be a double sandwich. The outer rings are indeed planar with a slight inclination toward the axis of the molecule, while the central ring is somewhat boat-shaped. The average Ti–C distance for the outer rings is about 2.35 Å. Each of the titanium atoms appears to interact with four carbon atoms only on the central ring; however, two of these, C-9 and C-9*, seem not to interact with either titanium, while two others, C-12 and C-12*, interact with both. The four carbon atoms interacting with a given titanium atom are in a plane essentially parallel to that of the adjacent outer ring with Ti–C distances ranging from 2.28 to 2.54 Å.

The complexes $(C_8H_8)_2Ti$, $(C_8H_8)_2V$, $(C_8H_8)_3Cr_2$, $(C_8H_8)_3Mo_2$, $(C_8H_8)_3W_2$, $(C_8H_8)Co$, and $(C_8H_8)Ni$ have been prepared also by reaction of the corresponding metal chloride with $(C_8H_8)Na_2$ (*84*).

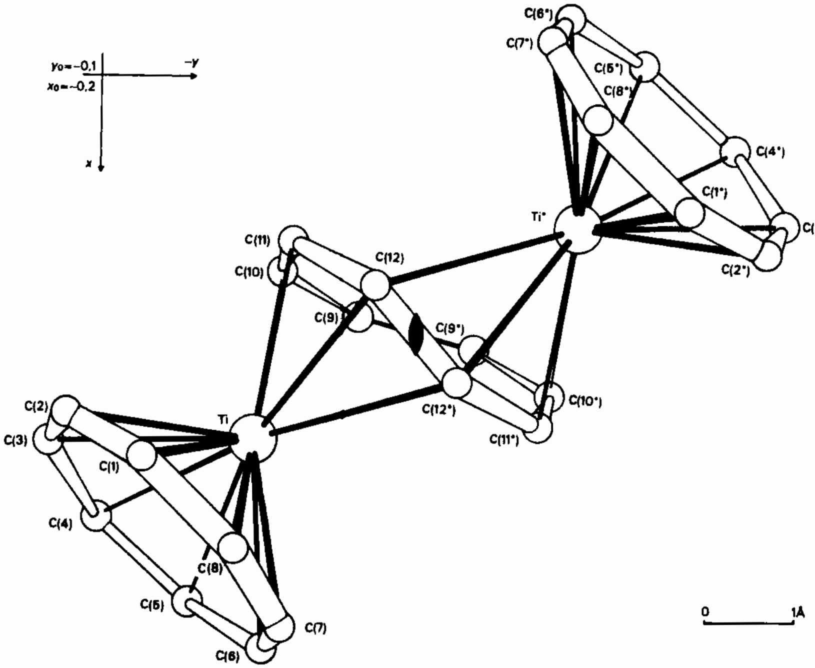
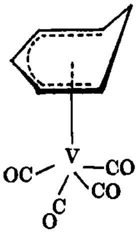


FIG. 1. Molecular structure of $(C_8H_8)_3Ti_2$ (*174*).

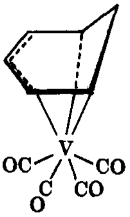
III. Group VB: Vanadium

Of the group VB elements, π complexes have been reported only for vanadium. The complexes (diolefin)$V(CO)_2(C_5H_5)$ obtained by UV irradiation of $V(CO)_4(C_5H_5)$ with butadiene, 2,3-dimethylbutadiene, and 1,3-cyclohexadiene have been reviewed earlier (*219*, *268*).

(Cyclohexadienyl)tetracarbonylvanadium complexes, $[(CH_3)_n\text{-}C_6H_{7-n}]V(CO)_4$ ($n = 0$, 2–6), have been prepared (*94*) by reduction of the corresponding arene complex cations with $NaBH_4$ at room temperature. The monomeric reddish-brown complexes are moderately stable in air and are soluble in organic solvents. On the basis of infrared and NMR spectra, structure (**1**), with bonding similar to that of the somewhat analogous manganese (*220*) and rhenium (*68*, *614*) complexes, has been postulated. There is an indication (*94*), however, that the bonding to the cyclohexadienyl system may involve two σ bonds and a π-allyl bond (*398*) instead (**2**).

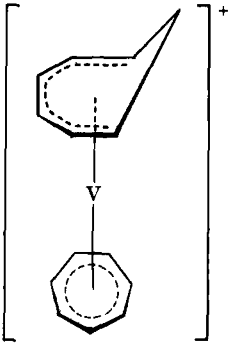


(1)



(2)

The reaction of $V(CO)_6$ with cycloheptatriene at 50°C under nitrogen has produced (*95*) in addition to the tropylium compound, $V(CO)_3(C_7H_7)$, the reddish-brown salt (π-cycloheptatriene)(π-tropylium)vanadium hexacarbonylvanadate, $[(C_7H_8)V(C_7H_7)]^+[V(CO)_6]^-$, insoluble in water and hydrocarbons. Upon reaction with $NaB(C_6H_5)_4$ in acetone, the tetraphenylborate salt is obtained. Both salts display a paramagnetism equivalent to one unpaired electron. The infrared spectrum indicates the presence of both the tropylium and the cycloheptatriene rings and suggests structure (**3**) for the cation.



(3)

IV. Group VIB: Chromium, Molybdenum, and Tungsten

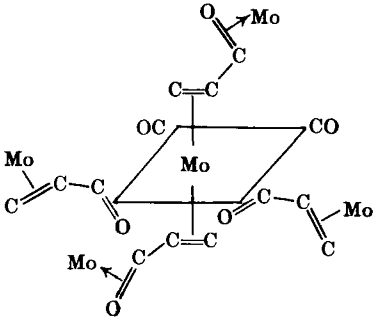
Although many stable cycloolefin complexes of the group VIB metals have been reported (*47*, *268*), it is only recently that π complexes of the simple monoolefins such as ethylene have been isolated (*148*, *195*, *203*, *572*).

The first ethylene complex of chromium(0) was prepared by heating (mesitylene)tricarbonylchromium with C_2H_4 under ultraviolet irradiation (*203*). The stable complex cations $[(C_2H_4)M(CO)_3(C_5H_5)]^+$ (M = Mo or W), have been prepared by the reaction of $BrM(CO)_3(C_5H_5)$ in benzene with gaseous C_2H_4 under pressure (*195*) or by the abstraction of a hydride ion from $(C_2H_5)M(CO)_3(C_5H_5)$ (*148*), the latter reaction being reversible. Stolz *et al.* (*559*) have prepared the ethylene π complexes of molybdenum and tungsten, $(C_2H_4)_nM(CO)_{6-n}$ ($n = 1$ or 2), *in situ* by replacement of the carbonyl groups in $M(CO)_6$ with ethylene under UV irradiation. The infrared spectra of $(C_2H_4)_2M(CO)_4$ indicate that the ethylene molecules are in trans positions (*559*).

With several functionally substituted ethylenes, stable π complexes of molybdenum and tungsten of the general form $L_nM(CO)_{6-2n}$ can be prepared, according to Eq. (1):

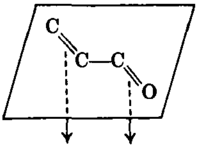
$$(CH_3CN)_3M(CO)_3 + nL \rightarrow L_nM(CO)_{6-2n} \qquad (1)$$

where L is vinyl methyl ketone (*348*, *354*, *355*, *573*) or acrolein (*573*). On the basis of the solubility properties and the infrared and NMR spectral data, Tate *et al.* (*573*) have shown that the complex (acrolein)$_2$Mo(CO)$_2$ is diamagnetic with the polymeric structure (**4**) wherein both the C=C and the C=O double bonds are coordinated at the molybdenum atoms. Of the three most probable configurations (**5a–c**) for the ligand, a near-planar arrangement (**5b**) is favored. The corresponding complexes of acrylonitrile, crotonaldehyde, and vinyl methyl ketone are considered (*573*) to have the same structure.



(**4**)

From the reaction of vinyl methyl ketone with $(CH_3CN)_3M(CO)_3$, (M = Cr or Mo), King (*348*) has isolated the complexes, (vinyl methyl ketone)$_3$M, as yellow volatile solids. Although the molybdenum complex



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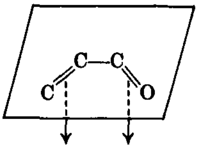
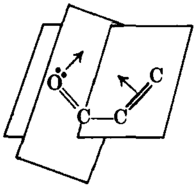
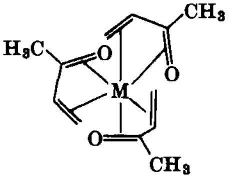


(5b)



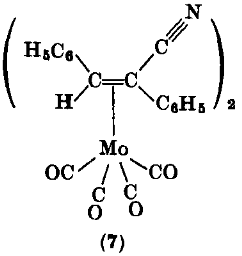
(5c)

was obtained in only 2% yield (*348*), the yield of the tungsten complex is about 60% (*354*, *355*). The complexes are monomeric and are considered to have the structure (**6**) in which the ligands are chelated to the metal through both the C═C and C═O double bonds. Direct substitution of acrylonitrile into the group VIB metal carbonyls has yielded only mono- and disubstituted complexes. With $Mo(CO)_6$ (*47*) one obtains the diamagnetic insoluble complex bis(acrylonitrile)dicarbonylmolybdenum in which the ligand apparently acts as a four π-electron donor through both C═C and C≡N bonds. Its structure is perhaps analogous to that of (**4**) (*573*). In contrast, the reaction of 1,2-diphenylacrylonitrile with $Mo(CO)_6$ (*522*) affords the complex bis(1,2-diphenylacrylonitrile)tetracarbonylmolybdenum, the infrared spectrum of which suggests complexing only at the olefinic double bond (**7**).



M = Mo or W

(6)

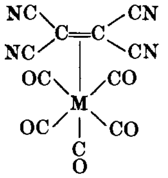


(7)

The failure to obtain complexes containing more than two acrylonitrile ligands by displacement of carbon monoxide from $M(CO)_6$ may be due to the fact that either the complex or the ligands cannot withstand the rigorous reaction conditions. It is possible, however, to prepare the series $(AN)_nM(CO)_{6-n}$ ($n = 1$, 2, or 3; AN = acrylonitrile; M = Cr, Mo, or W) in good yields by displacement of acetonitrile under mild conditions from its corresponding complexes (*508*, *571*).

On the basis of the carbonyl stretching frequencies, Kaesz and coworkers (*508*) have assigned to $(AN)M(CO)_5$ and $(AN)_2M(CO)_4$ an octahedral structure with C_{4v} and C_{2v} (cis configuration) symmetries, respectively. The nitrile stretching frequency in $(AN)W(CO)_5$ is at 2252 cm^{-1} (versus 2239 cm^{-1} for free ligand), while in $(AN)_2M(CO)_4$, (M = Cr, Mo, or W), it appears as a doublet at 2232 and 2249 cm^{-1}, consistent with the cis disubstitution. In both $(AN)W(CO)_5$ and $(AN)_2W(CO)_4$, the carbon–carbon double-bond stretching frequencies are essentially the same as that of free acrylonitrile (1610 cm^{-1}) suggesting coordination of the metal through the nitrogen lone-pair of electrons. However, in the tris-acrylonitrile complexes, which have been assigned a C_{2v} (trans) structure, the C═C stretching frequencies are at about 1440 to 1456 cm^{-1}, while the C≡N stretching frequencies are essentially unchanged from that of the free ligand, clearly indicating coordination through the olefinic double bond. This interpretation of the infrared data is supported by the proton resonance spectra (*508*). With Cr(III) (*335*) and Mo(III) (*550*), acrylonitrile complexes involve coordination only at the nitrile group.

The complex (tetracyanoethylene)$M(CO)_5$ (M = Cr, Mo, or W) is formed (*289*) by irradiation of the olefin with $M(CO)_6$ in benzene. The structure (**8**) is suggested by spectroscopic data.

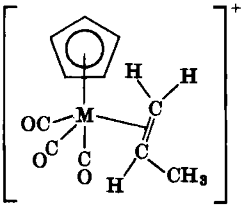


M = Cr, Mo, or W

(8)

The σ-allyl complexes of Mo (*148*) and W (*258*) react readily with hydrogen chloride in petroleum ether to produce with high yield a cation (**9**), which contains a π-complexed propylene molecule (*257*). The chloride (M = Mo) is readily soluble in water, reacting to form $(C_5H_5)Mo(CO)_3Cl$.

Reduction of the cation (M = W) with $NaBH_4$ affords a yellow oil identified as the isopropyl complex $(C_5H_5)W(CO)_3[CH(CH_3)_2]$ with none of the *n*-propyl isomer present. A hydride ion addition corresponding to that with the analogous iron complex (*255*) is postulated.



M = Mo or W

(9)

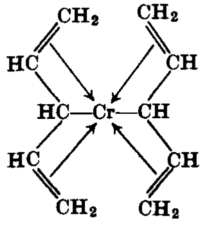
Formation of the relatively unstable complexes (olefin)$M(CO)_5$ and (olefin)$_2M(CO)_4$ (M = Mo or W) with propylene and butadiene has been accomplished (*559*) by UV irradiation of $M(CO)_6$ with olefin in *n*-hexane. From $W(CO)_6$, the complexes (*cis*-2-butene)$W(CO)_5$, (*trans*-2-butene)-$W(CO)_5$, and (*cis*-2-butene)$_2W(CO)_4$ have been produced similarly. As with the corresponding ethylene complexes, the olefin ligands in the bis-olefin complexes are in trans positions. Although, in these complexes, the butadiene molecule is coordinated at only one double bond, upon lengthy irradiation of (butadiene)$_2Mo(CO)_4$ (*559*), the previously reported (*268*) complex (butadiene)$_2Mo(CO)_2$ involving chelated butadiene molecules is produced.

The interaction of $Cr(CO)_6$ with 1,4-diphenylbutadiene produces only arene-type π complexes (*92*, *393*).

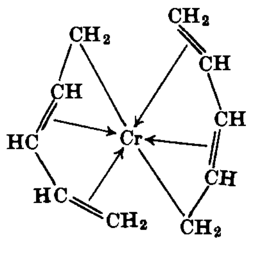
The stability of butatriene systems, which tend to form diradical species, can be improved by extensive conjugation with acyl groups, by introduction of bulky substituents, or by a charge-transfer process. Accordingly, the UV spectra of the stable yellow (tetraphenylallene)tricarbonylchromium and the red (tetraphenylbutatriene)tricarbonylchromium (*435*), produced by refluxing $Cr(CO)_6$ with the olefin in ether, have bands which can be ascribed to the charge transfer from the chromium tricarbonyl group to the olefinic system.

Only two examples of transition metal π complexes containing the pentadienyl group have been reported (*242*, *387*). The reaction of chromium(II) chloride with pentadienylsodium in tetrahydrofuran at −30°C yields green crystalline bis(pentadienyl)chromium(II), $(C_5H_7)_2Cr$, which demonstrates a paramagnetism corresponding to two unpaired electrons (*242*). The chemical, physical, and infrared spectral data suggest that the complex may have the structures (**10a**) or (**10b**), although a

π-allyl type of bonding should not be ruled out. The complex reacts slowly with CO, but not with Ph_3P, at room temperature and atmospheric pressure to yield $Cr(CO)_6$ and a green diamagnetic complex $(C_5H_7)_2Cr(CO)_2$.

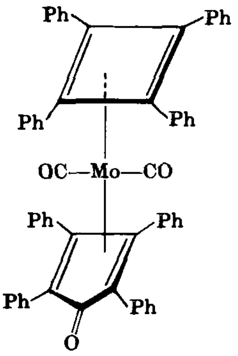


(10a)



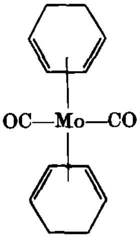
(10b)

Diphenylacetylene with $Mo(CO)_6$ (*298*) in a sealed tube at 160°–170°C produces, in addition to two cyclobutadiene complexes, a yellow compound with the empirical formula $[C_9(C_6H_5)_8O]Mo(CO)_2$, the infrared spectrum and chemical properties of which suit the tetraphenylcyclopentadienone complex of structure (**11**). On the other hand, the interaction of 3-hexyne with $(CH_3CN)_3Mo(CO)_3$ yields only the alkyne complex (*570*).



(11)

With $Mo(CO)_6$, 1,3-cyclohexadiene produces at ~100°C a low yield of yellow diamagnetic crystals, originally reported (*220*) as the first metal π complex having two diene ligands (**12**). Its proton NMR spectrum corresponds, however, to $(C_6H_9)(C_6H_7)Mo(CO)_2$ (**13**) (*229*). The true



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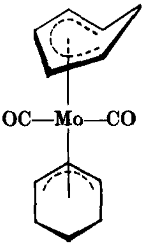
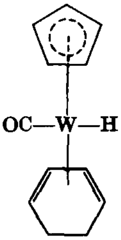


(13)

(1,3-cyclohexadiene)$_2$Mo(CO)$_2$ was obtained (*229*) by UV irradiation of (mesitylene)Mo(CO)$_3$ with the diene. The chromium analog $(C_6H_8)_2Cr(CO)_2$ can be obtained under the same conditions (*220*). Attempted preparation of this complex by direct substitution of $Cr(CO)_6$ led only to a small yield of (benzene)Cr(CO)$_3$, indicating the tendency of 1,3-cyclohexadiene to aromatize (*220*).

Similarly, because of the strength of the W–CO bonds, $W(CO)_6$ is unsuitable for the direct preparation of olefinic π complexes (*357*). However, substituted tungsten carbonyls with ligands involving little or no back-bonding can be employed. Accordingly, $(C_6H_8)_2W(CO)_2$ has been prepared in 50% yield by refluxing of (acetonitrile)$_3$W(CO)$_3$ with an excess of the diene in hexane (*357*). Heating this complex in boiling 2,2,5-trimethylhexane does not yield the tungsten analog of structure (**13**).

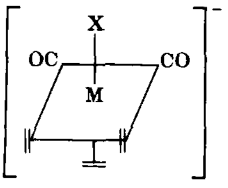
The interesting 1,3-cyclohexadiene metal hydride complex, $(C_6H_8)W(CO)H(C_5H_5)$, has been obtained by reduction of the benzene complex cation $[(C_6H_6)W(CO)(C_5H_5)]^+$ with $NaBH_4$ in aqueous methanol (*201*). On the basis of its infrared and NMR spectra structure (**14**) has been assigned. An infrared absorption band at 1851 cm^{-1} and a



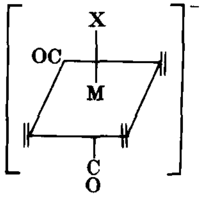
(14)

proton signal at a τ value of 18 ppm indicate the presence of the metal–hydrogen bond.

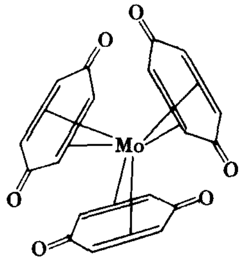
Halopentacarbonyl anions of group VIB metals react with olefins in a manner dependent seemingly upon the π-acceptor properties of the ligand. Thus, maleic acid and maleimide react with $[M(CO)_5X]^-$ ($M =$ Mo or W) to produce the complex $[(olefin)_3M(CO)_2X]^-$ which possibly has the isomeric structures (**15a**) and (**15b**) (*423*). The stronger π acceptors such as the quinones displace all the CO ligands, yielding the molybdenum and tungsten complexes $[(quinone)_3MX]^-$ for which, because of their insolubility, the bonding and structure have not been established (*96*). An uncharged *p*-benzoquinone complex $(C_6H_4O_2)_3Mo$ has also been prepared by reaction of $Mo(CO)_6$ with the quinone in toluene under reflux (*96*). The substantially diamagnetic, blue-black powder is insoluble in the common organic solvents. Although the infrared spectrum suggests the structure (**16**) in which all the quinone molecules are chelated to the metal atom, it is possible that, in view of its insolubility, the complex has a polymeric structure (**17**) in which some of the quinone molecules bridge between the molybdenum atoms.



(15a)



(15b)



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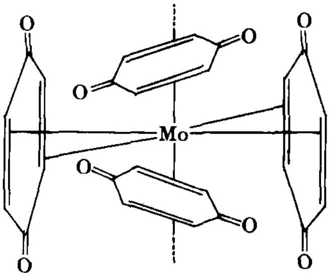
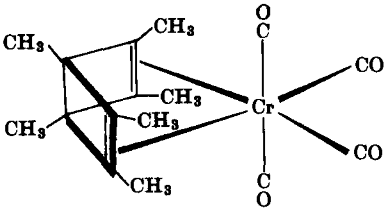


(17)

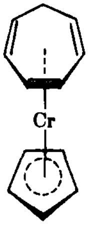
The first π complex of the Dewar benzene system was prepared by Fischer *et al.* (*202*) by reaction of $(CH_3CN)_3Cr(CO)_3$ with hexamethylbicyclo[2.2.0]hexa-2,5-diene. The monomeric, yellow, crystalline complex $(C_{12}H_{18})Cr(CO)_4$ has an NMR spectrum with two sharp absorptions at τ values of 8.26 and 9.1 ppm with relative intensities of 2:1. Structure (**18**), originally assigned on the basis of spectral data, has been confirmed



(**18**)

by X-ray analysis (*308*). The two double bonds occupy cis positions in a slightly distorted octahedral geometry with bonded C–Cr distances of 2.33 Å.

The reaction of 1,3,5-cycloheptatriene with $C_5H_5CrCl_2$ in the presence of iso-C_3H_7MgBr under UV irradiation, followed by treatment with methanol, yields the brown, paramagnetic ($\mu_{eff} = 1.63$ B.M.), air-sensitive complex, (1,3,5-cycloheptatriene)(cyclopentadienyl)chromium (**19**) (*207*). The complex is readily dehydrogenated with platinum to $C_7H_7Cr(C_5H_5)$ or oxidized with oxygen in acetone–water to yield the



(**19**)

cation $[(C_7H_7)Cr(C_5H_5)]^+$. When the reaction is effected with $CrCl_3$ and C_5H_5MgBr, the reddish-brown, paramagnetic ($\mu_{eff} = 1.67$ B.M.*) product $(C_{14}H_{17})Cr$ is considered (*211*) to be (1,3-cycloheptadiene)(π-tropylium) Cr(–I) (**20**).

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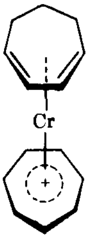
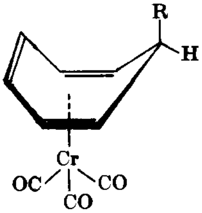
* B.M., Bohr magneton.

With various anions (R^-) such as hydride, methoxide, *t*-butylcyclopentadienide, etc., the (π-tropylium)tricarbonylchromium cation,



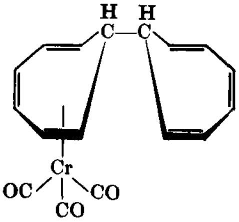
(20)

as well as the analogous molybdenum cation, is converted into the corresponding 1-substituted cycloheptatriene complex (**21**) (*420*, *421*). The chromium complexes have been identified by X-ray (*36*) and NMR



(21)

(*465*) studies as the exo isomers. The 1-phenylcycloheptatriene complex has a structure (*36*) closely resembling that of (cycloheptatriene)tricarbonylmanganese (*47*). When the chromium cation is reacted with ethanolic cyanide or other basic ions, the main products are the dicycloheptatrienyl complexes $(C_{14}H_{14})Cr(CO)_3$ (**22**) and $(C_{14}H_{14})[Cr(CO)_3]_2$ (**23**), presumably formed by reductive dimerization of the cation (*422*).



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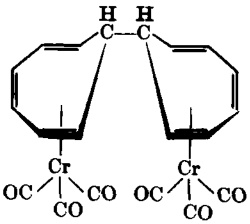
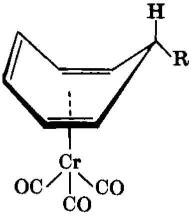


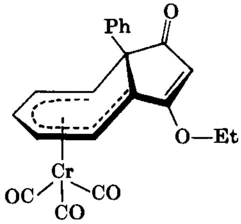
(23)

Pauson *et al.* (*466*) have also prepared the *endo*-1-substituted (cycloheptatriene)tricarbonylchromium (**24**) by reaction of $Cr(CO)_6$ or $Cr(CO)_3(Py)_3$ with the olefins in the presence of BF_3.



(24)

The reaction of diphenylketene with ethoxyacetylene gives a cycloheptatriene derivative which reacts in turn with $Cr(CO)_6$ to afford dark red needles of composition $(C_{18}H_{16}O_2)Cr(CO)_3$ (*44*, *45*). The proposed structure (**25**) has been confirmed by X-ray analysis (*87*) which shows the sp^3 carbon atom of the triene ring and the chromium atom on opposite



(25)

sides of an essentially planar six-carbon conjugated system. The average distance between the chromium atom and the sp^2 carbon atoms in the triene ring is 2.23 Å.

The migration of hydrogen in (cycloheptatriene)$Mo(CO)_3$ has been studied (*509*) by use of the labeled compound (1-d_1-cycloheptatriene)$Mo(CO)_3$ prepared by treatment of $(THF)_3Mo(CO)_3$ with the triene in hexane at room temperature. Between 80° and 120°C, the rate of migration, determined by NMR and mass spectra, is more than one thousand times greater than in the free olefin. The activation parameters are $\Delta H^{\ddagger} = 31.4$ kcal/mole and $\Delta S^{\ddagger} = 7.7$ cal/degree-mole.

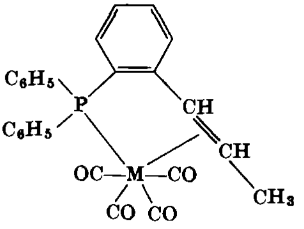
In the dark, the exchange reaction between cycloheptatriene-^{14}C, $C_7H_8{}^*$, and $(C_7H_8)Cr(CO)_3$ (*561*) appears to proceed both by S_N1 and S_N2 mechanisms (*566*). For the overall reaction [Eq. (2)] the rate expression

$$(C_7H_8)Cr(CO)_3 + C_7H_8{}^* \rightleftarrows (C_7H_8{}^*)Cr(CO)_3 + C_7H_8 \qquad (2)$$

is $K_1[(C_7H_8)Cr(CO)_3] + K_2[(C_7H_8)Cr(CO)_3][C_7H_8^*]$, where K_1 and K_2 are the rate constants for the S_N1 and S_N2 reactions, respectively. Whereas under UV irradiation, the chromium complex undergoes about 88% exchange, that observed with the molybdenum analog is only 10% (*565*).

The phosphines $PF_2(C_6H_5)$ (*515*), $PF(CH_3)[N(CH_3)_2]$, $PF(C_6H_5)[N(CH_3)_2]$, and $PF[N(CH_3)_2]_2$ replace the triene in $(C_7H_8(Mo(CO)_3$ (*516*). Similarly, cycloheptatriene in $(C_7H_8)M(CO)_3$ (M = Cr, Mo or W) undergoes ligand exchange with trimethylphosphite producing *cis*-$\{M(CO)_3[(CH_3O)_3P]_3\}$ exclusively. The kinetics of the latter reaction are first-order in each reactant and the activation parameters can be interpreted in terms of an S_N2 mechanism (*471*).

Norbornadiene (NBD) in $(NBD)M(CO)_4$ (*353*) is readily displaced by CO (*274*) or (2-allylphenyl)(diphenyl)phosphine (*50*, *312*). Although the latter reaction gives the compound of expected composition, $(C_{21}H_{19}P)M(CO)_4$, both the chemical and spectral data indicate that it has the structure (**26**) in which the $C_{21}H_{19}P$ ligand is the isomeric (2-propenyl)(diphenyl)phosphine. For the molybdenum complex this structure has been confirmed by X-ray diffraction (*379*).

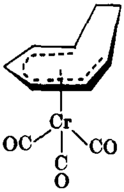


M = Cr, Mo, or W

(26)

The isomerization or rearrangement of diolefins upon complex formation is of particular interest. Leigh and Fischer (*375*) have confirmed earlier reports (*197*) that 1,5-cyclooctadiene interacts with $Cr(CO)_6$ in di-*n*-butyl ether to yield the *o*-xylene complex $[o\text{-}C_6H_4(CH_3)_2]Cr(CO)_3$, whereas in lower boiling solvents only $(1,5\text{-cyclooctadiene})Cr(CO)_4$ is obtained. Evidence indicates that the conversion to *o*-xylene occurs during complex formation rather than via decomposition of the diene complex. The analogous reactions with molybdenum and tungsten hexacarbonyls in di-*n*-butyl ether yield only the diene complex. With 1,3-cyclooctadiene, $Mo(CO)_6$ produces the 1,5-diene complex $(1,5\text{-}C_8H_{12})Mo(CO)_4$, while $W(CO)_6$ produces the complex of either the 1,5- or the 1,3-diene dependent on the solvent employed (*375*). There is a similar isomerization of the 1,3-diene in its interaction with $RhCl_3$ to yield $[(1,5\text{-}C_8H_{12})RhCl]_2$ (*499*). It has been suggested that the isomerization occurs via formation of a metal–hydrogen bond (*375*).

The suggestion by Fischer *et al.* (*210*) that (1,3,5-cyclooctatriene)tricarbonylchromium is a ferrocene-type metal–arene complex (**27**), has been confirmed by X-ray diffraction (*16*). The molecular structure resembles that of (cycloheptatriene)$Mo(CO)_3$ (*47*) in that the sp^3 carbon atoms and the metal atom are on opposite sides of the plane containing the sp^2 carbons. However, the nature of the bonding in the chromium may be different from that in the molybdenum complex. In (cycloheptatriene)$Mo(CO)_3$ the sp^2 carbon interatomic distances are approximately those expected for alternating double and single bonds in a triene system indicating coordination of the metal atom to three isolated double bonds (**28**). In contrast, in the chromium complex, these interatomic distances are nearly equal suggesting that the metal is bonded to a highly conjugated π sextet. The sp^2 carbon–chromium distances range from 2.12 to 2.28 Å.



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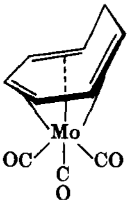
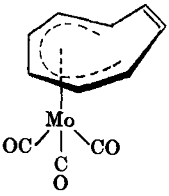


(28)

The π complexes of cyclooctatetraene, a nonaromatic but formally conjugated ring system, with many of the transition metals have been described (*220*). The first such complex of the group VIB metals was reported by Winstein *et al.* (*620*) who prepared $(C_8H_8)Mo(CO)_3$ (**29**), in good yield by reaction of the olefin with (diglyme)$Mo(CO)_3$ in hexane



(29)

at 50°C. The corresponding complexes of chromium and tungsten were later prepared by reaction of the olefin with $(NH_3)_3Cr(CO)_3$ (*366*) and $(CH_3CN)_3M(CO)_3$ [M = Cr (*348*) or W (*355*)].

The complexes $(C_8H_8)M(CO)_3$ represent a class in which the olefin has more π electrons than required by the metal atom. Consequently, (*i*) part or all of the excess π electrons may become involved in carbon–carbon σ-bond formation resulting in bicyclic ligands; (*ii*) the metal atom may coordinate with three olefinic double bonds leaving the other geometrically isolated; or (*iii*) the metal may be simultaneously linked to all the sp^2 carbon atoms with a fraction of each π electron involved in the bonding.

In the solid state the second case applies for $(C_8H_8)Mo(CO)_3$, the structural analysis (*405*) of which shows that six of the eight carbon atoms are associated with the metal, although not at equal distance (Fig. 2). Among these six carbon atoms, the C–C bond lengths are quite

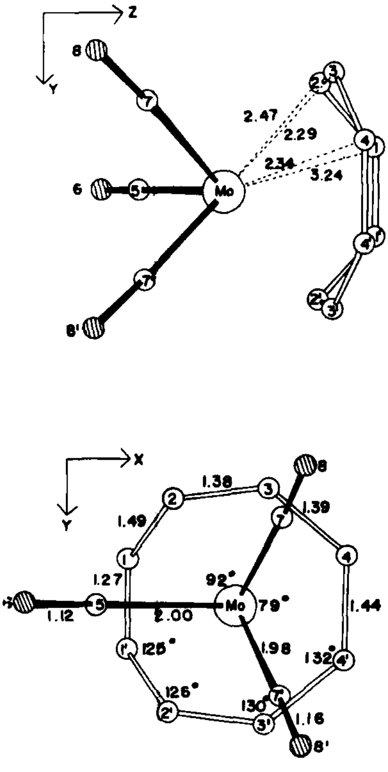
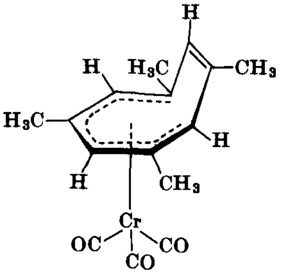


FIG. 2. Molecular structure of $(C_8H_8)Mo(CO)_3$ (*405*).

comparable (1.38–1.44 Å) indicating a conjugated system similar to that in (cyclooctatriene)$Cr(CO)_3$ (**27**), while the length of the uncoordinated double bond is 1.27 Å. The distances between the metal atom and the coordinated and uncoordinated carbons are 2.29–2.47 and 3.24 Å, respectively.

A very similar molecular structure has been observed (*56*) for the chromium complex of 1,3,5,7-tetramethylcyclooctatetraene (TMCOT), (TMCOT)$Cr(CO)_3$ (**30**). The $Cr(CO)_3$ group is linked to six of the ring



(30)

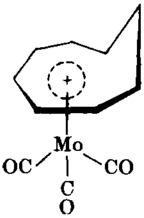
carbon atoms with Cr–C distances of 2.20–2.41 Å. The six "bonded" carbon atoms are nearly coplanar, while the free olefinic carbon atoms together with the adjacent ring carbons and the associated methyl groups are also essentially coplanar, the dihedral angle between the two planes being 119°. Again, there is no significant difference between the C–C bond lengths for the bonded carbon atoms indicating extensive delocalization of the π electrons.

It is noteworthy that the three complexes (TMCOT)$Cr(CO)_3$, $(C_8H_8)Mo(CO)_3$, and (1,3,5-C_8H_{10})$Cr(CO)_3$ all show the same carbonyl–metal–carbonyl angles, one being about 80° while the others are 91–94°. This further suggests a marked similarity in the bonding of the metal to the olefin in the three species.

At 30°C, the ^1H NMR spectrum of $(C_8H_8)Mo(CO)_3$ exhibits only a broad line, the fine structure of which is resolved at −30°C (*620*). A similar behavior is shown by $(C_8H_8)Cr(CO)_3$ (*347*, *366*) and $(C_8H_8)W(CO)_3$ (*347*). The effect has been attributed to a valence tautomerism in which the metal atom moves around the ring. Although there is some disagreement with respect to the magnitude of the activation energy for rotation of the metal atom about the C_8H_8 ring (*143*), the kinetic data (*347*) indicate that the rate of rotation decreases in the order $(C_8H_8)Mo(CO)_3 > (C_8H_8)Cr(CO)_3 \gg (C_8H_8)W(CO)_3$. A detailed discussion of valence tautomerism in organometallic complexes will be provided in the section on $(C_8H_8)Fe(CO)_3$.

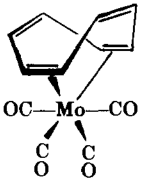
In order to elucidate further the process of valence tautomerism, Cotton *et al.* (*142*, *143*) have studied the ^1H NMR spectra of $(TMCOT)M(CO)_3$ (M = Cr, Mo or W) with the view that the alternation of hydrogen atoms and methyl groups in the ring would reduce the spin-spin coupling and thus simplify the spectra while retaining much of the symmetry of C_8H_8 itself. In the temperature range from −30° to 115°C, at least two and perhaps three phases of intramolecular rearrangement were observed. The first of these has been interpreted in terms of an oscillatory 1,2-shift mechanism. The relative rates of rearrangement are (*143*) $(TMCOT)Cr(CO)_3 \simeq (TMCOT)Mo(CO)_3 > (TMCOT)W(CO)_3$.

Protonation of $(C_8H_8)Mo(CO)_3$ yields $(C_8H_9)^+Mo(CO)_3$, shown by NMR to be the nonclassical homotropylium ion complex (**31**) (*620*).

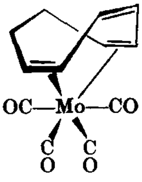


(31)

The molybdenum complexes $(olefin)Mo(CO)_3$ of C_8H_8 and C_8H_{10} react readily with CO to yield $(olefin)Mo(CO)_4$ in which the molybdenum atom is coordinated to the 1,5-double bonds (**32a**) and (**32b**) (*323*). Prolonged reaction with CO results in complete displacement of olefin



(32a)

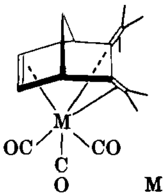


(32b)

from $(C_8H_{10})Mo(CO)_3$ and in formation of $(C_8H_8)[Mo(CO)_4]_2$ from $(C_8H_8)Mo(CO)_3$. An infrared study (*274*) of the substitution process with ^{13}C-enriched CO has revealed that the configuration of the carbonyls is not retained during the exchange reaction.

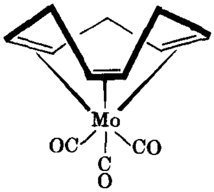
The reaction of bis(trifluoromethyl)tetramethylbicyclo[2.2.2]octatriene with $Mo(CO)_6$ (*343*) and of tetrafluorobenzobicyclo[2.2.2]octatriene with $Cr(CO)_6$ (*575*) affords the yellow (olefin)$M(CO)_3$ complexes with structures comparable to these of the analogous cobalt (*168*) and iron (*136*) complexes, respectively.

When 5,6-dimethylenebicyclo[2.2.1]hept-2-ene is refluxed with the metal hexacarbonyl in hydrocarbon solvents, the volatile, reddish-orange crystalline solid of composition $(C_9H_{10})M(CO)_3$ (M = Cr, Mo, or W) is obtained (*356*). These complexes (**33**) are air-stable, readily soluble in organic solvents, and show very similar spectral properties.



M = Cr, Mo, or W

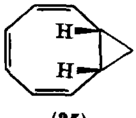
(33)



(34)

With *cis,cis,cis*-1,4,7-cyclononatriene, $Mo(CO)_6$ in an oxygen-free hydrocarbon yields the air-stable complex $(C_9H_{12})Mo(CO)_3$ (*592*) to which, on the basis of infrared and UV spectra, structure (**34**) has been assigned. The metal–olefin bonding is considered (*592*) to involve the inner convergent lobes of the π orbitals, in contrast to the silver(I) complex of the same olefin in which the silver ions are coordinated through overlap with the outer divergent lobes (*314*). The corresponding reaction with $Cr(CO)_6$ does not occur (*592*).

cis-Bicyclo[6.1.0]nona-2,4,6-triene (**35**) itself a thermally unstable olefin which undergoes conversion at about 90°C into structures (**36**) and (**37**) can be stabilized by reacting with (diglyme)$Mo(CO)_3$ to form the complex (triene)$Mo(CO)_3$ (*258*). The NMR spectrum suggests the exo complex (**38**). In the complex the ligand also undergoes rearrangement at 125°C to the complex of bicyclo[4.2.1]nona-2,4,7-triene (**39**).



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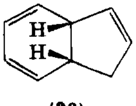

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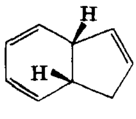
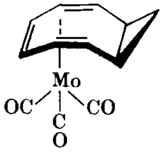


(37)

The ten π-electron system, bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (or 1,6-methanocyclodecapentaene) reacts with $Cr(CO)_6$ in octane under UV irradiation to give a reddish-violet complex, $(C_{11}H_{10})Cr(CO)_3$ (*213*).



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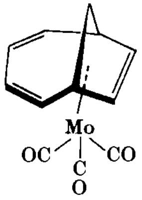
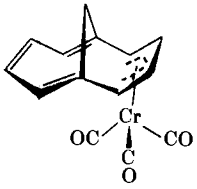


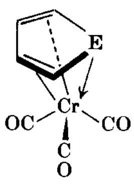
(39)

Although the NMR spectrum has been interpreted (*213*) as indicative of a cis configuration [i.e., with the $Cr(CO)_3$ moiety on the same side of the ring as the methylene bridge], a crystal analysis (*34*) has established the molecular structure (**40**) with a trans configuration. The metal atom is equally bonded to the four carbon atoms on one side of the bridgehead (Cr–C distance about 2.2 Å), while its distance from the bridgehead carbons (2.55 Å) indicates little interaction with these. The chromium atom thus appears to be two electrons short of an inert gas configuration (*34*). The corresponding reaction with $Mo(CO)_6$ produces two pale red complexes, one of which is thought to be analogous to that of structure (**40**) (*213*).



(40)

The heterocyclic olefins, thiophene and selenophene, also form π complexes upon reaction with $(pyridine)_3Cr(CO)_3$ in the presence of a Lewis acid (PF_3) (*447*). On the basis of spectral data, structure (**41**) has been assigned to the products.

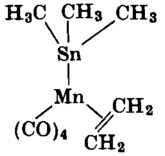


E = S or Se

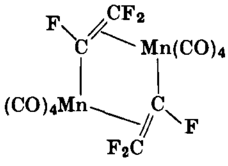
(41)

V. Group VIIB: Manganese and Rhenium

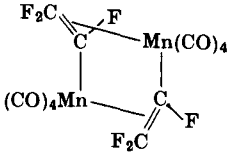
In the course of a study on the insertion of olefins into metal–metal bonds, Clark *et al.* (*115*) have obtained, as a yellow oil, an ethylene π complex $(CH_3)_3Sn\text{-}Mn(CO)_4(C_2H_4)$ (**42**), by UV irradiation of $(CH_3)_3Sn\text{-}Mn(CO)_5$ under ethylene pressure. Although the NMR spectrum indicates that the ethylene molecule is π-bonded to the manganese atom, it has not been possible to establish whether it occupies a cis or a trans position with respect to the tin atom. Upon reaction under comparable conditions, C_2F_4 breaks the Sn–Mn bond to produce two isomers of $[(C_2F_3)Mn(CO)_4]_2$ as well as the insertion product $(CH_3)_3SnCF_2CF_2Mn(CO)_5$ (*115*). On the basis of analytical and spectral data, the structures (**43a**) and (**43b**) have been proposed for the dimers.



(**42**)



(**43a**)

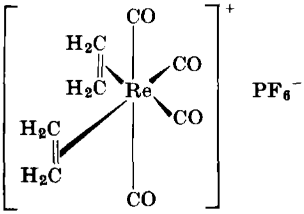


(**43b**)

A π complex of manganese $[(C_2H_4)Mn(CO)_5]^+$ can be prepared by reaction of ethylene at 140 atm with $Mn(CO)_5Cl$ (*208*) or of pure $C_2H_5Mn(CO)_5$ with $(C_6H_5)_3C^+BF_4^-$ (*255*). The π-complexed ethylene can be readily replaced by heating with triphenylphosphine to yield CO, C_2H_4, and $[\{(C_6H_5)_3P\}_2Mn(CO)_4]^+$ (*255*).

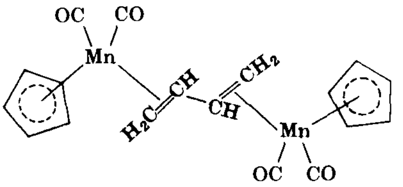
The analogous reaction of ethylene at 250 atm with $Re(CO)_5Cl$ affords the complex ion $[(C_2H_4)_2Re(CO)_4]^+$ (*209*) for which structure (**44**) having the olefinic ligands in cis positions has been postulated.

Acrylonitrile reacts with $(C_5H_5)Mn(CO)_3$ in hexane under UV irradiation to give stable, yellow crystals of $(CH_2CHCN)Mn(CO)_2(C_2H_5)$, the spectra of which unambiguously suggest coordination of the C=C double bond (*631*). The same reaction occurs with 1,3-butadiene (*631*)



(44)

to yield an unstable, orange oil $(C_4H_6)Mn(CO)_2(C_5H_5)$, as well as stable yellow crystals of $(C_4H_6)[Mn(CO)_2(C_5H_5)]_2$. The infrared spectrum indicates that in the former, the diene ligand is coordinated at one only of the double bonds, while in the latter, it acts as a bridge between two manganese atoms; structure (**45**) has been confirmed by an X-ray analysis (*628*) which shows Mn–C distances of 2.20 (Mn–CH_2) and 2.29 Å (Mn–CH). These results are not in accord with the earlier



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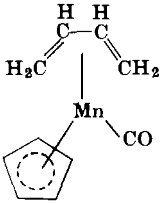
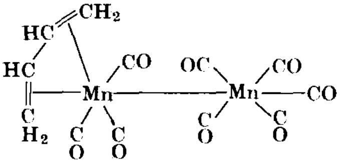


(46)

report (*220*) that the UV irradiation of $(C_5H_5)Mn(CO)_3$ with butadiene yields the cisoid complex (**46**).

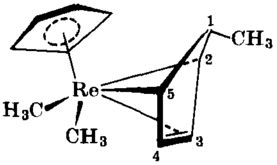
The direct substitution of the carbonyl groups in $Mn_2(CO)_{10}$ by 1,3-butadiene affords only 1% of orange, crystalline $(C_4H_6)Mn_2(CO)_8$ with cisoid configuration (**47**) (*630*). Reaction of butadiene with



(47)

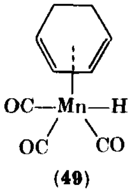
$RMn(CO)_5$, on the other hand, yields a π-allylic complex (*42*, *43*, *249*). Interaction of 2-chlorobutadiene (*18*) or 2-chlorobutene (*20*) with Mn(II) has been reported to form the corresponding π complex.

Treatment of an ethereal solution of lithiated bis(π-cyclopentadienyl)rhenium hydride, $(C_5H_4Li)_2ReH$, with an excess of methyl iodide yields a rather unstable yellow compound of composition $C_{13}H_{19}Re$ (*125*). The infrared and NMR spectra indicate that the complex is (methylcyclopentadiene)(cyclopentadienyl)dimethylrhenium for which the structure (**48**) has been deduced by X-ray analysis (*5*). The methylcyclopentadiene ring is nonplanar with an angle between the planes $C_2C_1C_5$ and $C_2C_3C_4C_5$ of 41°. This large bending of the ring suggests that the Re atom is σ-bonded to C-2 and C-5 and π-bonded to the C-3–C-4 double bond (*5*). This suggestion is consistent with the structural conclusion drawn from NMR studies (*147*).



(48)

The reduction of the benzene complex cation $[(C_6H_6)Mn(CO)_3]^+$ with $NaBH_4$ or $LiAlH_4$ gives (*612*) the previously reported (*220*) π-cyclohexadienyl complex $(C_6H_7)Mn(CO)_3$ in addition to a low yield of the (1,3-cyclohexadiene)tricarbonylmanganese hydride (**49**). Similarly, hydride ion ($LiAlH_4$) attack on the (hexamethylbenzene)tricarbonylrhenium cation, prepared by treatment of $Re(CO)_5Cl$ with $C_6(CH_3)_6$ and $AlCl_3$, affords the substituted π-cyclohexadienyl complex $[C_6(CH_3)_6H]Re(CO)_3$ (*614*) which has a broad, intense infrared band at 2790 cm^{-1}. A crystallographic analysis (*68*) shows a mean Re–trigonal carbon distance of 2.35 Å and places the hydrogen on the side of the ring away from the metal atom (**50**). The 2790 cm^{-1} band must be



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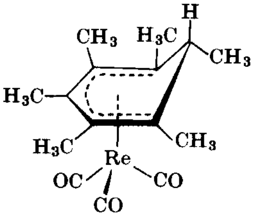
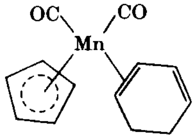


(50)

associated with the CH-stretching vibration of this exo hydrogen (*68*). Wilkinson and co-workers (Bennett, *47*) have attributed a similar anomalously low CH-stretching in $(C_5H_6)CoC_5H_5$ to the endo rather than the exo hydrogen of the CH_2 group in the cyclopentadiene ring. In view of structure (**50**), however, this conclusion may be incorrect. These complexes also react similarly with CCl_4 to produce $CHCl_3$ and the dehydrogenated complex cations (*47*, *614*). Similar π-hexadienyl rhenium complexes $(C_6R_6H)Re(C_6R_6)$ ($R = H$ or CH_3) have been prepared by the reaction of $[Re(C_6R_6)_2]PF_6$ with sodium in liquid ammonia followed by addition of hydride ion (*214*).

Fischer and Herberhold (*200*) have extensively investigated the reaction of $C_5H_5Mn(CO)_3$ with cyclic olefins, to produce (olefin)-$Mn(CO)_2(C_5H_5)$ and/or (olefin)$[Mn(CO)_2(C_5H_5)]_2$ wherein the olefin may be a C_5–C_9 cyclic monoolefin, 1,3-cyclohexadiene (*199*) (**51** and **52**), norbornadiene (**53** and **54**), or 1,5-cyclooctadiene (**55**). The structures have been assigned on the basis of infrared (*200*) and NMR (*200*, *228*) data.



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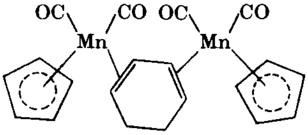

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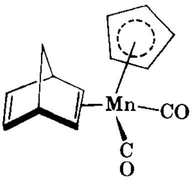

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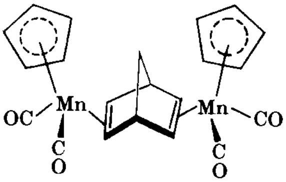

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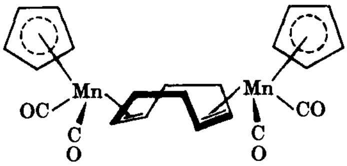
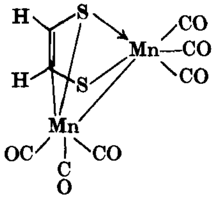


(55)

A kinetic investigation (*12*) of olefin replacement in (olefin)-$Mn(CO)_2(C_5H_5)$ by a ligand L [$L = $ phosphine, amine, or $(C_6H_5)_2S$] shows that the rate is independent of L and indicates an S_N1 reaction with dissociation of the olefin complex as the rate-determining step. In methylcyclohexane at 80°C the rate of olefin complex dissociation increases in the order: ethylene $<$ norbornadiene $<$ norbornylene $<$ cyclooctene $<$ propylene $<$ cyclopentene $<$ 1-pentene $\simeq$ cycloheptene. This order of complex stability is very comparable to that observed for the (olefin)Ag^+ series (*416*). The introduction of a methyl group into the cyclopentadienyl ring of the complex has very little effect on the rate of olefin replacement. The difference between the ethylene and propylene complexes has been attributed (*12*), however, to the steric and/or electronic effects of the methyl substituent in the latter. There is no measurable replacement of CO by L indicating that the Mn–CO bond is considerably stronger than the Mn–olefin bond.

The reaction of $Mn(CO)_5Br$ with disodium *cis*-1,2-ethylenedithiolate in an acetone–methanol solvent yields the dark red volatile $(C_2H_2S_2)Mn_2(CO)_6$ (*352*), shown by a preliminary X-ray analysis (*352*, footnote 11) to have the structure (**56**). This complex reacts at room temperature with $(C_6H_5)_3P$ to give the 1:1 adduct or under more vigorous conditions to form the CO replacement product $(C_2H_2S_2)Mn_2(CO)_4[(C_6H_5)_3P]_2$. In this instance the manganese–olefin bond appears to remain intact.



(56)

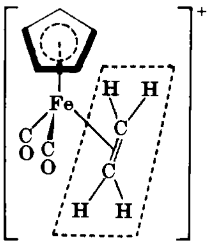
The reaction of $Mn_2(CO)_{10}$ with pyrrole in petroleum ether at 130°C affords bright orange crystals (m.p. 40.5°C) of a π-pyrrolyl complex $(C_4H_4N)Mn(CO)_3$ (*321*).

VI. Group VIIIA: Iron, Ruthenium, and Osmium

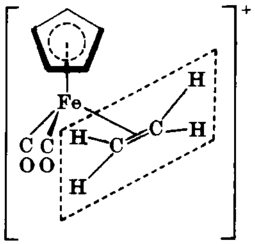
A. IRON

Treatment of a suspension of $Fe_2(CO)_9$ at room temperature with C_2H_4 (50 atm) in the dark results in formation of the simple ethylene complex $(C_2H_4)Fe(CO)_4$ (*425*) which decomposes rapidly in air or nitrogen. The reduction of tris(acetylacetonato)iron(III) with ethoxydiethylaluminum in the presence of ethylenebis(diphenylphosphine) (EDP) produces the π complex $(C_2H_4)Fe(EDP)_2$ (*280*) which exists in two isomeric forms. Interaction of the ethylene complex with hydrogen or iodine liberates ethylene, while UV irradiation results in formation of both ethylene and $HFe(EDP)[C_6H_4P(C_6H_5)CH_2CH_2P(C_6H_5)_2]$. The latter reaction is reversible under ethylene pressure.

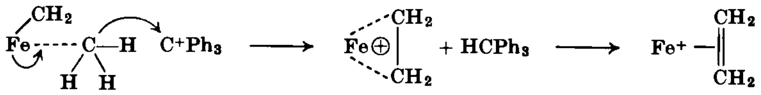
In the presence of trityl perchlorate the ethyliron complex $(C_2H_5)Fe(CO)_2(C_5H_5)$ undergoes a hydride elimination reaction to afford the corresponding ethylene complex cation (*253*). Molecular orbital calculations indicate that structure (**57a**) is a more stable configuration than structure (**57b**) (*255*). This reaction can also be reversed by reaction of the complex with sodium borohydride (*252*). A hydride elimination study (*255*) using the deuteroisopropyl complex indicates that the hydride abstraction involves a bimolecular mechanism in which the hydride is lost from the β-carbon atom [Eq. (3)]. In the reverse reaction, the hydride ion may attack either the metal, followed by hydrogen transfer to the ethylene ligand, or the ethylene directly (*255*).



(**57a**)



(**57b**)



(3)

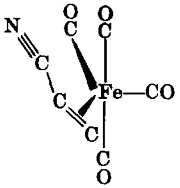
Although the analogous *n*-propyl and isopropyl complexes both give the π-propene complex cation, reversal of the reaction produces only the isopropyl species.

The analogous olefin complex cations

$$[(\pi\text{-}CH_2{=}CHCH_2R)Fe(CO)_2(C_5H_5)]^+ \quad (R = H \text{ or } CH_3)$$

can be readily formed (*254*) by protonation of the corresponding σ-allyl complexes, $(\sigma\text{-}CH_2CH{=}CHR)Fe(CO)_2(C_5H_5)$, with hydrogen chloride. Deuterium tracer studies suggest that protonation occurs at the γ-carbon atom followed by rupture of the Fe–C bonds. Similarly, protonation of $RFe(CO)_2(C_5H_5)$, where R = 3-propynyl (*14*, *316*), cyanomethyl (*13*), or formylmethyl (*15*), affords the corresponding π-olefin complex cations wherein the olefin is allene, ketenimine, or vinyl alcohol. The mechanism for these protonation–rearrangement reactions is evidently the same as that proposed for the σ-allyl complex. The ease of protonation of these complexes may be associated with the ability of the metal to provide intramolecular assistance by contributing electrons to the ligands (*119*).

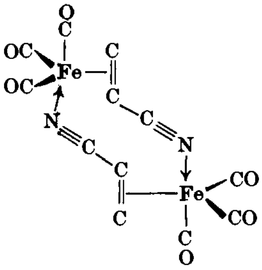
The structure (**58**) of the yellow, diamagnetic (acrylonitrile)$Fe(CO)_4$,



(**58**)

proposed (*340*) on the basis of its infrared spectrum, has been confirmed (*380*) by a single-crystal X-ray analysis. Coordination through the olefinic double bond results in a lengthening of that bond from 1.34 to 1.40 Å and a reduction of the C–C–C angle from 123° to 116° indicating increased *p*-character in that bond. The iron–trigonal carbon atom distances are about 2.10 Å. Viewing the olefin as a single ligand in a equatorial position, the overall structure can be regarded as approximating a trigonal bipyramid. The OC–Fe–CO angle in the equatorial plane is 110° and the angle subtended at Fe by the double bond is 39°. The angle between the normal to the apical axis and the plane containing the C–C–C–N skeleton is 76.4°, probably as a result of repulsion between the C≡N group and the apical CO ligand.

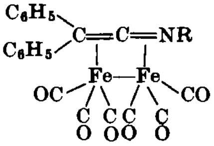
In addition to (acrylonitrile)$Fe(CO)_4$, Schubert *et al.* (*533*) have isolated two additional complexes of acrylonitrile: (*i*) a volatile yellow oil identified as another complex of the same stoichiometry in which coordination is through the nitrogen atom only and (*ii*) a yellow solid of composition $(C_3H_3N)Fe(CO)_3$ suggested by its infrared spectrum to be the dimer, di-μ-acrylonitrilehexacarbonyldiiron. A preliminary crystal analysis (*629*) shows structure (**59**) for the dimer, a structure somewhat analogous to that proposed (*115*) for the dimer $[(CF_2{=}CF)Mn(CO)_4]_2$



(59)

(**43**). Acrylonitrile acts therein as a bidentate ligand displaying both hard (nitrogen donor) and soft (π-donor) base character. It has been noted (*533*) that a hard base coordinates in the axial and a soft base in the equatorial position; this is exemplified by structure (**59**).

Complexes having both C=C and C=N bonds coordinated to the iron atom have been obtained by direct interaction of substituted ketenimines, $(C_6H_5)_2C{=}C{=}NR$ ($R = C_6H_5$ or CH_3), with $Fe_3(CO)_{12}$ (*453*) or of unsaturated imines, $RCH{=}CH{-}CH{=}NR'$ ($R = CH_3$, $R' = n\text{-}C_4H_9$; $R = R' = C_6H_5$), with either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ (*454*). On the basis of infrared and NMR spectra, the resulting complexes $[(C_6H_5)_2C{=}C{=}NR]Fe_2(CO)_6$ and $(RCH{=}CH{-}CH{=}NR')Fe(CO)_3$ have been assigned structures (**60**) and (**61**), respectively. The authors (*453*)



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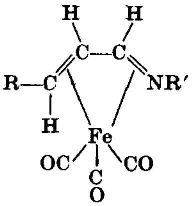


(61)

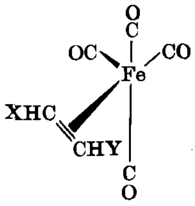
do not comment on the fact that structure (**60**) contains electron-deficient iron atoms. The latter compound ($R = R' = C_6H_5$), which can be prepared also by reaction of the cinnamaldehyde complex $(C_6H_5CH{=}CH{-}CHO)Fe(CO)_4$ with aniline (*454*), interacts with $P(C_6H_5)_3$ to give only the carbonyl displacement product

$$(C_6H_5CH{=}CH{-}CH{=}NC_6H_5)Fe(CO)_2P(C_6H_5)_3$$

In contrast, the alkyl-substituted imine complex ($R = CH_3$, $R' = n\text{-}C_4H_9$) reacts with $P(C_6H_5)_3$ to give free olefin and $CFe(O)_3[P(C_6H_5)_3]_2$ (*454*).

Gustorf and co-workers (*264–266*) have prepared complexes of the type $(\pi\text{-}CH_2{=}CHX)Fe(CO)_4$ [$X = OCOCH_3$ (*266*), Cl, CH_3, C_6H_5, or OCH_3 (*265*)] by irradiation of $Fe(CO)_5$ with the corresponding olefin. The complexes are very oxygen-sensitive and thermally unstable. At room temperature they decompose to yield the olefin and $Fe_3(CO)_{12}$. The order of thermal stability is vinyl chloride > styrene > propylene > vinyl methyl ether. The vinyl chloride and styrene complexes show catalytic activity for polymerization of methyl methacrylate in the presence of a small amount of halogenated hydrocarbon, e.g., CCl_4, at room temperature (*265*).

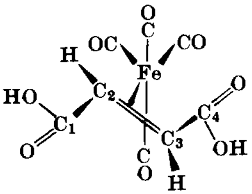
At ambient temperature without irradiation, $Fe_2(CO)_9$ readily reacts with β-chlorovinylketones (*440*) and unsaturated aldehydes or carboxylic acids (*601*) to produce the complexes $(XCH{=}CHY)Fe(CO)_4$, ($X = Cl$, $Y = COR$; or $X = H$, CH_3, C_6H_5, COOH; $Y = CHO$, COOH). Spectral data (*601*) indicate structure (**62**) in which only the olefinic double bond is involved in coordination. Upon heating (cinnamaldehyde)$Fe(CO)_4$ at 60°C in benzene, a red complex (cinnamaldehyde)$Fe(CO)_3$ is obtained (*555*). Although the infrared and NMR spectra suggest coordination through both the double bond and the aldehyde group, it is uncertain whether it is the oxygen lone-pair of electrons or the C=O double bond of the latter which is involved.



(**62**)

Although (maleic acid)Fe(CO)$_4$ has a symmetry plane perpendicular to the plane of the double bond, (fumaric acid)Fe(CO)$_4$ is clearly asymmetric and should thus be capable of resolution into its enantiomers (*457*). Accordingly, addition of the complex to a solution of brucine in acetone and crystallization of the diastereoisomeric salts followed by decomposition with hydrochloric acid yielded the two enantiomers having optical activities $[\alpha]_D^{25}$ −593 (acetone; C, 0.848) and $[\alpha]_D^{25}$ +587 (acetone; C, 0.921). Analyses and infrared spectra of individual enantiomers were identical to those of the racemic mixture.

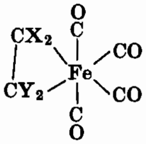
An X-ray analysis (*138*) of racemic (fumaric acid)Fe(CO)$_4$ shows a trigonal bipyramidal arrangement of the five ligands about the iron atom with the double bond at an equatorial position (**63**). The complex molecules are hydrogen-bonded through the fumaric acid ligands. Unlike the double bond in the corresponding acrylonitrile complex (*380*), that of this complex is tilted significantly from the equatorial plane (*139*). The carbon atoms C-1 and C-4 of the carboxylic acid groups are pushed away from the metal atom with the dehedral angle between the planes through C-1–C-2–C-3 and C-2–C-3–C-4 being 145°. It was suggested (*138*) that although this deviation from coplanarity of the carbon atoms may be due to repulsions between nonbonded atoms, it is also consistent with the introduction of more *p*-character into the hybridization of carbon atoms C-2 and C-3.



(63)

The crystal of (−)-(fumaric acid)Fe(CO)$_4$ contains three crystallographically distinct complex molecules, A, B, and C, each of which has C_2 symmetry (*139*). As in the racemate, the four carbon atoms of the fumaric acid are not coplanar, but show dihedral angles of 151°, 148°, and 146° in molecules A, B, and C, respectively. Although the axis of the double bond in molecules A and C is significantly tilted out of the equatorial plane of the complex, that of molecule B is not. The different coordinations are presumably stabilized by different arrangements of the hydrogen bonds (*139*).

Ultraviolet irradiation of $Fe(CO)_5$ with perhaloolefins (*194*) gives the moderately stable complexes (olefin)$Fe(CO)_4$ (olefin = C_2F_4, C_3F_6, C_2F_3Cl, $C_2F_2Cl_2$, cyclo-C_5F_8, or cyclo-C_6F_{10}). Although chemical evidence tends to favor a structure in which the double bond acts as a π donor at either an axial or equatorial position, one cannot rule out the possibility of σ bonding between the iron and carbon atoms (**64**). Similar bonding has been postulated (*69*, *70*, *250*, *511*) for the platinum complexes of these olefins.

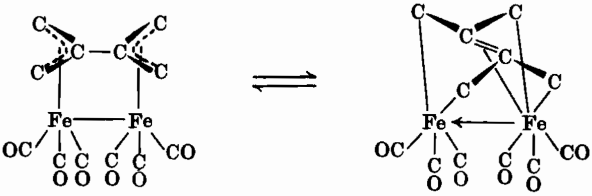


(64)

Reaction of allene with $Fe_3(CO)_{12}$ at atmospheric pressure in refluxing hexane (*428*) or at 120°C under pressure (*434*) produces red crystals of the 2,2′-bi-π-allylene complex

$$(OC)_3Fe[H_2C{=}C(\dot{C}H_2)—C(\dot{C}H_2){=}CH_2]Fe(CO)_3$$

In solution, this complex undergoes a rapid valence tautomerism (*428*, *432*) as indicated by structure (**65**). The π-allylic form appears to predominate at higher temperatures. The corresponding reaction with $Fe_2(CO)_9$ at 50°C under pressure produces, in addition to this same π-allylene complex, the σ,π-allyl complex $(C_3H_4)Fe_2(CO)_7$ (**66**) (*58*, *156*).



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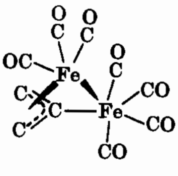
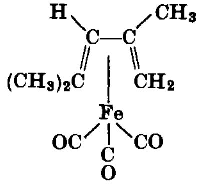
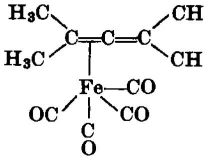


(66)

By contrast, the substituted allenes produce monomeric π complexes with iron carbonyls. Interaction of tetraphenylallene with $Fe(CO)_5$ in refluxing isooctane affords diamagnetic red crystals of $[(C_6H_5)_2C{=}C{=}C(C_6H_5)_2]Fe(CO)_3$ (*433*, *434*) while the reaction of tetramethylallene with $Fe_2(CO)_9$ produces both $[(CH_3)_2C{=}C{=}C(CH_3)_2]$-$Fe(CO)_4$ and a complex of molecular formula $(C_7H_{12})Fe(CO)_3$ (*57*) identified by NMR spectrum and oxidative degradation products as (2,4-dimethyl-1,3-pentadiene)tricarbonyliron (**67**). Although structure (**68**) has been assigned to $[(CH_3)_2C{=}C{=}C(CH_3)_2]Fe(CO)_4$, its NMR spectrum shows a temperature dependence indicating a valence tautomerism in which the $Fe(CO)_4$ group moves rapidly between the two π-molecular orbitals (*57*).

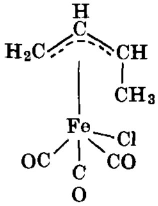

(**67**)


(**68**)

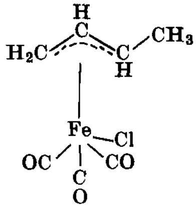
In the well-known complex (1,3-butadiene)$Fe(CO)_3$, the diene moiety has a planar and cisoid configuration which supports the suggestion of delocalized bonding (*47*, *220*, *443*). This view has been further supported by both ^1H (*487*) and ^{13}C (*487*, *498*) NMR spectra which indicate that all the C–H bonds are essentially sp^2 hybrids and that the bonding with the 1,4-carbon atoms differs somewhat from that with the 2,3-carbons, although both involve π orbitals.

Although earlier reports (*394*) indicated that triphenylphosphine replaced the diene rather than a CO ligand when heated with $(C_4H_6)Fe(CO)_3$, the corresponding reaction with $P(C_6H_5)(OR)_2$ ($R = C_2H_5$, C_3H_7, or n-C_4H_9) (*441*) or $P(OCH_3)_3$ (*496*) results in displacement of one CO ligand. Pauson and co-workers (*107*) have shown that under irradiation $P(C_6H_5)_3$ also replaces CO to produce $(C_4H_6)Fe(CO)_{3-n}$-$[P(C_6H_5)_3]_n$ ($n = 1$ or 2). Similar reactions have been effected with the cyclic dienes of C_4, C_5, and C_6 hydrocarbons (*107*).

The addition of hydrogen chloride to $(C_4H_6)Fe(CO)_3$ was initially reported (*311*) to yield a yellowish brown 1:1 π-allylic complex $[C_3H_4(CH_3)]Fe(CO)_3Cl$ with the methyl group in the anti position (**69a**). Pettit and co-workers (*189*) subsequently showed, however, that the methyl group occupied the syn position (**69b**), and suggested that this configuration arises as a result of addition of the HCl molecules to one



(69a)

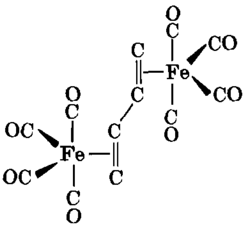


(69b)

of the complexed double bonds from the side distant from the iron atom followed by inversion of the methyl group in the intermediate in order to provide a favorable position for interaction of the chlorine atom with the metal.

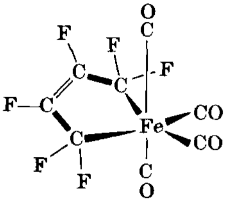
In the presence of a halogen acceptor such as $AlBr_3$, butadiene reacts with $BrFe(CO)_2(C_5H_5)$ to produce the cation $[(C_4H_6)Fe(CO)_2(C_5H_5)]^+$ which can be precipitated as the PF_6^- salt (*196*). Its infrared spectrum indicates that the diene acts as a monodentate ligand retaining one free double bond. Upon saturation with butadiene of a stirred suspension of $Fe_2(CO)_9$ in *n*-hexane, one obtains, in addition to a small quantity of $(C_4H_6)Fe(CO)_3$, a thermally unstable orange oil, $(C_4H_6)Fe(CO)_4$, and an air-stable yellowish-orange solid $(C_4H_6)[Fe(CO)_4]_2$ (*424*). In $(C_4H_6)Fe(CO)_4$, the diene again acts as a monodentate ligand which can be displaced by $P(C_6H_5)_3$. With dry HCl, the π-allylic complex $[(C_4H_7)Fe(CO)_4]^+Cl^-$ is formed (*424*).

The molecular structure (*362*) of the complex $(C_4H_6)[Fe(CO)_4]_2$ is similar to that of its manganese analog (**45**). It consists of a planar *trans*-1,3-butadiene moiety bonded in such a way to two $Fe(CO)_4$ groups that each of the double bonds occupies an equatorial position in a different trigonal bipyramid (**70**).



(70)

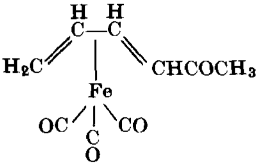
In contrast to the monodentate π bonding in $(C_4H_6)Fe(CO)_4$, the perfluorobutadiene analog $(C_4F_6)Fe(CO)_4$, obtained by reaction of the diene with $Fe(CO)_5$ (*300*), has been shown (*291*) to be a σ-bonded complex (**71**). The C_4 skeleton is linked to the Fe through the 1,4-carbon atoms



(**71**)

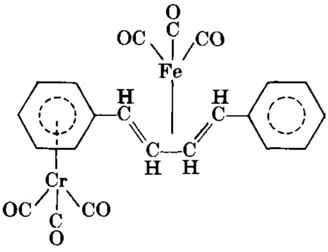
forming a planar five-membered ring with coordination about the iron being almost octahedral. This structure suggests that the electronegative substituents tend to promote the formation of a σ bond between the olefin and transition metal (*291*).

The reaction of $[Fe(CO)_3(NO)]^-$ with butadiene in the presence of methyl iodide followed by treatment with pyridine (*106*) has produced the complex (**72**) of the monosubstituted butadiene.

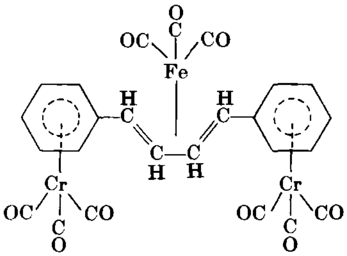


(**72**)

Although 1,4-diphenylbutadiene produces only the arene complexes $[C_4H_4(C_6H_5)_2]Cr(CO)_3$ (*106, 393*) and $[C_4H_4(C_6H_5)_2]Cr_2(CO)_6$ (*106*) upon interaction with $Cr(CO)_6$, the diene complex $[C_4H_4(C_6H_5)_2]Fe(CO)_3$ is obtained with $Fe_3(CO)_{12}$ (*393*). The chromium complexes react in turn with $Fe_3(CO)_{12}$ (*393*) or $Fe(CO)_5$ (*106*) to yield novel complexes (**73**) and (**74**), in which the olefin is bonded to different metals. It is interesting



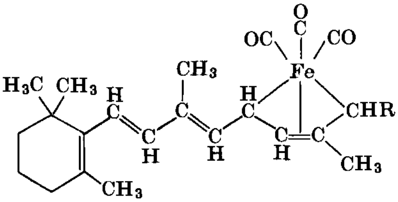
(**73**)



(**74**)

to note that under electron bombardment (*395*) these compounds give rise to the metal–metal bonded ions Cr–Fe$^+$.

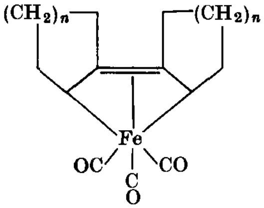
The first organometallic π complex of vitamin A acetate, (**75**) (R = CH_2OCOCH_3), obtained by reaction of the acetate with $Fe_3(CO)_{12}$



(75)

has been reported by Tsutsui and co-workers (*437*). Vitamin A aldehyde (*63*), β-carotene, and licopene, (*310*) react also with $Fe_3(CO)_{12}$ to yield the 1:1, 1:4, and 1:5 complexes, respectively.

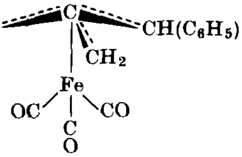
The crystal structure analysis (*64*) of the vitamin A aldehyde complex (**75**) (R = CHO), which confirms that suggested (*63*) on the basis of the NMR spectrum, shows a bonding of the $Fe(CO)_3$ to the polyene chain quite analogous to that observed in several butadiene–(or substituted butadiene–)metal complexes (*59*, *113*). The iron–carbon atom distances and the carbon–carbon bond lengths, clearly suggest (*64*) a σ,π-bonded rather than a two-π-bonded structure. A similar σ,π bonding has been proposed for the complexes 1,1′-bicyclopentenyl, -hexenyl, and -heptenyltricarbonyliron (**76**) (*391*), and for the tricarbonyliron complex



(76)

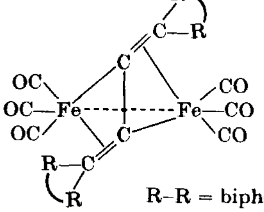
of 1,4-disubstituted butadiene (*93*, *267*, *604*), methyl linoleate (*224*, *448*, *449*), and substituted hexatrienes (*604–606*).

Trimethylenemethane achieves at its central carbon atom the maximum bond order and minimum free valence possible for an unsaturated carbon atom. This highly unstable molecule can be stabilized as the iron complex (trimethylenemethane)tricarbonyliron prepared by interaction of 3-chloro(2-chloromethyl)propene with $Fe_2(CO)_9$ in ether at room temperature (*187*). In contrast to some iron carbonyl complexes (*140*, *332*, *333*) this complex does not display facile valence tautomerism, as shown by its temperature independent ^1H NMR spectrum. Its phenyl-substituted analog (*109*, footnote 4) has been shown (*109*) to have an umbrella structure (**77**) in which the central carbon atom is 0.3 Å out of the plane of the three methylene carbons away from the iron. Both the methane ligand and the $Fe(CO)_3$ group adopt staggered conformations. It is apparent that the iron atom is π-bonded to all the carbon atoms with an iron–central carbon distance of 1.93 Å and iron–terminal carbon distances of 2.10 to 2.16 Å.



(**77**)

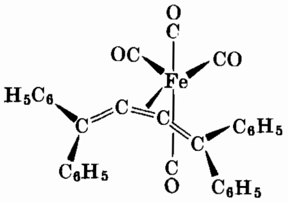
The products obtained by the interaction of tetraphenylbutatriene with $Fe(CO)_5$ (*433*) or of 1,4-dibromo- or substituted 1,4-dibromo-2-butyne with $Fe_3(CO)_{12}$ in the presence of zinc powder (*427*, *434*) were reported by Nakamura and co-workers to be $(RR'C{=}C{=}C{=}CRR')$-$Fe_2(CO)_5$ ($R = R' = H$; $R = H$, $R' = CH_3$; $R = R' = CH_3$; $R = R' = C_6H_5$). Joshi (*319*) subsequently showed, however, that the correct formulation of the product is $(RR'C{=}C{=}C{=}CRR')Fe_2(CO)_6$. This has been confirmed by both mass spectrometric (*346*, *436*) and crystal structure analyses (*319*, footnote 13). The preliminary structural analysis reveals a nonlinear carbon skeleton with each iron atom attached to the hydrocarbon by both a σ and a π bond (**78**).



R–R = biphenyl-2,2′-

(**78**)

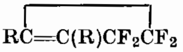
The analogous reaction of $Fe_2(CO)_9$ with tetraphenylbutatriene in benzene at room temperature affords, in addition to the hexacarbonyliron complex, the compound $[(C_6H_5)_2C{=}C{=}C{=}C(C_6H_5)_2]Fe(CO)_4$ which reacts with $FeCl_3$ in diethyl ether to release the butatriene (*320*). An X-ray analysis (*86*) of this complex (**79**) shows the hydrocarbon attached to the iron atom through the central double bond and occupying an



(**79**)

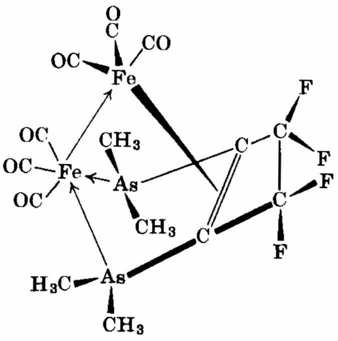
equatorial position in a trigonal-bipyramidal structure similar to that of (acrylonitrile)$Fe(CO)_4$ (*380*). The triene skeleton is symmetrically bent away from the iron atom at the central carbon atoms.

The fully substituted cyclobutenes



$RC{=}C(R)CF_2CF_2$ $[R{=}(CH_3)_2As$ or $(C_6H_5)_2P]$

readily displace carbon monoxide from iron carbonyls to yield the 1 : 1 adducts (*185*) as well as an interesting compound of molecular formula (olefin)$[Fe(CO)_3]_2$. A structural analysis of the compound (*185*, *186*) shows the molecular structure (**80**) involving a metal–metal bond

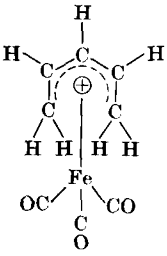


(**80**)

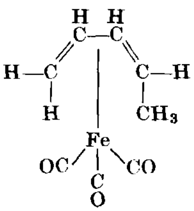
between the Fe atoms, one of which displays octahedral and the other trigonal-bipyramidal coordination. The olefinic double bond occupies an equatorial position in the trigonal bipyramid with iron-sp^2-carbon distances of 2.09 and 1.99 Å.

The preparation of (*trans*-1,3-pentadiene)$Fe(CO)_3$ by reaction of 1,4-pentadiene with $Fe_3(CO)_{12}$ has been reviewed (*47*, reference 160). Although earlier attempts to prepare the cis analog by direct interaction of *cis*-1,3-pentadiene with $Fe(CO)_5$ lead only to formation of the trans complex (*188*, *387*), it has been successfully prepared with $Fe_2(CO)_9$ (*363*). Although, in general, the cis-substituted dienes undergo isomerization upon interaction with $Fe(CO)_5$, *cis,trans*-2,4-hexadiene has been observed to retain its configuration (*188*). There may be a relationship between the effect of steric hindrance on complex stability and the tendency for isomerization to occur (*188*).

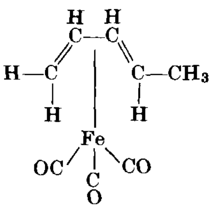
The complex of *cis*-1,3-pentadiene can be indirectly obtained by reaction of $NaBH_4$ with the *cis*-pentadienyl cation [*cis*-$C_5H_7Fe(CO)_3]^+$ (**81**), which is prepared by interaction of *trans*-1,3-pentadiene-5-ol with $Fe(CO)_5$ and treatment with $HClO_4$ (*387*). The product is a mixture comprised 80% of *cis*- and 20% of (*trans*-1,3-C_5H_8)$Fe(CO)_3$ (**82**) and (**83**), respectively (*387*). Although it does not react with the complex of



(**81**)



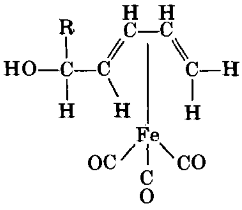
(**82**)



(**83**)

the trans isomer, the trityl cation abstracts a hydride ion from that of the cis isomer to yield the *cis*-pentadienyl cation (**81**) and triphenylmethane.

The *cis*-pentadienyl cation $[C_5H_7Fe(CO)_3]^+$ (*387*) and its 1-methyl-substituted analog (*386*) upon reaction with water undergo geometrical inversion leading to formation of the corresponding trans alcohol (**84**) ($R = H$ and CH_3, respectively). A mechanism involving a hydrated π-allylic complex as intermediate has been postulated (*386*). Solvolysis of the analogous *trans*-pentadienyl cations (**85**) does not involve inversion (*116*). The cis cation $[(syn\text{-}1\text{-methylpentadienyl})Fe(CO)_3]^+$ upon treatment with zinc dust yields a mixture of the diastereoisomers of (5,6-dimethyl-1,3,7,9-decatetraene)hexacarbonyldiiron (**86**) (*386*).



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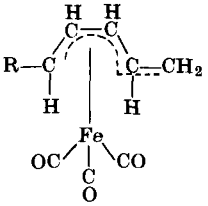

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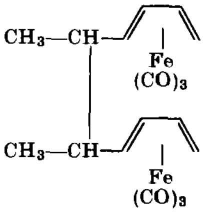
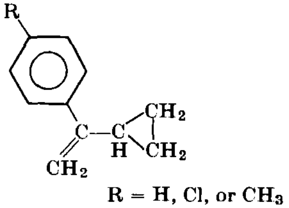


(86)

The vinylcyclopropanes (**87**) interact with $Fe(CO)_5$ to give the complexes $(trans\text{-}2\text{-aryl-}1,3\text{-pentadiene})Fe(CO)_3$ (**88**). A mechanism involving complex formation at the vinyl double bond followed by opening of the cyclopropane ring to give a π-allylic intermediate with an iron–carbon σ bond has been mentioned (*513*).



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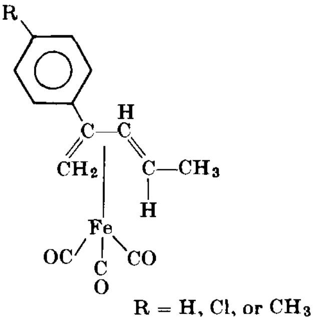
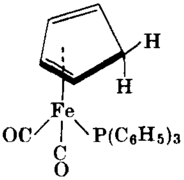


(88)

As with the pentadienes, the complex formed with cyclopentadiene is dependent upon the iron carbonyl employed.

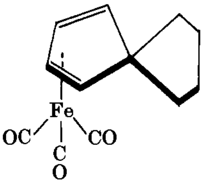
Reaction of cyclopentadiene with $Fe(CO)_5$ does not afford the π complex $(C_5H_6)Fe(CO)_3$, but rather $HFe(CO)_2(C_5H_5)$ which in solution loses hydrogen to produce the binuclear complex $[Fe(CO)_2(C_5H_5)]_2$ (*157*, references 2 and 3). Although an attempt to isolate the diene complex by reduction of $[Fe(CO)_3(C_5H_5)]^+$ with $NaBH_4$ gave only $HFe(CO)_2(C_5H_5)$, reduction of the $P(C_6H_5)_3$-substituted cation $[Fe(CO)_2(C_5H_5)P(C_6H_5)_3]^+$ did yield $(C_5H_6)Fe(CO)_2P(C_6H_5)_3$ (**89**) (*157*). A similar effect of phosphine substitution has been observed upon reduction of these cations with aryllithium (*583*).



(89)

The π complex $(C_5H_6)Fe(CO)_3$ has been prepared directly, however, in 30% yield by reaction of the diene with $Fe_2(CO)_9$ at 40°C (*363*). It is characterized by a strong infrared band at 2805 cm^{-1} attributed to the C–H (exo) stretching mode (*68*) and decomposes at 140°C to $[Fe(CO)_2(C_5H_5)]_2$ supporting the view (*157*, references 2 and 3) that it is an intermediate in the reaction of cyclopentadiene with $Fe(CO)_5$ which leads to the binuclear species. The stability of $(C_5H_6)Fe(CO)_3$ suggests that the reduction of $[Fe(CO)_3(C_5H_5)]^+$ to $HFe(CO)_2(C_5H_5)$ proceeds via direct attack of the hydride ion on the metal rather than initial attack at the C_5H_5 ring followed by transfer to the metal. The reduction of $[Fe(CO)_2(C_5H_5)P(C_6H_5)_3]^+$ must involve, on the other hand, attack of the hydride ion at the cyclopentadienyl ring to yield the diene complex.

Similarly, with spiro[4.4]nona-1,3-diene and spiro[2.4]hepta-4,6-diene, $Fe(CO)_5$ produces the π-cyclopentadienyl-type binuclear complexes (*248*, reference 3), while $Fe_2(CO)_9$ affords the π complexes (**90**) and (**91**), respectively. With the latter olefin, the complex of structure



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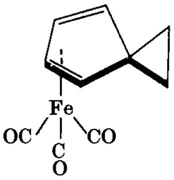

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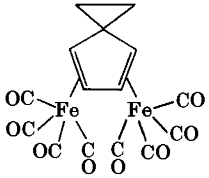
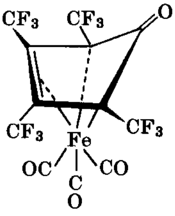


(92)

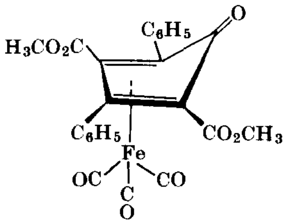
(**92**) is also obtained (*166*); upon standing at room temperature it rearranges to (6-methylfulvene)$Fe_2(CO)_6$. A ring-opening mechanism involving an initial hydrogen transfer to the metal has been suggested (*166*) for the rearrangement. It is possible (*166*) that the previously mentioned ring opening of vinylcyclopropanes upon reaction with $Fe(CO)_5$ may also involve a metal hydride intermediate rather than formation of an iron–carbon σ bond (*513*).

The products arising from reaction of alkynes with iron carbonyls are dependent upon the medium (*76*), but contain, in general, a cyclic olefin formed from the combination of two or three acetylene molecules with either a carbonyl group or an iron atom. Thus, with $Fe(CO)_5$, perfluoro-2-butyne produces the tetrasubstituted cyclopentadienone complex $[C_5(CF_3)_4O]Fe(CO)_3$ (*75*) which can be prepared also by direct interaction of the dienone with $Fe(CO)_5$ (*171*). A structural analysis (*38*) shows a nonplanar ring with a bending angle of about 20° and with metal-sp^2-carbon atom distances of 1.99 to 2.12 Å. These distances as well as the carbon–carbon bond lengths suggest again both σ and π bonding (**93**) between the metal and olefin.



(93)

Methyl phenylpropiolate $(C_6H_5)C{\equiv}CCO_2CH_3$ upon reaction with $Fe_2(CO)_9$ yields four complexes (*155*), one of which has been identified as the substituted cyclopentadienone complex $[C_5(C_6H_5)_2(CO_2CH_3)_2O]Fe(CO)_3$ (**94**). The olefinic ligand presumably arises from a head-to-tail condensation of the unsymmetrically substituted acetylene. By contrast, treatment of pentafluorophenylacetylene with $Fe(CO)_5$ gives only the 2,5-disubstituted cyclopentadienone complex $[C_5H_2(C_6F_5)_2O]Fe(CO)_3$, (**95**) (*172*). In this instance the ligand must result from a head-to-head condensation of the acetylene.



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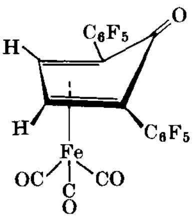
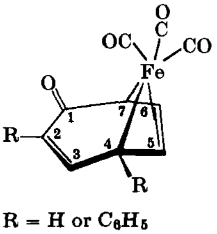


(95)

The complex $(C_6H_6CO)Fe(CO)_3$ can be obtained either by direct reaction of tropone with $Fe_3(CO)_{12}$ (*178*) or by reaction of acetylene with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ (*598*). The comparable complex of 2,4,6-triphenyltropone has also been obtained from phenylacetylene and $Fe_3(CO)_{12}$ (*297*). Because of the asymmetry in substitution of the latter tropone, two isomeric complexes, melting at 156°–158° and 162°–165°C, have been obtained. In solution at room temperature an isomerization equilibrium is attained (*80*).

Although on the basis of molecular orbital calculations and analogy with the cyclopentadienone complexes it has been suggested (*549*, reference 5) that the iron atom is bonded equally to the three double bonds of a planar tropone ring, Weiss and Hübel (*598*) have concluded from chemical evidence that the iron interacts with only two of these double bonds. Structural analysis of $(C_6H_6CO)Fe(CO)_3$ (*178*) and the higher melting isomer of $[2,4,6\text{-}(C_6H_5)_3C_6H_3CO]Fe(CO)_3$ (*549*) has established that the iron atom is indeed associated with only four carbon atoms and that the ring is nonplanar (**96**), with an angle between the planes describing the ring of 47° ($R = H$) and 41° ($R = C_6H_5$), respectively. In both complexes the C-5–C-6 bond distance (~1.39 Å) and the Fe–C-4–C-7 bond distances (2.09–2.17 Å) are quite comparable.

Even though the X-ray data suggest the presence of two σ bonds and one π bond between metal and olefin as was postulated for the butadiene–iron carbonyls, the UV spectra of the triphenyltropone complexes closely resemble that of the free olefin (*80*) suggesting that the bonding of the complex may indeed be intermediate between that of structure (**96**) and simple π bonding to two olefinic double bonds (*80*). This concept is more fully discussed in the section on cobalt (Section VII, A).



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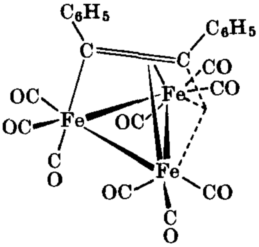
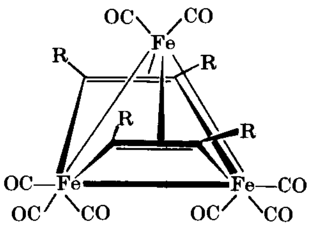


(97)

Diphenylacetylene reacts with $Fe_2(CO)_9$ in petroleum ether at room temperature to give, in addition to the known compounds $[C_2(C_6H_5)_2]_2Fe_2(CO)_6$ and $[C_4(C_6H_5)_4CO]Fe_2(CO)_6$ (*65*, *297*), a low yield of $[C_2(C_6H_5)_2]Fe_3(CO)_9$ (*71*). A structural analysis (*71*) of this species reveals that it can be regarded as resulting from displacement by the acetylene ligand of one terminal and two bridging carbonyls in $Fe_3(CO)_{12}$ (**97**). In accordance with the carbon–carbon distance of 1.41 Å, the diamagnetism of the electron-deficient molecule has been accounted for by considering the ligand as a π-coordinated olefin (*71*).

Reaction of this complex with an excess of diphenylacetylene produces under mild conditions the violet isomer of the known (*297*) compound $[C_2(C_6H_5)_2]_2Fe_3(CO)_8$ which rearranges (*297*) to the more stable black isomer (*71*). In the violet complex the acetylenic ligands are separately located on opposite sides of the triangular iron fragment, each being σ-bonded to the two $Fe(CO)_3$ groups and π-bonded to the $Fe(CO)_2$ group (**98**) (*179*). The average distance of the π-bonded Fe from the sp^2-carbons is 1.98 Å. The crystal structure of the black isomer (*179*) indicates that rearrangement of the violet complex involves formation of a ferracyclopentadiene ring (**99**), and π bonding of each of the olefinic double bonds to equivalent iron atoms on either side of the ring.



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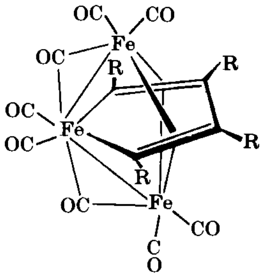
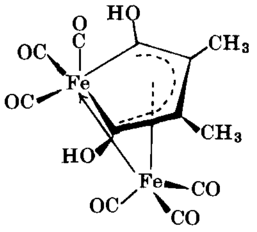


(99)

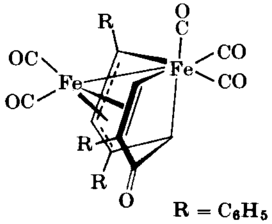
The distance from these iron atoms to the sp^2-carbons is about 2.14 Å. A similar type of ferracyclic ring formation (**100**) has been observed (*292*)



(100)

in the product obtained from the interaction of 2-butyne with an alkaline solution of $Fe(CO)_5$. The analogous compound (1,1,1-tricarbonyl-2,5-dimethoxyferracyclopentadiene)tricarbonyliron (*47*, *79*) reacts with *N*,*N*-dichloro-*p*-toluenesulfonamide to yield a novel iron carbonyl complex with a 1-aza-2-ferracyclohexadiene ring attached to an $Fe(CO)_3$ group via π-allylic bonding (*82*). This series of compounds illustrates the bond-breaking and bond-formation process resulting from the stereochemical requirement of the alkyne to form the complex involving most effective overlap of metal and ligand orbitals (*76*).

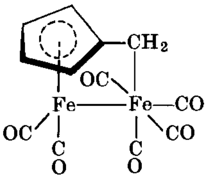
The black phenylacetylene complex $(C_2HC_6H_5)_3Fe_2(CO)_6$ (*297*) has been shown (*342*) to have the novel structure (**101**) which indicates the



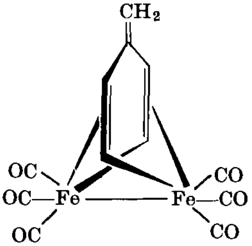
(101)

condensation of three phenylacetylene molecules with an iron atom and a carbonyl group to form a bicyclic[3.3,0] ring with the iron atom at one of the bridgehead positions. The ring is attached to an $Fe(CO)_2$ group through a π bond, a π-allylic bond, and a metal–metal bond.

Acetylene also reacts with $Fe_3(CO)_{12}$ to yield a red complex melting at 140°C and an orange complex melting at 62°C, both of which have the composition $(C_2H_2)_3Fe_2(CO)_6$ (*47*, *599*). The red complex has the structure (**102**) involving a π-cyclopentadienyl bond (*411*), whereas the orange complex involves a 3-methylene-1,4-pentadiene ligand. The diamagnetism in the molecule has been accounted for by postulation of σ bonding of each of the terminal carbon atoms and π bonding of each of the double bonds to an iron atom (*472*) as shown in structure (**103**). Complexes of composition $(alkyne)_3Fe_2(CO)_6$, analogous to those of structure (**102**) and (**103**), have been obtained (*80*, *81*) also from the interaction of $Fe_3(CO)_{12}$ with phenylacetylene and *p*-bromophenylacetylene, respectively.

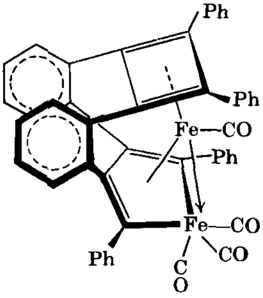


(**102**)



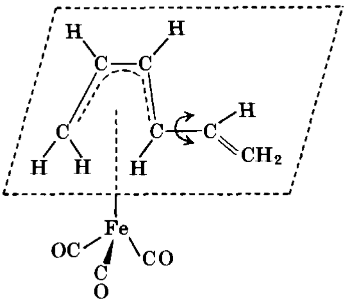
(**103**)

Another interesting complex, $(C_6H_5C{\equiv}C{-}C_6H_4{-}C{\equiv}CC_6H_5)_2$-$Fe_2(CO)_4$, has resulted from interaction of *o*-bisphenylethynylbenzene with $Fe(CO)_5$ for which a preliminary structural analysis has indicated structure (**104**) (*607*).



(**104**)

The reaction of 1,3,5-hexatriene in differing proportions with $Fe_2(CO)_9$ affords $(C_6H_8)Fe(CO)_4$, $(C_6H_8)Fe_2(CO)_8$, $(C_6H_8)Fe(CO)_3$, and $(C_6H_8)Fe_2(CO)_7$ (*425*). The structures (**105**) and (**106**) involving a (butadiene)$Fe(CO)_3$ moiety have been assigned to the last two complexes.



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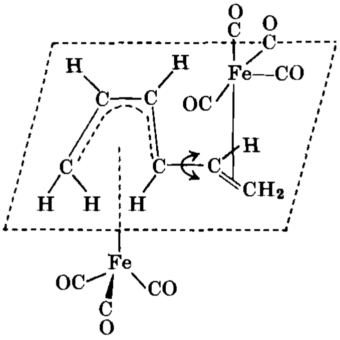
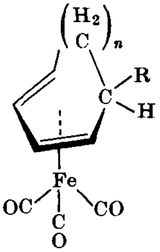


(106)

As with the analogous chromium complexes (*420*), anions (R^-) such as hydride, cyanide, alkoxide, etc., add to cyclohexa- or cycloheptadienyliron complexes to form the substituted species of structure (**107**) (*299*). Reduction of the cycloheptadienyliron cation with zinc dust



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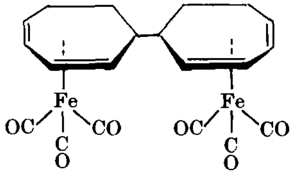
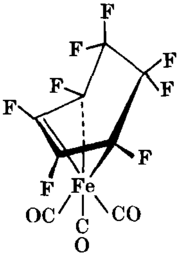


(108)

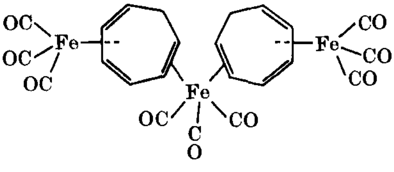
yields the dimeric complex (**108**) (*279*). This latter species has also been prepared (*386, 387*) by reaction of the cation with NaOH.

The reaction of $Fe(CO)_5$ with nonconjugated hexadienes results in isomerization of the olefin to give stable complexes with the conjugated ligands. Thus, 1,4-cyclohexadiene and 1, 5-hexadiene produce $(1,3\text{-}C_6H_8)Fe(CO)_3$ (*622*) and a mixture of $(1,3\text{-}C_6H_{10})Fe(CO)_3$ and $(2,4\text{-}C_6H_{10})Fe(CO)_3$, respectively (*17, 62*). Octafluoro-1,4-cyclohexadiene undergoes a similar isomerization upon reaction with $Fe_3(CO)_{12}$ to give colorless crystals of (1,3-C_6F_8)Fe$(CO)_3$ (*293*) in which the coordination again appears to involve two σ bonds and one π bond between the metal atom and a 1,3-butadiene moiety and the ring of the olefin is bent through about 47° (**109**) (*112*). From the interaction of $Fe_3(CO)_{12}$ with 1-methoxy-1,4-cyclohexadiene, however, the complex of the 1,4-diene $(C_6H_7OCH_3)Fe(CO)_3$ has been isolated in about 24% yield (*61*).



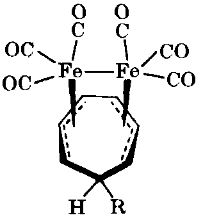
(**109**)

The reaction of 1,3-cyclohexadiene with $FeCl_3$ in an ether solution of iso-C_3H_7MgBr produces the complex with mixed ligands (1,3-C_6H_8)Fe-(C_6H_6) (*204*). Similarly by irradiation of $FeCl_3$ with a mixture of 1,3,5-cycloheptatriene and 1,3-cycloheptadiene in the presence of iso-C_3H_7MgBr, Fischer and Müller (*206*) have prepared the air-sensitive and thermally unstable complex with mixed ligands (1,3,5-C_7H_8)(1,3-C_7H_{10})Fe. $Fe(CO)_5$ reacts with cycloheptatriene to produce not only



(**110**)

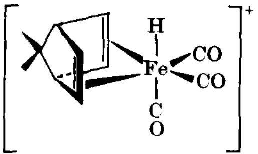
$(C_7H_8)Fe(CO)_3$ but also the diene complex $(C_7H_{10})Fe(CO)_3$ (*60*) and a trinuclear complex for which structure (**110**) has been suggested (*470*). Formation of the diene complex in this reaction obviously involves a rather uncommon intermolecular hydrogen transfer (*470*). The reaction of $Fe_2(CO)_9$ with either 1,3,5-cycloheptatriene or its 7-methoxy derivative yields the complex (triene)$Fe_2(CO)_6$ (*190*), the Mössbauer spectrum of which shows chemically equivalent iron atoms. This, with the NMR spectrum, suggests the structure (**111**) in which the $Fe(CO)_3$ groups are linked through the iron atoms which, in turn, are each coordinated to the ring through a π-allylic bonding. The cation $[(C_7H_7)Fe_2(CO)_6]^+$, obtained by reaction of the cycloheptatriene complex with trityl tetrafluoroborate, shows in solution a rapid valence tautomerism involving diene bonding to an iron atom and π-allylic bonding to the other.



(**111**)

Upon reaction with $[Fe(CO)_3CH_3S]_2$ in boiling benzene, norbornadiene replaces two carbonyl groups to yield $(C_7H_8)Fe(CO)_4(CH_3S)_2$ (*349–351*).

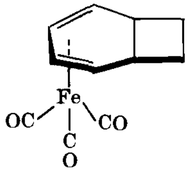
In a strongly acidic solution, (norbornadiene)$Fe(CO)_3$ undergoes protonation at the iron atom (*191*) to give structure (**112**). Its NMR spectrum shows a peak at $\tau = 17.3$ ppm attributable to the metal hydride. Several 7-substituted norbornadienes are stabilized by formation of their iron tricarbonyl complexes (*299*, *373*). The 7-norbornadienyl cation is destabilized, however, by complex formation (*299*); this is the first example of destabilization of a carbonium ion by attachment to a transition metal and probably results from inhibition in the complex of the homoallylic interactions which stabilize the free cation (*299*).



(**112**)

With several of the transition metals, i.e., Mo, W (*375*), Rh (*499*), Pd, or Pt (*233*), 1,5-cyclooctadiene forms a π complex quite normally, while the 1,3-diene undergoes isomerization to produce the 1,5-diene complex. Treatment of 1,5-cyclooctadiene with $Fe(CO)_5$, yields, however, no stable π complex, but results in quantitative isomerization of the olefin to the 1,3-diene (*17*). Because of this ready isomerization, it has been suggested (*470*) that the thermally unstable complex $(C_8H_{12})Fe(CO)_3$ obtained from the reaction of 1,5-cyclooctadiene with either $Fe_3(CO)_{12}$ in benzene or with $Fe(CO)_5$ in sunlight may indeed be the complex of the 1,3-diene. Although direct reaction of the 1,3-diene with $Fe(CO)_5$ does not yield a stable complex (*17*), the complexes of 1,3-cycloheptadiene and 1,3-cyclohexadiene have been reported (*47*). Only very recently has the isolation of $(1,5\text{-}C_8H_{12})Fe(CO)_3$, m.p. 61°–63°C, been mentioned (*152*, footnote 6).

A mixture of 1,3,5- and 1,3,6-cyclooctatrienes reacts with iron carbonyl to give the complexes (bicyclooctadiene)$Fe(CO)_3$ (**113**), (cyclooctatriene)$Fe(CO)_3$, and $(C_8H_{10})Fe_2(CO)_6$ (*430*, *470*). It was suggested



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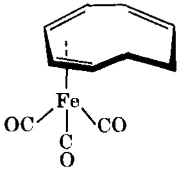
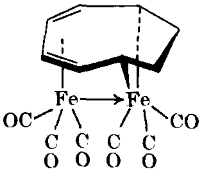


(114)

originally on the basis of relative stability of the isomers (*470*, reference 64) and subsequently confirmed by NMR spectroscopy (*401*) that $(C_8H_{10})Fe(CO)_3$ involved the 1,3,5-isomer (**114**). Although it was at first thought (*345*) that the orange-red binuclear complex $(C_8H_{10})Fe_2(CO)_6$ had the structure (**115**), a subsequent study of the Mössbauer spectrum (*190*) indicated the structure (**116**), analogous to structure (**111**), ob-



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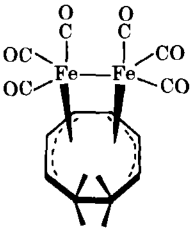
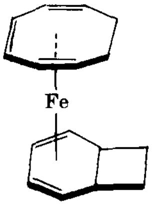


(116)

tained with 1,3,5-cycloheptatriene. A complex with mixed olefinic ligands, (1,3,5-cyclooctatriene)(bicyclo[4.2.0]octa-2,4-diene)iron (**117**), is obtained by UV irradiation of a mixture of $FeCl_3$, iso-C_3H_7MgBr, and 1,3,5-cyclooctatriene in ether. The diamagnetism in the complex is accounted for by involving bonding of the iron to all three double bonds in the cyclooctatriene ligand (*418*).



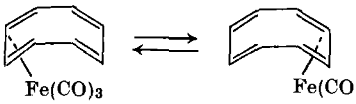
(117)

King (*345*) and Schrauzer and Thyret (*531*) have studied the reaction of 2,4,6-cyclooctatrienone and $Fe_3(CO)_{12}$ from which $(C_8H_8O)Fe(CO)_3$ and $(C_8H_8O)Fe_2(CO)_6$ have been obtained. Although both schools report identical infrared data for $(C_8H_8O)Fe(CO)_3$, they show remarkably different melting points and NMR data. It appears, however, that the $Fe(CO)_3$ group is coordinated to only two double bonds with perhaps a structure similar to that of (tropone)$Fe(CO)_3$ (**96**) rather than that of a bicyclodienone complex. The spectral data indicate that $(C_8H_8O)Fe_2(CO)_6$ may, on the other hand, have a structure similar to that of $(C_8H_{10})Fe_2(CO)_6$ (**116**).

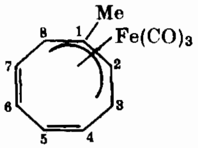
The reaction of cyclooctatetraene with $Fe(CO)_5$ produces the complexes $(C_8H_8)Fe(CO)_3$, $(C_8H_8)Fe_2(CO)_6$, and $(C_8H_8)Fe_2(CO)_7$ (*268*, reference 152). Complexes of substituted cyclooctatetraene have been similarly synthesized (*331*, *429*). Since their preparation in 1959 (*268*, references 152, 168, and 180) and especially since the reports of their crystal structure (*170*, *170a*), the nature of the bonding in $(C_8H_8)Fe(CO)_3$ and $(C_8H_8)Fe_2(CO)_6$ has been of particular interest to a number of investigators (*226*, *470*). Whereas chemical behavior and NMR and infrared spectra (the latter shows no C=C stretching bands) indicate a planar cyclooctatetraene ring in $(C_8H_8)Fe(CO)_3$, X-ray diffraction establishes that only six of the carbon atoms are coplanar and that the $Fe(CO)_3$ group is coordinated with the 1,3-diene moiety out of that plane. It was suggested (*170a*) that the single NMR absorption at $\tau = 5.76$ ppm could be explained by rapid migration of the $Fe(CO)_3$ group around the ring, probably involving, in turn, the various 1,3-diene positions. More detailed infrared investigations (*39*, *140*) have established, however, that the complex molecule has C_s symmetry and that the C–H stretching region in the solution spectrum is quite different from that in the solid, resembling more closely that of $(C_8H_8)PtI_2$ for which coordination through the 1,5-double bonds has been suggested (*268*). This result hence led to the conclusion (*140*) that in solution $(C_8H_8)Fe(CO)_3$ probably involves the 1,5-coordination.

Disagreement in interpretation of the low temperature NMR spectrum of $(C_8H_8)Fe(CO)_3$ has led to some further controversy regarding its structure in solution. The spectrum displays at $-140°$ to $-160°C$ two broad bands of equal intensity at $\tau \approx 4$ and 5.4 ppm, the latter having a shoulder on the high field side (*140*, *366*). Winstein and co-workers (*366*) have assigned the band at 5.4 ppm to the four protons in the coordinated 1,3-diene moiety and, because of the breadth of the bands at $-150°C$, have concluded that the 1,5-coordination should be ruled out. Cotton *et al.* (*140*), on the other hand, argue that the observed spectrum cannot arise from 1,3-coordination of C_8H_8, but that it is quite in accord with the 1,5-coordination suggested by their infrared studies. They attribute the shoulder on the high field band to a slight nonequivalence of the protons at the coordinated double bonds due to the C_s symmetry of the molecule.

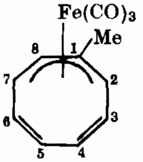
Although they agree with the 1,3-coordination, Pettit and co-workers (*333*) have suggested, on the basis of their study of the low-temperature NMR spectrum of the 1-methylcyclooctatetraene complex, that isomerization via a 1,5-shift (**118a**, **b**), still occurs at $-150°C$ and that at least two types of degenerate valence tautomerism are involved in the rearrangement in order to account for the single absorption in the room temperature spectrum. Winstein *et al.* (*11b*) question this interpretation, however, since reinvestigation of the NMR spectra of $(C_8H_7CH_3)Fe(CO)_3$ (*11b*) and its deuterated derivatives (*11a*) indicate that the $Fe(CO)_3$ group is attached at either the 3,2,1,8- or the 2,1,8,7-positions (**119a**, **b**). This 1,2-shift isomerization mechanism maintaining the 1,3-coordination at each step has been further substantiated by Breslow and co-workers (*262*) who have studied the NMR spectra of $(C_8H_8)Fe(CO)_3$ and of two 1,2-disubstituted complexes. Furthermore,



(**118a**) (**118b**)



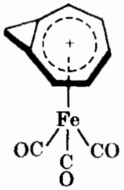
(119a)



(119b)

the Mössbauer spectra (*118*, *262*) of both the frozen solution and the crystalline complex of $(C_8H_8)Fe(CO)_3$ and $(C_8H_6R_2)Fe(CO)_3$ are all very similar.

The complex $(C_8H_8)Fe(CO)_3$ does not decompose in concentrated acids, but is protonated to yield the cation $[(C_8H_9)Fe(CO)_3]^+$ (**120**) (*158*, *159*). Comparison of the NMR spectrum of this cation with that of $[(C_8H_8D)Fe(CO)_3]^+$ indicates that the added proton becomes one of the



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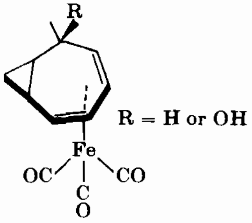
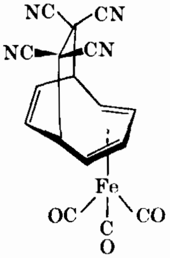


(121)

methylene hydrogen atoms (*159*). The cation is reduced with $NaBH_4$ in tetrahydrofuran (*158*, *159*) or with NaOH in aqueous acetone (*295*) to produce (bicyclo[5.1.0]octa-2,4-diene)tricarbonyliron (**121**) (R = H) or its hydroxy analog, respectively.

Although $(C_8H_8)Fe(CO)_3$ is inert to catalytic hydrogenation (*47*), it interacts with tetracyanoethylene in benzene at room temperature to give the Diels–Alder adduct (**122**). By a similar Diels–Alder addition



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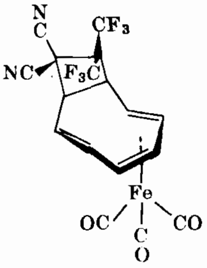
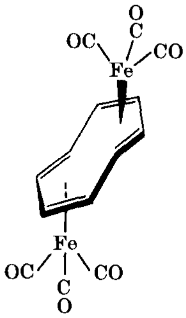


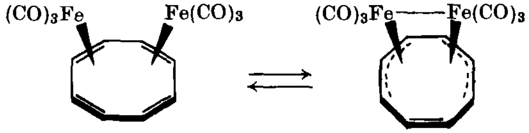
(123)

of substituted acetylenes to $(C_8H_8)Fe(CO)_3$, derivatives of bicyclo[4.2.2]deca-2,4,7,9-tetraene have been obtained (*367*). The reaction of $(CF_3)_2C{=}C(CN)_2$ with $(C_8H_8)Fe(CO)_3$ yields (*251*), on the other hand, the complex (**123**) resulting from 1,2-addition to the C_8H_8 ring.

With $Fe_2(CO)_9$, cyclooctatetraene produces (*332*), in addition to $(C_8H_8)Fe(CO)_3$, three isomeric complexes of composition $(C_8H_8)Fe_2(CO)_6$ one of which is identical to that obtained with $Fe(CO)_5$ (*268*, reference 152) for which the trans structure (**124**) has been established (*170a*). Infrared, NMR, and Mössbauer spectra (*190*, *332*, *602*) all suggest the



(**124**)



(**125**) (**126**)

cis structures (**125**) and (**126**) for the remaining two isomers, the former being similar to structure (**124**), whereas the latter is more analogous to the $(triene)Fe_2(CO)_6$ (**116**). The NMR spectra indicate that in solution an equilibrium between isomers (**125**) and (**126**) is established.

Heating of either isomer (**125**) or (**126**) in CCl_4 or C_6H_6 produces shiny black crystals of composition $(C_8H_8)Fe_2(CO)_5$ having a marked resemblance (*382*) to those of $(C_8H_8)Fe_2(CO)_7$ isolated (*47*, reference 173) from the reaction of C_8H_8 with $Fe(CO)_5$. The NMR spectrum of this complex has a single band at $\tau = 5.33$ ppm. A structural analysis (*222*) of $(C_8H_8)Fe_2(CO)_5$ shows (Fig. 3) that the molecule is bisected by a mirror plane through C-4 and C-8. The iron atoms, each of which carries two terminal carbonyls, are linked via a metal–metal bond and a bridging carbonyl, the latter lying in the mirror plane. The interatomic distances suggest π-allylic bonding of each iron to three carbon atoms, e.g., C-5, C-6, and C-7 and interaction of each of C-4 and C-8 with both iron atoms through electron-deficient three-center bonds.

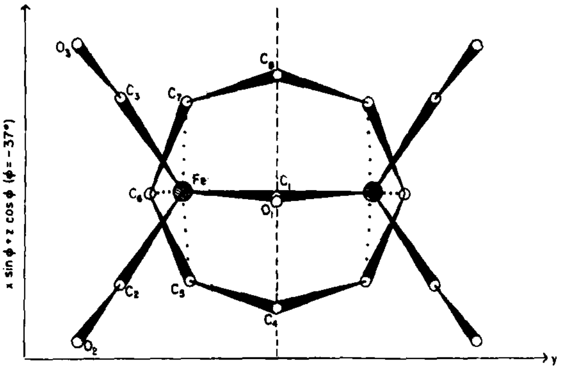
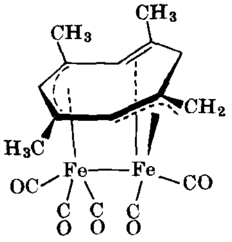
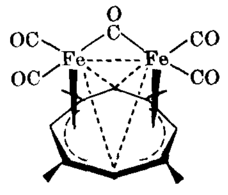


FIG. 3. Molecular structure of $(C_8H_8)Fe_2(CO)_5$ (*222*).

The reaction of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with 1,3,5,7-tetramethylcyclooctatetraene (TMCOT) in refluxing octane yields four π complexes (*145*). The first, a yellow oil of composition $(C_{12}H_{16})Fe(CO)_3$, is thought to be a complex of tetramethylbicyclooctatriene with bonding analogous to that of structure (**113**); the second, comprising yellow crystals of $(TMCOT)Fe_2(CO)_6$, is the TMCOT analog of *trans*-$(C_8H_8)Fe_2(CO)_6$ (**124**); the third, obtained as a low yield of red crystals, and the fourth, black crystals, are isomers of $(TMCOT)Fe_2(CO)_5$. The red isomer, has been shown by structural analyses (*146*) to be (1,3,5-trimethyl-7-methylene-1,3,5-cyclooctatriene)pentacarbonyliron (**127**). In this complex the isomerized TMCOT ring is bonded to $Fe(CO)_3$ through a π-allylic linkage and to $Fe(CO)_2$ through both a double bond in the ring and a π-allylic segment involving the 7-methylene group, with an Fe–Fe bond accounting for the observed diamagnetism. The Fe–C distances range from 2.08 to 2.17 Å for the π-allylic bonding and are 2.21 and 2.28 Å for coordination at the double bond.



(**127**)

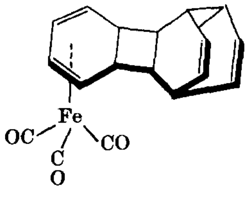


(**128**)

The black isomer is in every respect analogous to $(C_8H_8)Fe_2(CO)_6$. Although the methyl substitution offers the possibility for two isomeric structures, that having the methyl groups at the terminal carbons of the π-allylic segments (**128**) prevails in the solid state (*144*). The NMR spectrum of the complex in solution shows, however, only one band for the ring protons suggesting again valence tautomerism via a 1,2-shift (*144*).

With $Fe_2(CO)_9$ in refluxing hexane, TMCOT produces in low yield orange crystals of $(TMCOT)Fe_2(CO)_6$ which readily loses CO to yield compound (**128**) (*145*). A comparison of NMR and infrared spectra indicates that this complex is analogous to *cis*-$(C_8H_8)Fe_2(CO)_6$ (**126**) (*332*). From this reaction, the complex $(TMCOT)Fe(CO)_3$ was not obtained (*145*).

Under UV irradiation cyclooctatetraene adds to $(C_8H_8)Fe(CO)_3$ to give two mononuclear isomers (**129**) and (**130**) of $(C_{16}H_{16})Fe(CO)_3$ melting at 118° and 172°C, respectively (*524*, *525*). Although (**129**) has a temperature-dependent NMR spectrum (*525*), a preliminary X-ray analysis suggests no valence tautomerism in the solid state (*525*, footnote 20). Since it, as well as $(C_{16}H_{16})Fe(CO)_4$, is also a product of the reaction at 30°C of the cyclooctatetraene dimer (m.p. 76°C) with either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$, it has been assigned the structure shown. Complex (**130**), which has a temperature-independent NMR spectrum, has been shown by X-ray diffraction (*504*, *505*) to involve the dimer of m.p. 53°C (*525*, reference 23), which has been found (*525*) also to produce both (**129**) and (**130**) with $Fe(CO)_5$ under irradiation. As shown, the $Fe(CO)_3$ group is bonded to one of the six-membered rings at a highly conjugated 1,3-diene moiety with iron–carbon distances of 2.07 to 2.14 Å. Since $(C_{16}H_{16})Fe(CO)_4$ (m.p. 112°–114°C) loses CO upon standing in solution to yield (**129**), it has been assigned structure (**131**) (*525*).



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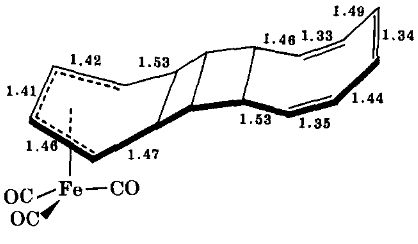

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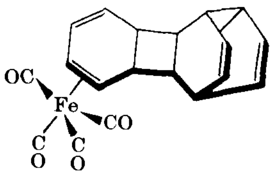

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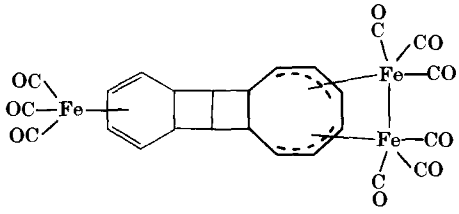
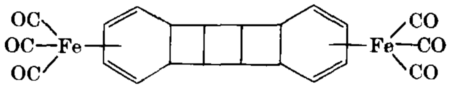


(132)

Reaction at 160°–170°C between the 76°C dimer and $Fe(CO)_5$ (*526*) produces in addition to complex (**129**), the trinuclear complex $(C_{16}H_{16})Fe_3(CO)_9$ (m.p. 170°C), the binuclear species $(C_{16}H_{16})Fe_2(CO)_6$ (m.p. 191°C), and a small amount of another isomer of $(C_{16}H_{16})Fe(CO)_3$ melting at 175°–180°C. On the basis of its Mössbauer spectrum and its temperature-independent NMR spectrum, structure (**132**) has been assigned (*525*) to the trinuclear complex. Thermal decomposition of $(C_{16}H_{16})Fe_3(CO)_9$ yields two isomeric forms of $(C_{16}H_{16})Fe_2(CO)_6$, one identical to that mentioned above and another possessing the same melting point. To these complexes the structures (**133**) and (**134**), respectively, based on NMR data, have been assigned.



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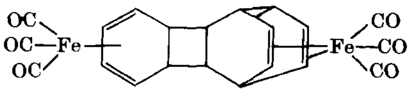
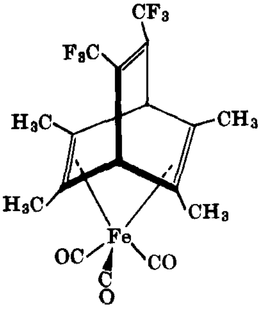


(134)

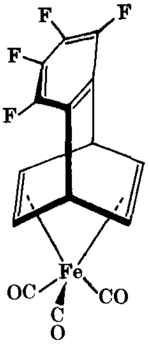
In view of the fact that $(C_8H_8)Fe_2(CO)_6$ exists as trans and cis isomers (**124**) and (**125**), it is reasonable to assume that the binuclear species (**133**) and (**134**) and the trinuclear complex (**132**) of $C_{16}H_{16}$ might have also trans and cis modifications. These have not been distinguished by the investigators.

Although the reaction of bis(trifluoromethyl)tetramethylbicyclo[2.2.2]octatriene with $Mo(CO)_6$ or $Co(CO)_2(C_5H_5)$ gives a single product, e.g., (**168**), its reaction with $Fe(CO)_5$ produces two tricarbonyliron complexes, one with a structure analogous to (**168**) and another with structure (**135**), the latter being the major product (*343*). Similarly, reaction of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with tetrafluorobenzobicyclo[2.2.2]-octatriene under reflux produces an orange-yellow complex (**136**) (*575*).

Bicyclo[3.2.1]octadiene reacts with $Fe(CO)_5$ to yield yellow (bicyclo[3.2.1]octadiene)tricarbonyliron which on treatment with trityl

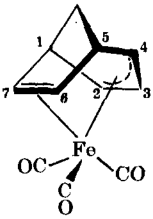


(135)



(136)

fluoroborate produces the corresponding cation (*396*). A structural analyses of the salt (*396*) shows structure (**137**) for the cation with the iron atom coordinated through the isolated C-6–C-7 double bond and



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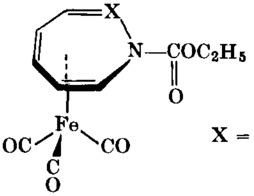


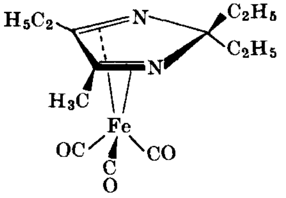
(138)

X = C or N

the C-2–C-3–C-4 segment which resembles an electron-deficient allylic group.

The UV irradiation of ethylazepine-1-carboxylate with $Fe(CO)_5$ gives the orange-yellow tricarbonyliron complex (**138**) (X = C), m.p. 87°C (*212*). Saponification of this complex with a methanolic solution of sodium methoxide affords the air-sensitive, orange complex of the unsubstituted azepine $(C_6H_6NH)Fe(CO)_3$, m.p. 41°–42°C. Similar complexes of 2,4,6-trimethylazepine and its *N*-carbethoxy derivative also have been prepared (*212*). Interaction at room temperature of a solution of ethyl-1*H*-diazepine-1-carboxylate in petroleum ether with $Fe_2(CO)_9$ also gives a complex of structure (**138**) (X = N) (*560*).

Cyclic diazobutadienes react under mild conditions with $Fe_2(CO)_9$ to give air-sensitive, orange-red complexes (*574a*) such as (methyltriethylimidazolenine)tricarbonyliron, m.p. 66°C, for which structure (**139**) has been proposed. The complex (pentamethylpyrrolenine)tricarbonyliron has been similarly prepared (*574a*).



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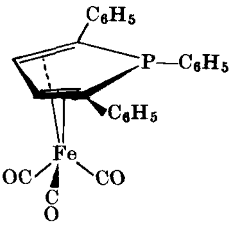
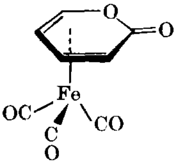


(140)

Triphenylphosphole reacts with $Fe(CO)_5$ in a sealed tube at 140°C to yield the red complex of structure (**140**). The analogous complex of triphenylphosphole oxide has also been isolated. By contrast the reaction of the phosphole with $Fe_2(CO)_9$ under mild conditions yields the P-bonded complex $[C_4H_2P(C_6H_5)_3]Fe(CO)_4$ (*124*).

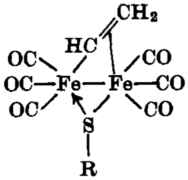
The irradiation of α-pyrone in the presence of $Fe(CO)_5$ results in formation of (cyclobutadiene)tricarbonyliron and the yellow (α-pyrone)-tricarbonyliron, m.p. 140°–141°C (**141**). This latter complex can also be prepared by reaction of the pyrone with $Fe_2(CO)_9$ in warm heptane (*506*). Similar complexes of substituted α-pyrones have also been reported (*294*).



(141)

The interaction of vinyl sulfides, $RSCH{=}CH_2$ ($R = CH_3$, C_2H_5, or $CH{=}CH_2$), with $Fe_3(CO)_{12}$ affords red complexes of composition $(RSCH{=}CH_2)Fe_2(CO)_6$ which appear to result from breaking of the sulfur–carbon bond and to involve both a vinyl group and a RS group as bridging ligands between the metal–metal-bonded iron atoms (**142**) (*358*). Similarly, treatment of 2,2′-dithienyl with $Fe_3(CO)_{12}$ gives the red hexacarbonyliron complex (*392*) which by analogy with structure (**142**) and on the basis of its NMR spectrum may have the structure (**143**). One cannot exclude, however, a structure in which the sulfur–carbon bond is still intact (*392*).

Schiff bases with structure (**144**) react readily under mild conditions with $Fe_2(CO)_9$ to form complexes apparently involving a π bond between



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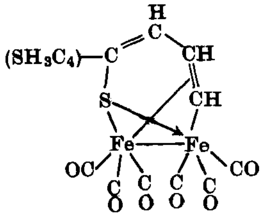
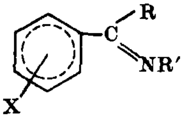


(143)

one of the double bonds in the aromatic ring and an iron atom (*33*). When the Schiff base is prepared from benzaldehyde and *p*-toluidine, Baikie and Mills (*35*) have obtained the complex for which structure (**145**) has been established.



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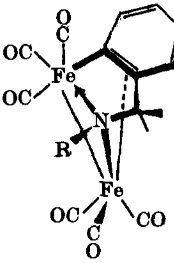


R = MeC_6H_4–

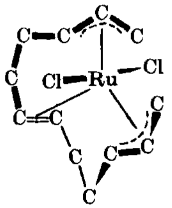
(145)

B. Ruthenium and Osmium

Although ruthenium(II) chloride does not catalyze the hydrogenation of ethylene, an aqueous HCl solution of the salt absorbs ethylene in an amount corresponding to formation of a 1:1 complex (*272*). The kinetics of the process indicate that the complex formation proceeds via an S_N1 mechanism involving initial rupture of a ruthenium–chlorine bond (*272*). By contrast, maleic and fumaric acids are catalytically hydrogenated to succinic acid (*271a*). The reaction intermediate involves both metal–olefin and metal hydride bonds. Tracer studies have shown (*271a*) that the hydrogen atoms involved arise from the solvent rather than from the gaseous hydrogen added.

Catalytic dimerization of acrylonitrile with $RuCl_3 \cdot 3H_2O$ in ethanol at 150°C under hydrogen pressure yields a yellow complex considered (*413*) to be a metal–olefin π complex, while the corresponding reaction under nitrogen pressure produces only the nitrogen-bonded complex $(CH_2CHCN)_3RuCl_3$. The former complex itself catalyzes the dimerization reaction (*413*)

When butadiene is treated with $RuCl_3$ in 2-methoxyethanol at 100°C, yellow-brown crystals of composition $(C_4H_6)_3RuCl_2$ are obtained (*381*). Crystal structural analysis has identified (*381*, *382*) the complex as (2,6,10-dodecatriene-1,12-diyl)dichlororuthenium (**146**), analogous to the nickel complex (**194**) suggested (*608*) as the catalytic intermediate in the nickel-catalyzed cyclic trimerization of butadiene. In this complex, the ruthenium atom has a trigonal-bipyramidal configuration with the chlorine atoms at axial positions and the organic moiety, attached through two π-allylic and one π-olefin bonds, lying in the equatorial plane. Pyrolysis (*445*) of the complex produces a mixture of *all-trans*- and *trans,trans,cis*-1,5,9-cyclododecatrienes.



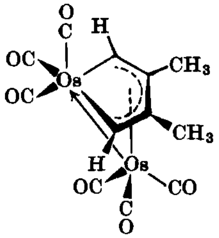
(**146**)

Substitution of isoprene in the above reaction yields a diamagnetic, brownish complex of composition $(C_4H_5CH_3)_2RuCl_2$ (*473*) which has been identified as a chloro-bridged dimer in which the organic ligands are tail-to-tail dimers of isoprene attached to the metal through terminal π-allylic groups.

The reaction between acetylenes and ruthenium carbonyls produces a series of π complexes with cyclic ligands which, as in the iron system, have either the metal or a CO group incorporated into the ring. Accordingly, 3-hexyne (*536*) and hexafluoro-2-butyne (*90*) react with $Ru_3(CO)_{12}$ to give the (substituted cyclopentadienone)tricarbonylruthenium complexes with structures presumably comparable to those of the iron complexes (**93**–**95**). Although diphenylacetylene will not react directly with $Ru_3(CO)_{12}$ to produce this type of complex (*536*), it can be prepared (*90*) by treating $Ru_3(CO)_{12}$ with tetracyclone in benzene under reflux.

Dependent upon the reaction conditions, diphenylacetylene (L) reacts with $Ru_3(CO)_{12}$ to produce either purple $L_3Ru_3(CO)_9$ or yellow $L_2Ru_2(CO)_6$ (*536*). The former complex produced at 70°C in hexane probably has the structure of $Ru_3(CO)_{12}$ with one CO ligand at each ruthenium atom replaced by a diphenylacetylene molecule, whereas the latter complex obtained at 200°C in decalin probably has a structure similar in form to structure (**100**). The analogous reaction with *p,p'*-dichlorodiphenylacetylene (L') produces dark red $L'_3Ru_3(CO)_9$ and orange $L'_2Ru_3(CO)_8$ for which a structure similar to that of the black isomer of $[O_2(C_6H_5)_2]_2Fe_2(CO)_8$ has been proposed (*536*).

The colorless sublimable complex $[C_4H_2(CH_3)_2]Os_2(CO)_6$ obtained from the reaction of $Os_3(CO)_{12}$ with 2,3-dimethylbutadiene (*194a*) has the structure (**147**) with one metal atom incorporated into a five-membered ring (*178a*). The prime difference between this structure and that (**100**) of $(CH_3C{\equiv}COH)_2Fe_2(CO)_6$ is that the π-coordinated $Os(CO)_3$ group is rotated through 60° relative to the corresponding $Fe(CO)_3$ group. Consequently, while the coordination polyhedron of the iron atom is a distorted trigonal prism (*292*) that of the osmium atom is a distorted octahedron (*178a*). In both cases, the metal atom in the ring has a distorted octahedral configuration.

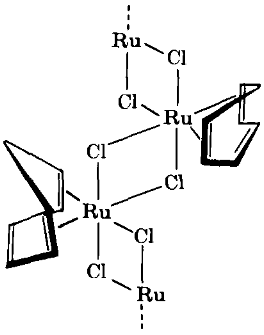


(**147**)

With $RuCl_3$ in ethanol, 1,3-cyclohexadiene undergoes dehydrogenation to form a polymeric benzene complex $[(C_6H_6)RuCl_2]_x$ (*619*). Similar dehydrogenation of 1,3-cyclohexadiene to benzene has been observed upon UV irradiation of MCl_3 [M = Fe (*220*), Ru, or Os (*205*)] or $[(\text{olefin})RuCl_2]_x$ (olefin = norbornadiene or 1,5-cyclooctadiene) (*418*) with the diene in the presence of iso-C_3H_7MgBr from which the mixed olefin complexes $(C_6H_8)M(C_6H_6)$ have been isolated.

With $RuCl_3$ and cycloheptatriene a polymeric complex $[(C_7H_8)RuCl_2]_x$, soluble only in dimethyl sulfoxide, is obtained (*619*). The complex has been assigned the structure (**148**) in which the olefin molecule assumes the boat configuration with coordination at the 1,5-double bonds (*619*). Upon UV irradiation in the Grignard system 1,3,5-cycloheptatriene and $[(\text{olefin})RuCl_2]_x$ (olefin = norbornadiene or 1,5-cyclooctadiene) react to produce $(1,3,5\text{-}C_7H_8)(\text{olefin})Ru$ (*418*).

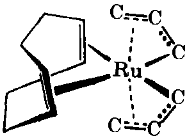
The deep red solution of ruthenium carbonyl, obtained by passing CO through a refluxing ethanolic solution of $RuCl_3$, slowly reacts with



(148)

norbornadiene at room temperature to afford the stable, insoluble, brick-red complex $[(C_7H_8)RuCl_2(CO)]_2$ (*503*). An attempt to split the chlorine bridges by treatment with pyridine or 3-methylpyridine under vigorous conditions results in replacement of the diene as well (*503*). The comparable reaction of ruthenium carbonyl with 1,5-cyclooctadiene proceeds only upon refluxing to give the brown, insoluble $[(C_8H_{12})RuCl_2(CO)]_2$ (*503*).

The action of allylmagnesium chloride on the polymeric $[(C_8H_{12})RuCl_2]_x$ in refluxing diethyl ether followed by hydrolysis with water produces (1,5-cyclooctadiene)bis(π-allyl)ruthenium(II) in good yield (*482*). The 2-methylallyl analog and the norbornadiene complex $(C_7H_8)Ru(C_3H_5)_2$ have been similarly prepared. NMR spectra suggest for the cyclooctadiene complex the structure (**149**) in which the allylic groups are asymmetrically bonded to the metal atom.



(149)

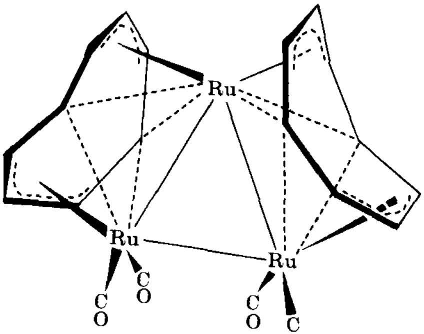
The reaction between $Ru_3(CO)_{12}$ and 1,3-cyclooctatriene has been reported (*97*) to give a yellow complex of composition $(C_8H_{12})Ru_3(CO)_{10}$.

By UV irradiation of a mixture of $RuCl_3$ or $[(\text{norbornadiene})RuCl_2]_x$, 1,3,5-cyclooctatriene, and iso-C_3H_7MgBr in ether, Müller and Fischer (*418*) have prepared (1,3,5-cyclooctatriene)(bicyclo[4.2.0]octa-2,4-diene)ruthenium, analogous to structure (**117**). The irradiation of $[(1,5\text{-}C_8H_{12})RuCl_2]_x$ with the Grignard and 1,3,5-cyclooctatriene affords $(1,3,5\text{-}C_8H_{10})(1,5\text{-}C_8H_{12})Ru$ (*418*). The latter complex can be prepared also by direct interaction of $RuCl_3$ with a 1:1 mixture of 1,5-C_8H_{12} and 1,3,5-C_8H_{10} in the presence of the Grignard (*205*).

Cyclooctatetraene interacts with $Ru_3(CO)_{12}$ in benzene under irradiation (*88, 89*) or in refluxing hexane (*141*) to produce $(C_8H_8)Ru(CO)_3$, m.p. 75°C, and $(C_8H_8)Ru_2(CO)_5$, m.p. ~160°C (decomposes). The $(C_8H_8)Ru(CO)_3$ is isostructural with its iron analog (*141*), and also exhibits a valence tautomerism involving a 1,2-shift mechanism (**119**), while the ruthenium atom is attached to a 1,3-diene segment of the ring (*88, 141*). The relative rates of rearrangement are $(C_8H_8)Fe(CO)_3 > (C_8H_8)Ru(CO)_3$, in reverse order to that observed for the chromium and molybdenum complexes (*347*). The complex $(C_8H_8)Ru_2(CO)_5$ has a structure identical to those of $(C_8H_8)Fe_2(CO)_5$ (Fig. 3) and $(TMCOT)Fe_2(CO)_5$ (**128**).

When carried out in refluxing xylene, the above reaction also produces $(C_8H_8)Ru_2(CO)_6$ (*88*) for which the spectral data suggest (*88, 141*) a structure in solution identical to that of the iron analog (**126**). The ruthenium compound does not appear to undergo the isomerization in solution demonstrated by the iron compound (*332*). A preliminary X-ray analysis (*141*, footnote 11a) establishes, however, that in the solid state the complex does not have the structure (**126**) in that there is no symmetry plane and the Ru–Ru bond is nearly perpendicular to the direction of that suggested for the Fe–Fe bond.

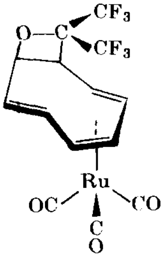
In refluxing octane, the reaction of C_8H_8 with $Ru_3(CO)_{12}$ produces exclusively $(C_8H_8)_2Ru_3(CO)_4$, m.p. 165°–170°C (decomposes) (*141*). This complex can be regarded as a derivative of the parent metal cluster with eight CO groups replaced by two C_8H_8 ligands contributing eight π-electron pairs. The NMR spectrum indicates valence tautomerism in the molecule. An X-ray analysis (*55*) reveals that the mode of bonding between the rings and the metal atoms (**150**) is essentially the same as that in $(C_8H_8)Fe_2(CO)_5$ (Fig. 3) with some distortion caused by intra-



(150)

molecular repulsions. This appears to be the first stereochemically nonrigid molecule with two moving rings (*55*).

As does its iron analog, $(C_8H_8)Ru(CO)_3$ reacts readily at room temperature with $(CN)_2C{=}C(CF_3)_2$ to give the ruthenium analog of the 1,2-addition complex of structure (**123**) together with another complex of composition $[C_8H_8CO(CF_3)_2]Ru(CO)_3$ for which structure (**151**) has been suggested (*251*).



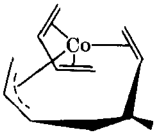
(**151**)

VII. Group VIIIB: Cobalt, Rhodium, and Iridium

A. Cobalt

The passage of allene into a benzene solution of dicobalt octacarbonyl at room temperature produces air-sensitive yellow crystals of composition $[(C_3H_4)Co(CO)_3]_2$ (*428*). The spectral data indicate a π-allyl complex in which a CO grouping has been transferred to the 2-position of each allylic moiety. Although $Co_2(CO)_8$ does not form a π complex with tetraphenylallene, cyclopentadienyldicarbonylcobalt does react under reflux in isooctane to yield the product $[C_3(C_6H_5)_4]Co(CO)(C_5H_5)$ in which the olefin appears to be a monodentate ligand (*434*).

Reduction with $NaBH_4$ of $CoCl_2$ in ethanol solution at −30°C in the presence of 1,3-butadiene results in formation of a complex of empirical formula $C_{12}H_{19}Co$ melting at 35.5°–37°C (*439*). This complex, which catalyzes the dimerization of butadiene to 3-methyl-1,4,6-heptatriene, reacts with CO to produce butadiene and $(C_8H_{13})Co(CO)_3$ (*439*). A crystallographic analysis (*7*) of $C_{12}H_{19}Co$ has shown the conjugated 1,3-butadiene ligand with cisoid conformation and the methylheptadienyl ligand π-coordinated through a terminal vinyl and an allylic grouping (**152**). The carbon atom–cobalt distances indicate that the



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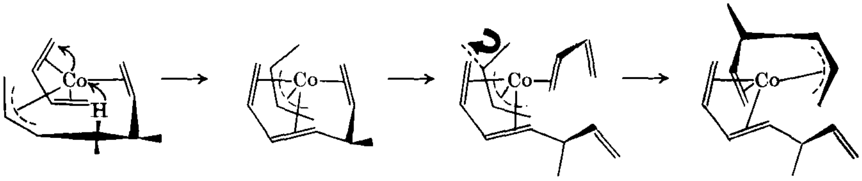
internal carbons of the butadiene molecule and the allylic grouping are closest to the metal at 2.04 and 1.99 Å, respectively. It is possible that $C_8H_{13}Co(CO)_3$ involves only π-allylic coordination of the methylheptadienyl ligand. On the bases of both the molecular structure (*7*) and the chemical reactivity (*439*) of the complex, a mechanism for the catalysis of butadiene dimerization has been suggested (**153**). In step (**153a**) to (**153b**) a hydrogen atom, only 3.10 Å distant from the metal, migrates from the methylcycloheptadienyl ligand to the butadiene ligand, perhaps through an intermediate cobalt hydride, to produce butenyl and 3-methyl-1,4,6-heptatriene ligands. This is probably an equilibrium process if there is no further change of ligand configuration. Through step (**153b**) to (**153c**) another butadiene molecule could then displace the vinyl end group of the triene ligand from the coordination sphere of the metal and in turn, (**153c** to **153d**), react with the butenyl ligand to produce another methylheptadienyl ligand. Still another butadiene molecule could then replace the methylheptatriene and again form the complex of structure (**152**).

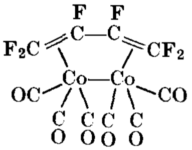


(153a) **(153b)** **(153c)** **(153d)**

Another cobalt complex having only hydrocarbon ligands, (1,3-butadiene)cyclopentadienylcobalt, has been obtained as a volatile red solid melting at 103°–105°C by reaction of the diene with dicyclopentadienylcobalt or (1-benzoyl-1,3-cyclopentadiene)cyclopentadienylcobalt (*489*). The compound decomposes slowly in air.

Although butadiene reacts with $Co_2(CO)_8$ to yield the diene complexes (diene)$CO_2(CO)_6$ and (diene)$_2Co_2(CO)_4$ (*268*), with alkyl- or acylcobalt tetracarbonyls it produces only the π-allylic species, 1-alkyl- or 1-acylmethyl-π-allylcobalt tricarbonyls (*281*). These will react, in turn, with $P(C_6H_5)_3$ which displaces one CO ligand to form monotriphenylphosphine derivatives (*281*).

Reaction of perfluorobutadiene at 100°C with $Co_2(CO)_8$ has produced (*300*) an uncharacterized red nonvolatile substance and yellow, crystalline, diamagnetic $(C_4F_6)Co_2(CO)_6$. Unlike the iron complex $C_4F_6Fe(CO)_4$, which involves σ bonding of the olefin to the metal (*291*, *300*), the cobalt complex involves π-coordinate bridging of the ligand between the two cobalt atoms and a cobalt–cobalt bond (**154**). Upon reaction with ligands such as phosphines or arsines, the metal–metal bond is ruptured producing the paramagnetic species of structure (**155**) (*300*).



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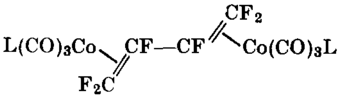
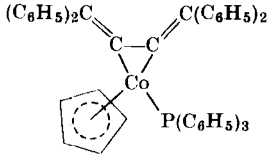


L = $P(C_6H_5)_3$, $P(C_4H_9)_3$, or $As(C_6H_5)_3$

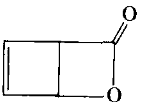
(**155**)

The addition of an excess of isopropylmagnesium bromide to a mixture of $Co[P(C_6H_5)_3](C_5H_5)I_2$ and tetraphenylbutatriene gives reddish-brown crystals melting at 214°C of the compound (**156**) involving two Co–C σ bonds (*341a*). This complexing of butatriene is analogous to that (**79**) obtained with $Fe_2(CO)_9$ (*320*).

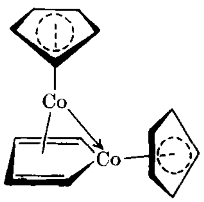


(**156**)

Photolysis of an ethereal solution of photo-α-pyrone (**157**) and cyclopentadienyldicarbonylcobalt yields, in addition to the air-stable, yellow crystalline (cyclobutadiene)cyclopentadienylcobalt, a dark green, air-sensitive crystalline species melting at 121°–122°C with the empirical



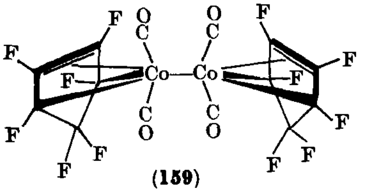
(**157**)



(**158**)

formula $C_{14}H_{14}Co_2$ (*507*). On the basis of the mass, infrared, and NMR spectra the structure (**158**) involving σ bonding of one cobalt atom to the C-4 moiety and dative bonding between the cobalt atoms has been tentatively suggested. The bonding to the metal in this complex is considered to be similar to that in the somewhat analogous iron (**100**) and osmium (**147**) complexes (*507*).

Upon reaction at room temperature with $Co_2(CO)_8$, perfluorocyclopentadiene produces in 65% yield an air-stable, weakly paramagnetic, crystalline, orange-yellow complex $[(C_5F_6)Co(CO)_2]_2$ considered on the basis of spectral data to involve one π and two σ bonds between the metal and olefin (**159**) (*41*). This bonding is quite similar to that observed in (octafluorocyclohexa-1,3-diene)tricarbonyliron (**109**) and [tetrakis(trifluoromethyl)cyclopentadienone]cyclopentadienylcobalt (**162**). Photochemical reaction of this perfluoroolefin with $Co(CO)_2(C_5H_5)$ at room temperature gives a low yield of $(C_5F_6)Co(CO)(C_5H_5)$ consisting of a mixture of two conformational isomers (*41*). The infrared spectrum of this mixture indicates the presence of an uncoordinated double bond (**160**).



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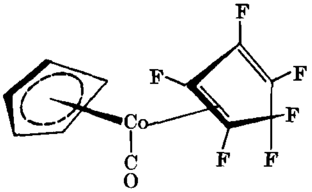

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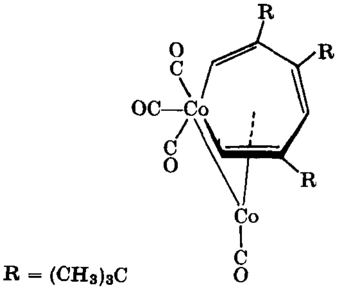
The reaction of excess 3,3-dimethyl-1-butyne with $Co_2(CO)_8$ yields violet crystals of $(C_2HR)_3Co_2(CO)_4$ [$R = C(CH_3)_3$], which upon reaction with a CCl_4 solution of bromine at 0°C produce 1,2,4-tri-*tert*-butylbenzene, the first benzene derivative with ortho *tert*-butyl substituents (*368*). This latter reaction, coupled with the infrared spectral and magnetic moment data, indicates structure (**161**) for the complex.



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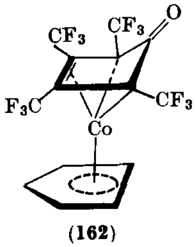
Although it was originally reported (*75*) that the reaction of perfluoro-2-butyne with cyclopentadienyldicarbonylcobalt produced [tetrakis(trifluoromethyl)cyclobutadiene]cyclopentadienylcobalt, a study of the crystal structure of the orange-red air-stable product has shown (*241*) that the complex is instead [tetrakis(trifluoromethyl)cyclopentadienone]cyclopentadienylcobalt. The structure (**162**) with localized σ and π bonds between metal and olefin was postulated (*241*). The carbonyl group of the cyclopentadienone ligand is bent away from the cobalt to produce a dihedral angle of 21° between the planes of the ligand containing the carbon atoms. This bending is somewhat greater than that in the analogous iron tricarbonyl complex (**93**), and much greater than that in (tetramethylcyclopentadienone)cyclopentadienylcobalt (**163**), (*37*, *268*, *527*). Marked bending of the C_5 diene ring occurs also in (1-phenylcyclopentadiene)cyclopentadienylcobalt (*111*) and (1-benzoylcyclopentadiene)cyclopentadienylcobalt (*108*).



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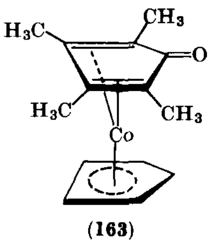

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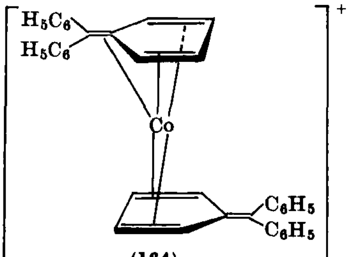
Although in valence bond terminology structures (**162**) and (**163**), in which the cobalt has formal oxidation states of +3 and +1 respectively (*37*), may represent extremes of bonding types with the conjugated diene ligands, the similarity of their electronic absorption spectra (*520*) and the evidence for conjugated diene character in both (*470*) suggests similarity in the bonding. A molecular orbital approach (*108*, *339*) indicates that the prime difference between the complexes may be in the amount of back donation of *d*-electrons from the metal, this being greater when the ligand carries electron-withdrawing substituents. It has been suggested (*108*) that the distortion from planarity of the cyclic diene results from the deformation of the antibonding π orbital necessary to maximize the overlap with the metal *d*-orbital. This distinction between structures (**162**) and (**163**) is very analogous to that between the transition metal complexes of tetrafluoro- or tetracyanoethylene and ethylene, the former having structures indicative of σ bonding to the metal (*461*). With these species also, there is probably a greater back-bonding to the olefin with electron-withdrawing substituents.

A somewhat similar reaction of 3-hexyne with acyltetracarbonylcobalt produces the π-allyl complex 3,4-alkeno-4-lactonyltricarbonylcobalt (*282*).

Bis(6,6-diphenylfulvene)cobalt(I) cation has been isolated as the PF_6^- salt by reaction of the olefin with $CoCl_2$ and isopropylmagnesium bromide followed by hydrolysis and air oxidation (*216*, *217*). On the basis of the infrared and NMR spectra structure (**164**), in which the two ligands are not identically bonded to the metal, has been assigned to the cation.



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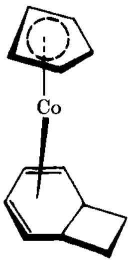
An attempt to prepare the corresponding complex of 6,6-dimethylfulvene via the Grignard reaction resulted in hydrogen addition to yield the bis(π-isopropylcyclopentadienyl)cobalt cation (*216*).

Duroquinone reacts with $Co(CO)_2(C_5H_5)$ to give $[C_6(CH_3)_4C_2]$-$Co(C_5H_5)$. The corresponding complexes of the other transition metals in this group also have been prepared (*521*). These complexes have well-defined electronic spectra and from the infrared spectra it has been concluded that the π-bonded duroquinone molecule must be nonplanar.

Cyclopentadienyldicarbonylcobalt reacted in ethylcyclohexane under reflux with 1,3-cyclohexadiene, norbornadiene, and 1,5-cyclooctadiene yields the corresponding complexes $(C_6H_8)Co(C_5H_5)$, $(C_7H_8)Co(C_5H_5)$, and $(C_8H_{12})Co(C_5H_5)$ (*357*) with no evidence for isomerization of the olefins. When the same reaction is carried out with 1,3,5-cyclooctatriene, however, the product is either (1,3,5-cyclooctatriene)cyclopentadienylcobalt (*401*) or (bicyclo[4.2.0]octa-2,4-diene)-cyclopentadienylcobalt (**165**) (*357*, *401*), dependent upon the conditions employed. This reaction is quite analogous to that of 1,3,5-cyclooctatriene with iron carbonyls (*268*). The reaction of $HgBr_2$ with $(C_7H_8)Co(C_5H_5)$ produces the 1:1 adduct $(C_7H_8)Co(C_5H_5)\cdot HgBr_2$ (*123*) which is probably a Lewis acid: base adduct involving Hg–Co bonds and Hg–Br bridging.

The trityl cation as the tetrafluoroborate reacts with (1,3-cyclohexadiene)cyclopentadienylcobalt to produce $[(C_6H_6)Co(C_5H_5)]^{2+}$ (*220*)



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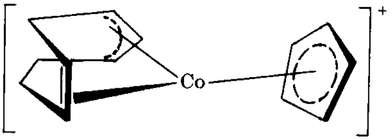
and with the corresponding complex of 1,5-cyclooctadiene to yield predominantly $[(C_8H_{11})Co(C_5H_5)]^+$ (**166**) (*376*). The latter cation has been obtained also by protonation of (1,3,5-cyclooctatriene)cyclopentadienylcobalt in concentrated H_2SO_4 (*401*); it reacts readily with nucleophiles such as cyanide or acetylacetonate to produce substituted diene complexes (**167**) (*376*) and with methylmagnesium iodide to yield



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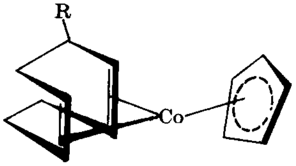

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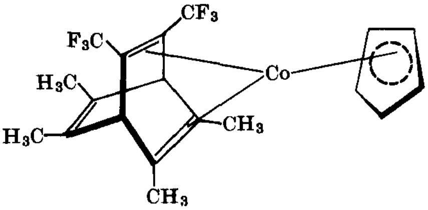
the dimer bis(cyclopentadienyl)-3,3′-bis(cycloocta-1,5-dienyl)dicobalt analogously to the dimerization of chromium (*422*) and iron (*401*) complexes.

Upon treatment with 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen), the 1,3-cyclohexadiene complex $[(C_6H_8)Co(CO)_2]_2$ disproportionates to produce $[CoL_3]^+[Co(CO)_4]^-$ (L = bipy or phen); the analogous norbornadiene complex, however, undergoes only ligand displacement to yield $[Co(CO)_2L]_2$ (*46*).

The complex (tetraphenylcyclobutadiene)iododicarbonylcobalt reacts upon heating with 1,3,5-cycloheptatriene to give the cation [(1,3,5-cycloheptatriene)(tetraphenylcyclobutadiene)Co]$^+$, isolated as the I^-, PF_6^-, or $[Co(NCS)_4]^{2-}$ salts (*184*). This cation is also very susceptible to nucleophilic attack to yield the π-cycloheptatrienyl complex.

When bis(trifluoromethyl)tetramethylbicyclo[2.2.2]octatriene, obtained from the reaction of durene with hexafluoro-2-butyne, interacts with $Co(CO)_2(C_5H_5)$, the only product obtained is that of structure (**168**) (*343*).



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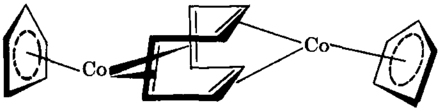
Cyclooctatetraene reacts with $Co(CO)_2(C_5H_5)$ to produce $(C_8H_8)Co(C_5H_5)$ (*158*, *268*, *431*) and $(C_8H_8)[Co(C_5H_5)]_2$ (*227*). Preparation of the complexes by reaction of cyclooctatetraene with cobaltous acetylacetonate and ethoxydiethylaluminum has also been reported (*611*). Spectral data indicate that in the mononuclear complex the olefin is coordinated as a 1,5-diene with the tub conformation (*158*, *226*, *227*, *268*). X-Ray data (*220*) show structure (**169**) for the binuclear complex.



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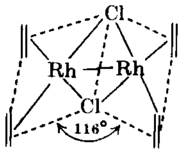
Although at room temperature the ^1H NMR spectrum of $(C_8H_8)Co(C_5H_5)$ in *p*-xylene shows no evidence of valence tautomerism, at 133°C all the C_8H_8 protons are equivalent (*452*). It has been suggested (*452*) that this tautomerism may occur between the two different 1,5-diene structures only or may, on the other hand, involve 1,3-coordination as an intermediate for the two 1,5-forms. The NMR spectrum shows as well the production of some $(C_8H_8)[Co(C_5H_5)]_2$ and free C_8H_8 upon heating the solution of $(C_8H_8)Co(C_5H_5)$ (*452*).

B. RHODIUM AND IRIDIUM

The first monoolefin complex of rhodium(I) was reported by Cramer (*148a*) who prepared orange-red crystals of μ-dichloro(tetraethylene)dirhodium(I) $[(C_2H_4)_2RhCl]_2$ by reaction of C_2H_4 with hydrated $RhCl_3$ in aqueous methanol. Single crystal studies (*362*) of the complex have established that the planes containing the square-planar rhodium atoms intersect along the line joining the bridging chlorine atoms with a dihedral angle of 116° (**170**). The rhodium–rhodium distance indicates an



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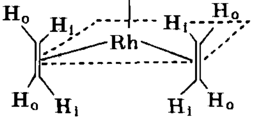
intramolecular metal–metal bond. The reduction of Rh(III) to Rh(I) is accompanied by some oxidation of ethylene to acetaldehyde. The ethylene is quite readily displaced from the rather insoluble complex by such ligands as cyclooctadiene, acrylonitrile or triphenylphosphine. The more soluble but less stable propylene analog has been similarly prepared (*148a*). The rather unstable bromo analog $[(C_2H_4)_2RhBr]_2$ also has been isolated by reaction of ethanolic $RhCl_3$ and excess LiBr with C_2H_4 (*49*). The infrared spectrum of the chloro and bromo complexes show bands at 399 and 393 cm^{-1}, respectively, which have been assigned (*49*) to the Rh–C_2H_4 stretching mode.

The reaction of $[(C_2H_4)_2RhCl]_2$ with C_5H_5Na yields yellow crystals of $(C_2H_4)_2Rh(C_5H_5)$ that melt at 72°C (*344*). The NMR spectrum of this complex at 25°C shows broad bands of equal area at $\tau = 7.23$ and 8.88 ppm due to protons in the coordinated ethylene (*149*, *344*). The probability that the ethylene ligands are equivalent suggests then that each carries two different types of protons. At −20°C, each of these bands in the NMR is split into two pairs of doublets while at 57°C they converge into a single band at $\tau = 8.07$ ppm (*149*). The proton equilibration is considered (*149*) to result from rotation of the ethylene ligand about the axis of the coordinate bond, the energy barrier being about 6 kcal/mole. By comparison of the NMR spectrum with that of $(C_2H_4)_2Rh(acac)$ (acac = acetylacetonate), obtained by reaction of $[(C_2H_4)_2RhCl]_2$ with acetylacetone and KOH at −80°C (*149*), the nonequivalent protons have been identified as those occupying inner (H_i) and outer (H_o) positions (**171**). The NMR spectrum of the 1,5-hexadiene complex (C_6H_{10})-



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$Rh(C_5H_5)$ (*149*) suggests that the protons H_i are the more highly shielded perhaps as a result of long-range shielding by the other coordinated ethylene molecule.

Although neither C_2D_4 nor CO displace ethylene from $(C_2H_4)_2Rh(C_5H_5)$, both displace it readily from $(C_2H_4)_2Rh(acac)$. The different behavior of these complexes is attributed to the fact that in $(C_2H_4)_2Rh(C_5H_5)$, rhodium has an inert gas configuration, whereas in $(C_2H_4)_2Rh(acac)$ it can accommodate another pair of electrons and thus form an activated complex for an S_N2 exchange reaction (*149*).

When equimolar quantities of $[(C_2H_4)_2RhCl]_2$ and $[Rh(CO)_2Cl]_2$ are reacted in benzene solution followed by cooling to −30°C, dark red prisms of $[(C_2H_4)Rh(CO)Cl]_2$ that melt at 113°C are obtained (*480*). This complex probably has a bridged structure very analogous to structure (**170**) with the olefin molecules in trans positions. Addition of dry HCl to a solution of the complex yielded the rhodium(III) product $[Rh(C_2H_5)(CO)Cl_2]_x$ which upon treatment with dimethylphenylphosphine gave $Rh(C_2H_5)(CO)Cl_2[P(CH_3)_2(C_6H_5)]_2$ (*480*).

Displacement of ethylene from $(C_2H_4)_2Rh(acac)$ by excess vinyl chloride and propylene at low temperature has yielded the corresponding complexes $(olefin)_2Rh(acac)$ melting at 42° and 40°C, respectively (*152*).

The stability of a number of rhodium(I)–olefin complexes relative to that of the ethylene complex has been established by spectrophotometric determination of the extent of displacement by another olefin of C_2H_4 from $(C_2H_4)_2Rh(acac)$ in a closed system according to Eq. (4).

$$(C_2H_4)_2Rh(acac) + olefin \rightleftharpoons (olefin)(C_2H_4)Rh(acac) + C_2H_4 \qquad (4)$$

The results, expressed as the equilibrium constant for Eq. (4) at 25°C (Table I) indicate that substitution of ethylenic hydrogen by methyl

TABLE I

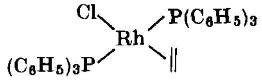
EQUILIBRIUM CONSTANT AT 25°C FOR DISPLACEMENT OF ETHYLENE FROM $(C_2H_4)_2Rh(acac)$[a]

Olefin	K_e	Olefin	K_e
Propylene	0.078	Vinyl chloride	0.17
1-Butene	0.092	Vinyl fluoride	0.32
cis-2-Butene	0.004	1,1-Difluoroethylene	0.10
trans-2-Butene	0.002	*trans*-1,2-Difluoroethylene	1.24
Isobutene	0.0004	*cis*-1,2-Difluoroethylene	1.59
Vinylmethyl ether	0.018	Trifluoroethylene	88
Styrene	0.08	Tetrafluoroethylene	59
Acrylonitrile	>50		

[a] From Eq. (4) (*152*).

groups leads to a lower stability of the complex. A similar (*416*, *621*) but much smaller (*152*) effect has been observed with silver complexes in solution. Substitution by fluorine, however, increases the rhodium complex stability; the stability of the 1,2-difluoroethylene complex is comparable to that of the ethylene complex while that of the tri- or tetrafluoroethylene complex is considerably greater. Since any substituent would offer some steric destabilization, it appears that electronegative substituents strengthen whereas electropositive substituents weaken the coordination of olefins to rhodium(I). It has been concluded (*152*) that, since the π component of the coordinate bond would be expected to respond similarly to these substituents, the electrical effect in this system acts principally through the π component, either because it is the stronger component or because it is more susceptible to inductive effects. The displacement of C_2H_4 by C_2F_4 is a very slow process suggesting that the rate-determining step may be the nucleophilic addition of the olefin to the Rh(I) complex and that formation of the activated complex is more dependent upon formation of the σ bond than of the π bond (*152*).

Passage of ethylene through a chloroform solution of $RhCl[P(C_6H_5)_3]_3$, obtained by reaction of $RhCl_3$ with an excess of triphenylphosphine in ethanol, yields yellow crystals of $(C_2H_4)RhCl[P(C_6H_5)_3]_2$ in which the olefin is trans to chlorine (*450*) (**172**). The corresponding, but less stable, bromo complex has also been isolated, but the iodo complex was not obtainable (*450*). Although both the chloro and bromo complexes are stable in the solid state, they lose ethylene rapidly in solution. Their solution NMR spectra indicate rapid exchange between free and coordinated ethylene even at –50°C. As with $(olefin)_2Rh(acac)$ complexes (*152*), the complexation constants for formation of $(olefin)RhCl[P(C_6H_5)_3]_2$ are very much smaller with the other monoolefins than with ethylene (*450*).

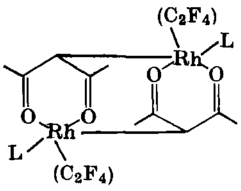


(**172**)

By contrast, the analogous complex of tetrafluoroethylene, $(C_2F_4)RhCl[P(C_6H_5)_3]_2$, is very stable in solution showing a temperature-independent ^{19}F NMR spectrum with all fluorines equivalent (*400*). Although it can be prepared by direct interaction of C_2F_4 with $RCl[P(C_6H_5)_3]_3$, the corresponding reaction will not satisfactorily produce the complex of chlorotrifluoroethylene $(C_2F_3Cl)RhCl[P(C_6H_5)_3]_2$.

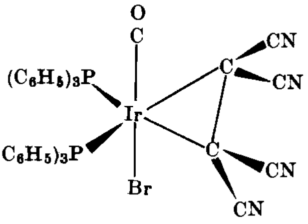
The latter complex can be obtained, however, by the reversible replacement of ethylene from (**172**) (*400*). The arsine complexes (olefin)-$RhCl[As(C_6H_5)_3]_2$ (olefin = C_2H_4, C_2F_4) have also been described (*385*). Although the reaction at room temperature of C_2F_4 with $[RhClL_2]_2$ ($L = P(C_6F_5)(C_6H_5)_2$) in benzene yields the anticipated C_2F_4 complex (*334*), at higher temperature and, in particular, in the presence of some water the product of this, and other reactions in which L is one of a number of phosphines with fluorinated substituents, is $RhCl(CO)L_2$. It is thought that the C_2F_4 complex is formed initially and that the olefin is then displaced by CO generated during the reaction (*334*). The solvolysis of $(C_2F_4)(C_2H_4)Rh(acac)$ in protonic solvents has been observed (*463*) to produce CO.

The reaction of C_2F_4 with $(C_2H_4)_2Rh(acac)$ (*153*, *463*) or $[(C_2H_4)_2RhCl]_2$ (*153*) at room temperature results in partial displacement of ethylene to produce $(C_2F_4)(C_2H_4)Rh(acac)$ and $[(C_2F_4)(C_2H_4)RhCl]_2$, respectively. The former complex reacts with phosphines, amines, and dimethyl sulfoxide to yield $(C_2F_4)Rh(acac)L_2$ and with nitriles and dimethylformamide to yield the dimeric species $[(C_2F_4)Rh(acac)L]_2$ in which bridging is through a tridentate acetylacetonate ligand (**173**) (*463*). The infrared and NMR spectra suggest that, although (C_2F_4)-$(C_2H_4)Rh(acac)$ probably involves square planar coordination about Rh(I), the complexes derived therefrom by displacement of C_2H_4 with the other ligands may involve a distorted octahedron about Rh(III) with two coordination sites occupied by the carbon atoms of C_2F_4 (*463*). A similar Rh(III) structure has been suggested (*23*) for the tetracyanoethylene complexes $[C_2(CN)_4]RhX(CO)[P(C_6H_5)_3]_2$, (X = Cl, Br, or NCS), obtained by reaction of the olefin at room temperature with $RhX(CO)[P(C_6H_5)_3]_2$.



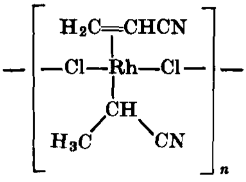
(**173**)

The analogous iridium complexes $(C_2F_4)IrCl(CO)[P(C_6H_5)_3]_2$ (*153*, *463*) and $[C_2(CN)_4]IrX(CO)L_2$ [X = Cl, L = $As(C_6H_5)_3$; X = Cl, Br, I, CNO, or CNS, L = $P(C_6H_5)_3$] (*23*, *24*) have been described. The somewhat unstable acrylonitrile and the more stable fumaronitrile complexes also have been prepared (*24*). The infrared carbonyl-stretching frequencies indicate decreasing electron density on the metal with increasing number of electron-withdrawing olefin substituents (*24*). With ethylene there is a small net electron transfer from olefin to metal, but with C_2F_4 and $C_2(CN)_4$ the olefins act as the electron acceptors (*594a*). Although hexacoordinate Ir(III) structure with σ bonding of the olefinic carbon atoms to the metal to produce an iridacyclopropane ring has been suggested (*23*, *463*) for some of these complexes, a pentacoordinate Ir(I) structure appears to be more valid (*594a*). A molecular orbital assessment of the coordinate bonding shows (*24*) that successive introduction of electron-withdrawing cyano groups into the ethylene molecule results in a progressive weakening of the σ component with corresponding strengthening of the π component of the metal–olefin bond. Consequently, these olefins may be attached to the metal by essentially pure π bonding. A structural study of $[C_2(CN)_4]IrBr(CO)[P(C_6H_5)_3]_2$ (*402*) indeed establishes a trigonal-bipyramidal geometry about Ir with cis phosphine ligands and with the olefin lying in the equatorial plane (**174**). This contrasts to some extent with the platinum(0) complex $[C_2(CN)_4]Pt[P(C_6H_5)_3]_2$ in which the olefin is about 10° out of the equatorial plane (*461*). The Ir–C and C–C (olefin) distances are 2.15 and 1.51 Å, respectively, and the cyano groups are displaced from the olefin plane away from the metal. A consideration of the various C–C bond lengths indicates that the central carbon atoms are still sp^2-hybridized (*402*).



(**174**)

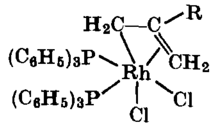
The reaction of acrylonitrile with ethanolic $RhCl_3$ yields a product of approximate composition $(CH_2{=}CH{-}CN)_2RhCl_2$ in which one of the acrylonitrile moieties is σ-bonded to Rh(III) and the other perhaps π-bonded as indicated by the chlorine-bridged structure (**175**) since it can be displaced by pyridine to yield $(CH_3CHCN)RhCl_2(C_5H_5N)_3$ (*168*). The reaction is thought to involve an intermediate Rh(III) hydride. The comparable reaction with crotononitrile, methacrylonitrile, cinnamonitrile, methyl vinyl ketone, methyl vinyl sulfone, and isoprene does not occur (*168*).



(175)

Prolonged reaction of rhodium(III) chloride or bromide (RhX_3) with tri-*o*-tolylphosphine (OTP) in high boiling alcohols or ketones has produced yellow, monomeric, diamagnetic complexes $RhX(OTP)_2$ in which the ligand $(OTP)_2$ has been identified as *trans*-2,2′-di(di-*o*-tolylphosphine)stilbene (*48*). There is uncertainty as to whether the ligand, which results presumably from a coupling–dehydrogenation reaction, is σ- or π-bonded to the rhodium.

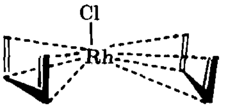
Reaction at room temperature of $RhCl[P(C_6H_5)_3]_3$ with allyl or 2-methallyl chloride produces crystalline Rh(III) complexes (**176**) in which a terminal carbon atom of the allylic group is σ-bonded and the double bond is π-bonded to the rhodium atom (*374*). In solution, the π bond is broken and, a solvent molecule enters the octahedral coordination sphere. When the reaction is conducted at reflux temperature, the only product is the π-allylic complex.



R = H or CH_3

(176)

Butadiene reacts slowly with $RhCl_3$ in ethanol at –5°C to yield the yellow, diamagnetic air-sensitive complex $(C_4H_6)_2RhCl$ (*475*) stable in the solid but not in solution at room temperature. The same complex is rapidly formed by reaction of C_4H_6 with the cyclooctene complex $[(C_8H_{14})_2RhCl]_2$. X-Ray studies (*475*) show that the molecule (**177**) has C_{2v} symmetry with Rh–C distances of about 2.2 Å. The butadiene ligands

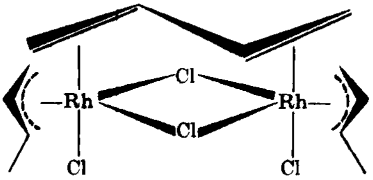


(177)

are readily displaced by triphenylphosphine. Interaction of C_4H_6 with $RhCl[P(C_6H_5)_3]_3$ in ethanol–chloroform produces, however, the monomeric complex $(C_4H_6)RhCl[P(C_6H_5)_3]_2$, m.p. 85°C (decomposes) (*510*).

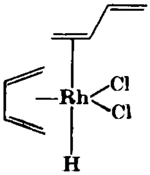
Although butadiene and *trans*-1,3-pentadiene displace both cyclooctene molecules from $[(C_8H_{14})_2RhCl]_2$ to form (diolefin)$_2$RhCl, isoprene and 2,3-dimethylbutadiene displace only one yielding (diolefin)-$(C_8H_{14})RhCl$. However, these latter diolefins will completely displace butadiene for $(C_4H_6)_2RhCl$ to give the corresponding bisdiolefin complexes (*474*).

At 20°C, the reaction of C_4H_6 with $RhCl_3$ in ethanol (*478*, *481*) or with $[(C_2H_4)_2RhCl]_2$ or $(C_2H_4)_2Rh(acac)$ in HCl-saturated ethanol (*151*) produces $(C_4H_6)[(C_4H_7)RhCl_2]_2$ identified as the chloro-bridged, butadiene-bridged π-crotyl complex (**178**). Reaction of (**178**) with pyridine (L) (*478*) results in displacement of C_4H_6 to give $(C_4H_7)RhCl_2L_2$, while reaction with 1,5-cyclooctadiene (*481*) yields $[(C_8H_{12})RhCl]_2$.

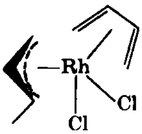


(**178**)

Complex (**178**) results also from the saturation with HCl of a suspension of $(C_4H_6)_2RhCl$ in methanol (*481*) or from the reaction of 1-methallyl chloride with $[(C_2H_4)_2RhCl]_2$ in methanol followed by saturation with C_4H_6 (*481*). It has been suggested (*169*) that alcoholic reduction of $RhCl_3$ in the presence of butadiene may produce an unstable hydride (**179**) which at lower temperatures loses HCl to produce (**177**) and at room temperature undergoes hydride addition to produce the π-crotyl complex intermediate (**180**) which can then dimerize with elimination of



(**179**)



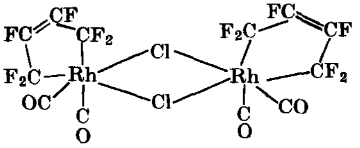
(**180**)

one molecule of C_4H_6 to yield (**178**). The methyl-substituted 1,3-butadienes do not form comparable complexes nor do they displace the bridging C_4H_6 molecule from (**178**). The reaction of C_4H_6 with hydrated $RhCl_3$ in ethanol in the presence of zinc metal has been reported (*567*) to give a hydrated chloro-bridged π-crotyl complex.

Although the main products of the reaction of isoprene with $RhCl_3$ in alcohols are the ethers resulting from addition of alcohol across a double bond, the polymeric complexes $[(C_5H_8)_xRhCl_2]_n$ ($x = 2$, 3, or 4) have been isolated (*169*). Treatment of these with triphenylphosphine gives the dimer $\{(C_5H_8)_xRhCl_2[P(C_6H_5)_3]\}_2$, whereas treatment with pyridine yields the hydrated monomer $(C_5H_8)RhCl_2(H_2O)(C_5H_5N)_2$. The ethers are also produced but in smaller quantity in the butadiene reactions (*169*).

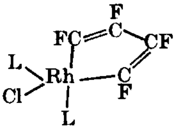
Butadiene reacts with chloroiridous acid in sodium bromoiridate in ethanol to give the iridium analog of (**178**), $(C_4H_6)[(C_4H_7)IrX_2]_2$ (X = Cl or Br) (*541*). The butadiene ligand can be displaced from these complexes by phosphines and arsines, but not by CO and 1,5-cyclooctadiene. This suggests that butadiene is more strongly coordinated to iridium than to rhodium.

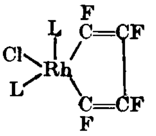
Perfluorobutadiene and dicarbonylchlororhodium(I) dimer react to give the chloro-bridged rhodium(III) dimer $[(C_4F_6)RhCl(CO)_2]_2$ (**181**) with a metallocyclopentene ring similar to that in $(C_4F_6)Fe(CO)_4$ (**71**) (*510*). With $RhCl[P(C_6H_5)_3]_2$ in benzene, however, C_4F_6 produces with loss of fluorine the monomeric $(C_4F_4)RhCl[P(C_6H_5)_3]_2$ (*510*). On the basis of its NMR spectrum this complex is considered to have either a trigonal-bipyramidal (**182a**) or a tetragonal-pyramidal (**182b**) structure. The arsine analog also has been prepared (*510*).



(**181**)

Rhodium–olefin complexes have been identified as intermediate species in rhodium-catalyzed olefin-to-olefin addition reactions (*5a, 150a, 151*) and olefin hydrogenation reactions (*450*). Although the ethylene–Rh(I) complexes are not in themselves catalysts for dimerization of ethylene, both $[(C_2H_4)_2RhCl]_2$ and $(C_2H_4)_2Rh(acac)$ react with


(182a)


(182b)

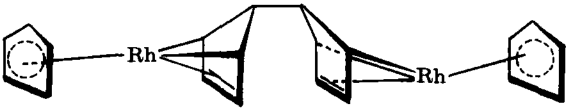
L = $P(C_6H_5)_3$ or $As(C_6H_5)_3$

alcoholic HCl to produce $[(C_2H_4)_2RhCl_2]^-$ which is converted by reaction with additional HCl into the ethylrhodium(III) compound $[(C_2H_4)C_2H_5RhCl_3(S)]^-$ (S = solvent) which is the catalytic species. The rate-determining step is the rearrangement of this species to the *n*-butylrhodium(III) complex $[CH_3CH_2CH_2CH_2RhCl_3(S)_2]^-$ which then rapidly loses HCl to yield the 1-butene complex of Rh(I). The coordinated 1-butene and solvent molecules are rapidly displaced by ethylene to yield again the initial rhodium(I) complex $[(C_2H_4)_2RhCl_2]^-$ (*150a*).

The rhodium-catalyzed addition of ethylene to 1,3-butadiene to yield 1,4-hexadiene (*5a*, *151*) proceeds via a similar mechanism (*151*) with the exception that, upon formation of the alkylrhodium(III) species, the hexadiene synthesis proceeds without further change in the oxidation state of the metal. In these reactions with butadiene the coordinated alkyl groups are either chelate or π-allyl structures which appear to stabilize Rh(III) (*151*). The addition of propylene to butadiene and isoprene to produce *trans*-2-methyl-1,4-hexadiene and 2,4-dimethyl-1,4-hexadiene, respectively, has been similarly accomplished (*5a*).

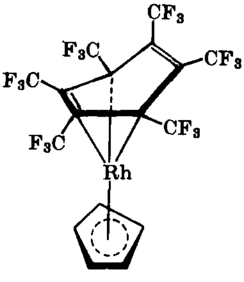
In benzenelike solvents, $RhX[P(C_6H_5)_3]_3$, which loses one phosphine ligand to yield $RhX[P(C_6H_5)_3]_2(S)$ (S = solvent), is a very efficient catalyst for hydrogenation of nonconjugated olefins at ambient temperature and atmospheric pressure (*450*). The mechanism of hydrogenation involves (*450*), in turn, the activation of hydrogen by formation of the *cis*-dihydride complex of Rh(III), $H_2RhX[P(C_6H_5)_3]_2(S)$, displacement of the solvent ligand by the olefin, simultaneous cis transfer of the two bonded hydrogens to the coordinated olefin, and diffusion of the saturated species away from the catalytic site. If the olefin is a strong π acid, e.g., C_2H_4 or C_2F_4, the ability of the metal to activate hydrogen is markedly reduced and catalytic hydrogenation is not achieved. The much slower olefin hydrogenation experienced with $H_2IrCl(CO)[P(C_6H_5)_3]_2$ (*595*) than with $H_2RhCl[P(C_6H_5)_3]_2(S)$ (*450*) is due to the lesser tendency for the former complex to dissociate in solution to produce a coordination site for the olefin molecule. By contrast with its iridium analog $RhCl(CO)[P(C_6H_5)_3]_2$ will not activate hydrogen to produce the *cis*-dihydride (*450*).

Reduction with molten sodium of the hexafluorophosphate salts of $[M(C_5H_5)_2]^+$ (M = Rh or Ir) produces the dicyclopentadienylmetal(II) which exist as paramagnetic monomers at very low temperatures and in the gas phase above 150°C, but as diamagnetic dimers (**183**) at room temperature (*215*).



(183)

The interaction of hexafluoro-2-butyne with $Rh(CO)_2(C_5H_5)$ at about 110°C gives two products in about equal yield: [tetrakis(trifluoromethyl)-cyclopentadienone]cyclopentadienylrhodium $[(CF_3)_4C_5O]Rh(C_5H_5)$ and [hexakis(trifluoromethyl)benzene]cyclopentadienylrhodium $[C_6(CF_3)_6]$-$Rh(C_5H_5)$ (*171a*). The very stable, yellow cyclopentadienone complex is essentially identical to its cobalt analog (**162**). The orange-yellow air-stable benzene complex has been observed (*110*) to have the structure (**184**) in which the C_6 ring is bent away from the metal through 48°, one C_4 segment being σ,π-bonded to rhodium while the double bond in the other segment is free. The Rh–σ-bonded carbon and Rh–π-bonded carbon distances are 2.15 and 2.04 Å, respectively. This structure which is in accord with that suggested by infrared and ^{19}F NMR spectra (*171a*) represents the first unequivocal example of localized bonding from a C_6 aromatic compound to a transition metal (*110*).

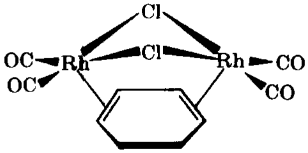


(184)

The chloro-bridged 1,5-hexadiene complex $[(C_6H_{10})RhCl]_2$, m.p. 115°–117°C, has been prepared by reaction of the olefin with $[(C_2H_4)_2RhCl]_2$ in diethyl ether at room temperature (*149*). When reacted with cyclopentadienylsodium, this complex produces

$(C_6H_{10})Rh(C_5H_5)$, a liquid melting at 10°C (*149*). In general, the rhodium complexes $[(diene)RhCl]_2$ and $[(olefin)_2RhCl]_2$ can be prepared by reaction of the diolefins or monoolefins, respectively, with $RhCl_3$ in aqueous alcohol (*617*) at room temperature. In addition to those reviewed earlier (*268*), complexes are produced by 1,3-cyclohexadiene, octafluoro-1,3-cyclohexadiene, 1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene, norbornene, cycloheptene (*301*, *617*), and cyclooctene (*475*, *617*). With 1,3-pentadiene, isoprene, 2,3-dimethyl-1,3-butadiene, and cycloheptatriene, however, no complex has been isolated (*617*). Similarly, by reaction of the olefin with $Na_2IrCl_4 \cdot 6H_2O$ in aqueous ethanol, the iridium complexes $[(diene)IrCl]_2$ are obtained with norbornadiene and 1,5-cyclooctadiene (*615*, *618*), while $(diene)_2IrCl$ is produced with 1,3-cyclohexadiene and 2,3-dimethyl-1,3-butadiene (*618*). With $H_2IrCl_6 \cdot 6H_2O$ in aqueous ethanol, cycloheptene and cyclooctene both yield $(olefin)_3Ir(CO)Cl$, while cyclooctene produces also $[(C_8H_{14})_2Ir(CO)Cl]_2$ (*540*, *618*). The carbonyl ligand in these complexes is formed by breakdown of the alcohol and methane is liberated. The cyclooctene ligands are readily displaced from $[(C_8H_{14})_2Ir(CO)Cl]_2$ by phosphines and 1,5-hexadiene, while allylic chlorides add on to the complex breaking the chloro bridges and displacing one C_8H_{14} molecule from each metal. Ethylene also adds to the complex in solution to the extent of two molecules per Ir atom apparently without displacement of cyclooctene (*540*).

Upon reaction with $[Rh(CO)_2Cl]_2$, 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene produce $(diolefin)[Rh(CO)_2Cl]_2$ with structures much like that of $[Rh(CO)_2Cl]_2$, but with a bridging of the rhodium atoms by the diolefin ligand (**185**) (*616*).

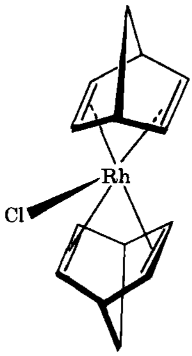


(**185**)

With $[Rh(CO)_2Cl]_2$, 3-allylacetylacetone gives in addition to $Rh(CO)_2(C_8H_{11}O_2)$, the red binuclear complex $[Rh(CO)_2(C_8H_{11}O_2)]Rh(CO)_2Cl$ in which the $Rh(CO)_2Cl$ segment is linked to the other by π bonding between the rhodium atom and the double bond of the allyl group (*74*). An excess of 1,5-cyclooctadiene readily displaces the carbonyl groups to form the known complexes $[(C_8H_{12})RhCl]_2$ and $(C_8H_{12})Rh(C_8H_{11}O_2)$ (*268*).

Cycloheptadiene interacts slowly with $Rh(CO)_2(acac)$, simultaneously undergoing isomerization, to give the norbornadiene complex $(C_7H_8)Rh(acac)$ (*74*).

A study of the temperature dependence of the NMR spectrum of a solution of norbornadiene and $[(C_7H_8)RhCl]_2$ indicates the formation at low temperature of the five-coordinate rhodium complex (**186**) (*596*). The kinetics of norbornadiene exchange suggest that the slow reaction of $[(C_7H_8)RhCl]_2$ with C_7H_8 gives complex (**186**) and an intermediate $(C_7H_8)RhCl$ which reacts with another molecule of C_7H_8 to produce additional (**186**). Complex (**186**) can be isolated at −100°C from the above system or at 0°C under N_2 from the reaction of norbornadiene with $(1,3\text{-}C_4H_6)RhCl$ (*596*).



(186)

Although the interaction of an ethanolic solution of $RhCl_3$ and $SnCl_2$, which has been shown (*625*) to form the Sn–Rh-bonded dimer $[Rh(SnCl_3)_2Cl]_2^{4-}$, with 1,5-cyclooctadiene and other diolefins gives the known chloro-bridged dimer $[(diene)RhCl]_2$, that with norbornadiene affords $(C_7H_8)_2Rh(SnCl_3)$ (*625*). By contrast, the corresponding reaction with $IrCl_3$ gives the diolefin complexes $(diene)_2Ir(SnCl_3)$ in all cases (*625*). In $(C_7H_8)_2Rh(SnCl_3)$ and $(C_8H_{12})_2Ir(SnCl_3)$, one diene ligand can be replaced by two phosphine, arsine, or stibene ligands and upon reaction of the complexes with sodium tetraphenylborate, one obtains $[(diene)_2M]^+ \, B(C_6H_5)_4^-$. In the iridium–tin system, cycloheptatriene undergoes an isomerization comparable to that found in the $Rh(CO)_2(acac)$ system (*74*) to give the norbornadiene complex, whereas both 1,3-cyclooctadiene and 4-vinylcyclohexene isomerize, as in the palladium(II) halide system (*233*, *234*), to give the 1,5-cyclooctadiene complex (*625*).

The interaction of 1,3-C_8H_{12} with $RhCl_3$ in ethanol also results in isomerization of the diene to give $[(1,5\text{-}C_8H_{12})RhCl]_2$ (*499*). This effect, the opposite to that observed with iron carbonyls (*17*), is thought to result from rapid transfer of hydrogen from the 5,6- to the 3,4-positions on the ring of the coordinated diene perhaps via a Rh–H bond (*499*). $IrCl_3 \cdot 4H_2O$ also interacts with the 1,3-diene to produce small quantities of $[(1,5\text{-}C_8H_{12})IrHCl_2]_2$ (*499*). Deuteration experiments (*539*) indicate the occurrence of cis addition of hydride to a coordinated double bond in $[(1,5\text{-}C_8H_{12})IrHCl_2]_2$ in solution followed by trans elimination of a proton. Interestingly, some Rh(III) and Ir(III) compounds have been found (*444*) to be active catalysts for the isomerization of 1,5- to 1,3-cyclooctadiene.

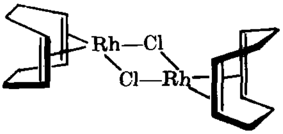
Hexachloronorbornadiene (1, 2, 3, 4, 7, 7 - hexachloro - bicyclo[2.2.1]-hepta-2,5-diene) complexes of rhodium and iridium, $[(C_7H_2Cl_6)MCl]_2$, have been obtained from the reactions of the olefin with $RhCl_3$ or $[Rh(CO)_2Cl]_2$ and H_2IrCl_6, respectively (*613*). Complex formation results in a shift to lower frequency of the C=C-stretching vibration in the olefin by 224 and 249 cm^{-1} for the rhodium and iridium systems respectively. This shift is markedly greater than that observed upon complexing of norbornadiene (*1*, *618*) probably as a result of greater d–π^* overlap in the complex of the olefin containing the electronegative chlorine atoms (*613*). The relative shift for the two metals is the inverse of that reported for the norbornadiene complexes (*618*) and suggests stronger complexing to iridium than to rhodium. This suggestion is supported by the higher magnetic shielding of the protons in $C_7H_2Cl_6$ in the iridium than in the rhodium complex (*613*). Recent investigation of the far infrared spectra of $[(C_7H_8)RhCl]_2$, $[(1,5\text{-}C_8H_{12})RhCl]_2$, and $[(1,5\text{-}C_8H_{12})IrCl]_2$ have shown lower metal–chlorine and metal–diene stretching frequencies for the rhodium than for the iridium complexes (*49*). Although there is some uncertainty about the assignment of the metal–diene stretching band in the iridium complex, these data too suggest that iridium complexes more strongly than does rhodium (*49*).

An NMR study (*597*) of ligand exchange in the system (diene)MCl(L) (diene = norbornadiene or 1,5-cyclooctadiene; M = Rh or Ir; L = tertiary phosphine, arsine, or stibene) shows a first-order dependence of the rate upon both L and the olefin complex in the temperature range from −70° to −10°C. The exchange involves an S_N2 mechanism with the five-coordinate complex $(\text{diene})MCl(L)_2$ as intermediate. The intermediate iridium complexes $(1,5\text{-}C_8H_{12})IrCl(L)_2$ can be isolated from ethanolic solution. The activation energy for the process ranges from 4 to 10 kcal/mole (*597*).

By analogy with the cobalt analogs, the complexes $(\text{diene})Rh(C_5H_5)$

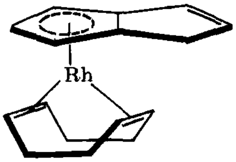
(diene = norbornadiene or 1,5-cyclooctadiene) interact with HgX_2 (X = Cl or Br) to form 1:1 halogen-bridged polymeric complexes (*123*). Similar 1:1 adducts have been obtained with $(1,5\text{-}C_8H_8)Ir(C_5H_5)$ (*161*).

The structure (**187**) of the dimeric π complex $[(1,5\text{-}C_8H_{12})RhCl]_2$ prepared from $[Rh(CO)_2Cl]_2$ and the diene (*268*, reference 45) has been shown by X-ray diffraction (*309*) to be significantly different from that of the chlorocarbonylrhodium dimer (*309*, reference 1). In the latter complex rhodium has an octahedral coordination achieved by formation of bent intramolecular and straight intermolecular Rh–Rh bonds; in the diene complex it shows square-planar coordination. The C_8 ring in boat form is π-bonded through both double bonds to the rhodium atom with average C=C bond lengths of 1.44 Å.



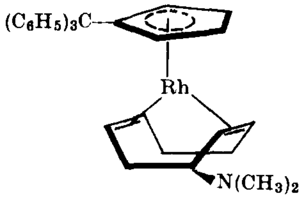
(**187**)

Allylmagnesium bromide reacts with $[(1,5\text{-}C_8H_{12})RhI]_2$ at 0°C in tetrahydrofuran to produce upon hydrolysis with aqueous NH_4Cl (*328*) the yellow, diamagnetic $(1,5\text{-}C_8H_{12})Rh(\pi\text{-}C_3H_5)$. Similarly, $[(1,5\text{-}C_8H_{12})RhCl]_2$ reacts with thallium hydropentalenide to form yellow (1,5-cyclooctadiene)hydropentalenylrhodium (**188**), which reacts with *n*-butyllithium to yield the corresponding anion (*329*, *415*).



(**188**)

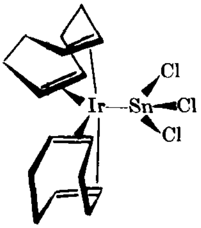
Upon reaction with $RhCl_3$ in methanol, Dewar hexamethylbenzene undergoes a ring contraction to produce pentamethylcyclopentadienyldichlororhodium(III) (*324*), which upon refluxing with 1,5-cyclooctadiene in ethanol with added Na_2CO_3 yields (1,5-cyclooctadiene)pentamethylcyclopentadienylrhodium(I). Reaction of $(1,5\text{-}C_8H_{12})Rh(C_5H_5)$ in 1:1 ratio with trityl fluoroborate gives (1,5-cyclooctadiene)tritylcyclopentadienylrhodium (*376*), in contrast with the analogous reaction of the corresponding cobalt complex from which a cyclooctadienyl complex cation (**166**) is obtained. However, when reacted in 1 : 2 mole ratio with $(C_6H_5)_3CBF_4$, the rhodium complex does produce the cyclooctadienyl complex cation $[(C_8H_{11})RhC_5H_4C(C_6H_5)_3]^+$ which reacts with dimethylamine to give the substituted diene complex of structure (**189**). With the rhodium complex there is initial electrophylic substitution of the trityl cation on the C_5 ring followed by hydride abstraction from the coordinated C_8 ring (*376*).



(189)

The iridium hydride complex $[(1,5\text{-}C_8H_{12})IrHCl_2]_2$ mentioned above can be prepared in 70% yield by interaction of the diene with chloroiridic acid (*500*) or chloroiridous acid prepared *in situ* by reduction of chloroiridic acid in boiling ethanol (*502*). In the chloro-bridged dimer the iridium has an octahedral coordination with the diene molecules occupying equatorial positions. Although the dienes ligands are readily displaced by tertiary phosphines (L) to give $IrHCl_2L_3$, the Ir–Cl and Ir–H bonds are ruptured by sodium carbonate in methanol, by cyclopentadienylsodium, and by thallous acetylacetonate to form $[(diene)Ir(OCH_3)]_2$, $(diene)Ir(C_5H_5)$, and (diene)Ir(acac), respectively (*500, 502*).

With $Na_2IrCl_6 \cdot 6H_2O$ and $SnCl_2$ in boiling ethanol, 1,5-cyclooctadiene affords $(1,5\text{-}C_8H_{12})_2Ir(SnCl_3)$ (*477, 625*) which has been shown (*477*) to have a distorted trigonal-bipyramidal structure (**190**) with the $SnCl_3$ group and one olefinic double bond from each of the diene ligands

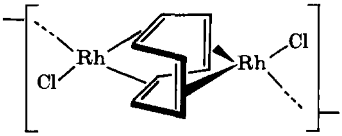


(190)

in the equatorial plane. The iridium–trigonal carbon atom distances are 2.22 Å for the axial and 2.17 Å for the equatorial double bonds.

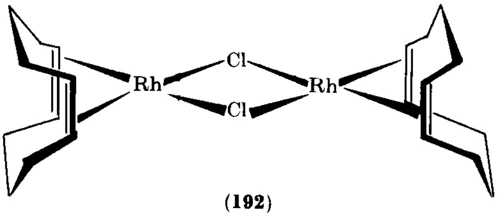
While in refluxing light petroleum cyclooctatetraene interacts with $Rh(CO)_2(C_5H_5)$ to give the air-stable yellow $(C_8H_8)Rh(C_5H_5)$, m.p. 106°C (*158*), in refluxing decane under UV irradiation it produces the yellow $(C_8H_8)[Rh(C_5H_5)]_2$ (*85*). The latter complex can be prepared also by reaction of the former with $[Rh(CO)_2Cl]_2$ (*85*). The NMR spectra of these C_8H_8 complexes indicate that, like their cobalt analogs, they do not undergo valence tautomerism in solution. Infrared spectra suggest (*85*, *158*) and structural analyses confirm (*220*, reference 505) the suggestion that the olefin has the tub conformation with a structure for $(C_8H_8)[Rh(C_5H_5)]_2$ like that of the cobalt analog (**169**). Unlike the iron complex $(C_8H_8)Fe(CO)_3$, the C_8H_8 ring in $(C_8H_8)Rh(C_5H_5)$ is not protonated in concentrated sulfuric acid (*159*). It also fails to form a Diels–Alder adduct with tetracyanoethylene, perhaps as a result of the absence of a nonbonded 1,3-diene segment in the ring (*159*).

The preparation of the known dimer $[(C_8H_8)RhCl]_2$ from C_8H_8 and $RhCl_3$ (*47*, references 5 and 19) has been found (*54*) to be nonreproducible. It can be prepared, however, by treatment of $[(C_8H_{14})_2RhCl]_2$ with C_8H_8 (*54*). Its spectra suggest a structure quite similar to that of $[(1,5\text{-}C_8H_{12})RhCl]_2$ (**187**). The presence of an infrared band at 1630 cm^{-1} indicates free double bonds both in the dimer and in its products of reaction with phosphines or arsines and acetylacetone. Upon standing in solution in CCl_4 or $CHCl_3$, $[(C_8H_8)RhCl]_2$ deposits an insoluble orange-brown compound of composition $(C_8H_8)Rh_2Cl_2$ which shows no infrared band near 1630 cm^{-1} and which reacts with the above donor ligands to give $[(C_8H_8)Rh_2Cl_2]_2$ and $(C_8H_8)Rh_2(acac)_2$. These observations suggest the structure (**191**) for the complex (*54*).



(191)

In an ethanol solution of $RhCl_3$, *cis,trans*-1,5-cyclodecadiene is converted to its *cis,cis*-1,6-isomer with subsequent formation of the dimeric rhodium complex $[(1,6\text{-}C_{10}H_{16})RhCl]_2$ which can also be prepared by direct interaction of the 1,6-olefin with $RhCl_3$ in ethanol (*579*, *582*). Spectral evidence suggests a configuration (**192**) much like that of the 1,5-cyclooctadiene complex with the $1,6\text{-}C_{10}H_{16}$ rings in a boat conformation.



(192)

VIII. Group VIIIC: Nickel, Palladium, and Platinum

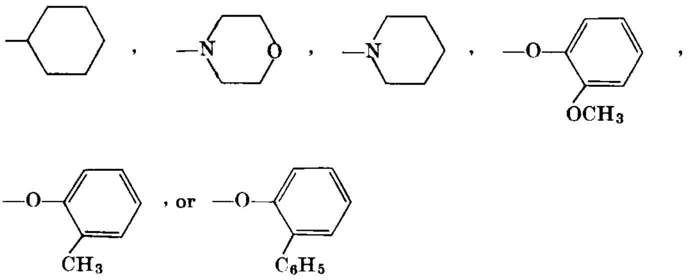
A. NICKEL

A number of nickel–olefin complexes have been described in recent years, many of these having nickel in its zero oxidation state.

Reduction of nickel acetylacetonate with $(C_2H_5)_2AlOC_2H_5$ in the presence of triphenylphosphine (*610*) produces yellow, crystalline (ethylene)bis(triphenylphosphine)nickel(0). An X-ray analysis of this complex $(C_2H_4)Ni[P(C_6H_5)_3]_2$ (*122*) has shown a Ni–C distance of about 2.01 Å and a C=C length of about 1.46 Å. In the crystal, the C–Ni–C plane is reported to be inclined at an angle of 12° to the P–Ni–P plane. It is suggested (*122*) that this indicates a low-energy barrier to out-of-plane rotation and that, in solution, the complex may exhibit rotation of the ethylene molecule about the coordinate bond. This suggestion must be accepted with some reservation, however, since an independent structural analysis (*183*) has indicated that the ethylene carbon atoms are coplanar with the nickel and phosphorus atoms.

Similar yellow ethylene complexes have been obtained (*608*, *610*) with the phosphines R_3P, wherein R is

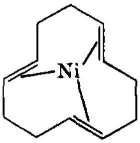
—C_2H_5,



Displacement of ethylene from $(C_2H_4)Ni(R_3P)_2$ and formation of the corresponding olefin complex has been accomplished with styrene, α-methylstyrene, and stilbene (R = phenyl) and with 1-hexene and propylene (R = cyclohexyl).

The reaction of (ethylene)bis(triphenylphosphine)nickel(0) with tetrafluoroethylene (*153*, *463*) involves a rearrangement of the triphenylphosphine ligands to produce the air-sensitive compound $(C_2F_4)Ni[P(C_6H_5)_3]_3$.

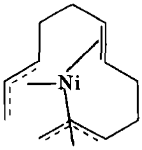
Another interesting complex in which the Ni(0) is three-coordinate is *all-trans*-1,5,9-cyclododecatrienenickel(0), $C_{12}H_{18}Ni$ (*73*). This structure (**193**) is the only known Ni(0) complex in which the nickel atom is coordinated only to three olefinic double bonds. The complex, formed as described above by reduction of nickel acetylacetonate in the presence of the triene at 0°C, is monomeric, sublimes *in vacuo*, and crystallizes as dark red, lustrous needles melting at 102°C (*173*). It is sensitive to air but stable in water. X-Ray analysis (*177*) shows that the nickel atom sits at the center of the ring with a planar trigonal hybridization; the Ni–CH distance is about 2.11 Å.



(**193**)

Because in this complex the nickel is electron-deficient, it will add another ligand. Reaction with carbon monoxide at −78°C produces white, crystalline $(C_{12}H_{18})Ni(CO)$ which decomposes at about −15°C to produce the olefin, nickel metal, and $Ni(CO)_4$. Triphenyl- and triethylphosphine produce 1:1 complexes with $(C_{12}H_{18})Ni$ melting with decomposition at about 90° and 100°C, respectively.

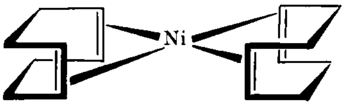
Reaction of excess butadiene with $(C_{12}H_{18})Ni$ results in displacement of the triene and trimerization of C_4H_6 (*608*). At 20°C a new molecule of cyclododecatriene is produced while at −40°C the product, illustrated by structure (**194**), is considered to involve a C_{12} chain with a trans double bond and two terminal π-allyl groupings.



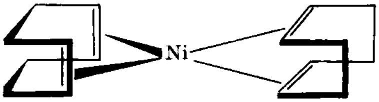
(**194**)

Stable olefin–Ni(0) complexes are formed also with 1,5-cyclooctadiene (COD) and cyclooctatetraene (COT), by displacement of cyclododecatriene from $(C_{12}H_{18})Ni$ (*608*) or by reduction of nickel acetylacetonate (*73*). The COD complex has also been produced (*419*) by treating anhydrous $NiCl_2$ with an excess of iso-C_3H_7MgBr and COD in ether under UV irradiation.

The complex bis(1,5-cyclooctadiene)nickel(0) is obtained as yellow crystals which sublime *in vacuo* at 90°C and melt with decomposition at 142°C. The infrared (*73*) and NMR spectra (*419*) indicate that all double bonds are coordinated to the nickel atom (i.e., Ni is 4-coordinate); the C═C bands at 1656 and 1490 cm^{-1} in the free diene are replaced by a strong band at 1328 cm^{-1} in the complex, while the NMR spectrum shows only two signals (intensity ratio 1 : 2) at $\tau = 5.64$ (olefinic protons) and $\tau = 7.84$ (methylene protons). The absence of a center of symmetry (infrared) suggests that configuration (**195b**) is more probable than (**195a**), indicating a tetrahedral rather than square planar coordination about Ni(0). X-Ray analysis of the compound (*173*) shows a distorted configuration with some distortion of the COD molecule as well. The C═C length is about 1.38 Å, while the average Ni–CH distance is 2.12 Å.



(195a)



(195b)

$(COD)_2Ni$, in conjunction with certain metal chlorides, has been described (*160*) as a catalyst for cis polymerization of 1,3-butadiene.

Reaction of $(COD)_2Ni$ with acetylacetone (*73*) produces orange crystalline π-(4-cyclooctenyl)acetylacetonatonickel(II) which sublimes *in vacuo* at about 60°C and melts with decomposition at 75°C. The reaction involves a proton transfer from acetylacetone to the COD ring with a concomitant change of the nickel oxidation number from zero to two. A structural analysis (*412*) has shown an essentially square planar coordination about the nickel (Fig. 4) with a C═C length of 1.42 Å and a Ni–C distance of 2.03 Å, [these values are very close to those observed for the complex $(C_2H_4)Ni[P(C_6H_5)_3]_2$ (*122*)], and a Ni–CH_2 distance of 1.95 Å.

With carbon monoxide, this compound reacts as shown in Eq. (5) to produce 1,2-bis(cyclooctenyl)glyoxal.

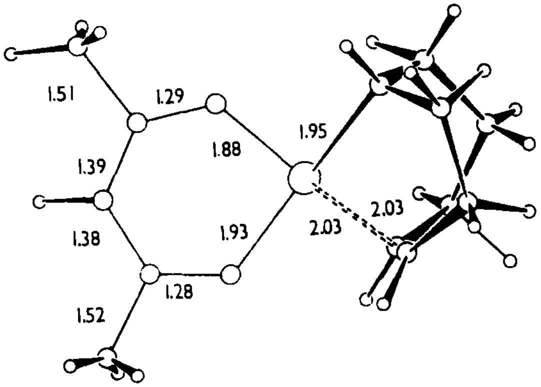
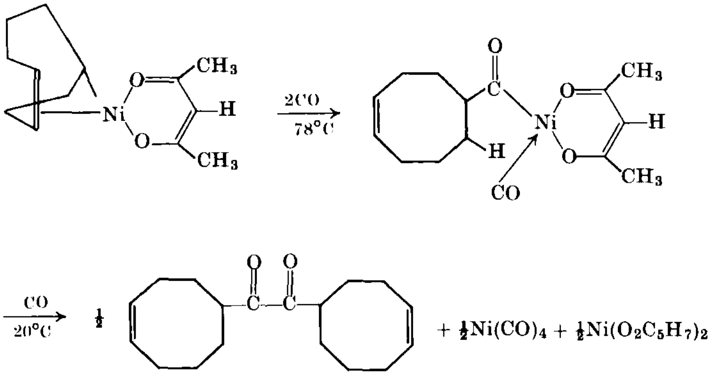
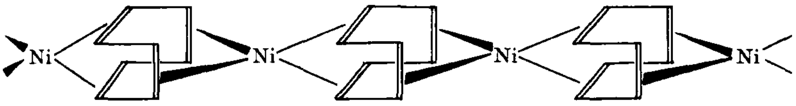


FIG. 4. Molecular structure of (4-cyclooctenyl)acetylacetonatonickel (*412*).



(5)

With cyclooctatetraene, the complex formed above −20°C has the stoichiometry $(C_8H_8)Ni$. The black lustrous crystals are only slightly soluble. Although the infrared spectrum of the solid shows no evidence of uncomplexed double bonds, the NMR of a benzene solution shows two different types of protons leading to the suggestion (*73*) that the solid compound has a polymeric structure (**196**) which is dissociated upon dissolution.



(196)

With excess COT at –60° to –40°C, golden-yellow crystals of stoichiometry $(C_{16}H_{16})Ni$ are obtained. The infrared spectrum of these shows both free and complexed double bonds. Above –20°C, $(COT)_2Ni$ rapidly loses COT to produce (**196**).

Schrauzer and Thyret have described (*528*, *529*, *531*) the synthesis of olefin–Ni(0) complexes containing a quinone, in particular, duroquinone, as a ligand. The red, diamagnetic duroquinone complexes are obtained by reaction of nickel carbonyl with the quinone in excess olefin. They are stable in air and soluble in polar organic solvents and water. Those olefins which form the complex contain essentially parallel double bonds, e.g., norbornadiene, dicyclopentadiene, 1,5-cyclooctadiene, 1,3,5-cyclooctatriene, or cyclooctatetraene.

The dipole moment (ranging from 3.5–4.3 *D*) and the infrared and UV (charge-transfer) spectra indicate that much of the charge on the metal, resulting from donation from the olefin, is transferred to the quinone. The NMR spectra show, with symmetric olefins, a splitting of the duroquinone protons, indicating a hindrance to rotation of the ligands about the axis through the nickel atom. Ligand exchange reactions have established that the order of complex stability, (C_8H_8)-Ni(duroquinone) < (nor-C_7H_8)Ni(duroquinone) < $(C_{10}H_{12})$Ni(duroquinone) < (1,5-C_8H_{12})Ni(duroquinone), corresponds with the order of dipole moments.

Crystallographic analysis (*245*) of the (COD)Ni(duroquinone) complex has shown discrete monomeric molecules with the nickel atom located between the boat form of the COD ring and the duroquinone ring (Fig. 5). The respective orientation of the ligands is indicative of a

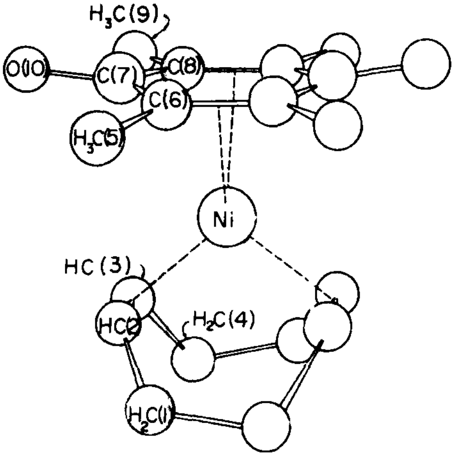


FIG. 5. Molecular structure of (1,5-cyclooctadiene)duroquinonenickel (*245*).

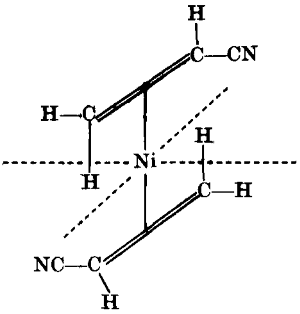
tetrahedral configuration. The double bonds of COD are shorter (1.32 Å) than those of duroquinone (1.40 Å) indicating stronger bonding to the latter. Although the nickel atom is closer to the double bonds of COD (2.00 Å) than of duroquinone (2.11 Å), this is considered to be a consequence of the effect of the difference in stereochemical configuration of the ligands and not a simple function of the metal–olefin bond strength.

With other quinones, the only olefin yielding stable complexes is 1,5-cyclooctadiene. The quinones employed have been trimethyl-*p*-benzoquinone, 2,5- and 2,6-dimethyl-*p*-benzoquinone (*531*), and vitamin E quinone (*530*). In general, these complexes show higher water solubility, higher dipole moments, and more marked paramagnetism than do the duroquinone complexes. The paramagnetism suggests that there is some electron transfer from nickel to quinone and that the nickel may indeed have an oxidation state midway between Ni(0) and Ni(II).

Two COD-Ni(I) complexes, $(C_8H_{12})NiBr$ and $(C_8H_{12})NiI$, obtained by treating the π-allylnickel halide with a large excess of COD in the presence of norbornene, have been reported (*476*). The complexes are very sensitive to air and decompose rapidly in solution (unless excess COD is present) to produce COD, nickel metal, and nickel halide. Reaction with triphenylphosphine yields $NiX[P(C_6H_5)_3]_3$ having a magnetic moment of about 1.9 Bohr Magneton corresponding to one unpaired electron and confirming the presence of Ni(I). The COD complexes were observed to catalyze the polymerization of butadiene, allene, or acetylene to linear polymers.

Schrauzer (*517*, *518*) has prepared, by reaction of the olefin with $Ni(CO)_4$, red, crystalline bis(olefin)nickel(0) complexes in which the only olefins satisfactorily employed were those having α-substituents demonstrating large inductive and mesomeric effects, e.g., acrylonitrile, acrolein, fumaronitrile, and cinnamonitrile. The small energy difference between antibonding molecular states of these ligands and the nickel atom was considered to account in part for the stability of the complexes. The infrared spectra (*230*) indicate that the complexes have a centrosymmetric arrangement of the ligands, e.g., bis(acrylonitrile)nickel(0) (**197**), and that, while the nitrile group does not appear to interact directly with the nickel atom, the carbonyl oxygen of acrolein does. The nickel atom can coordinate additionally either one or two molecules of triphenylphosphine.

Both bis(1,5-cyclooctadiene)nickel(0) and bis(acrylonitrile)nickel(0) catalyze the polymerization of allene to highly crystalline linear polymers (*451*). With compounds such as tri-*o*-tolyl phosphite, bis(acrylonitrile)nickel in hydrocarbon catalyzes the cyclodimerization of butadiene to 1,5-cyclooctadiene, whereas in alcohols it catalyzes the



(197)

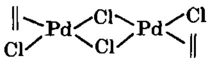
linear dimerization to *n*-octatrienes or 3-methyl-*n*-heptatrienes. With compounds such as pyridine or quinoline, however, it produces a catalyst for the cyclotrimerization of butadiene to 1,5,9-cyclododecatriene (*417*).

Bis(maleic anhydride)nickel(0), an orange air-sensitive compound, soluble in acetone but not in benzene, is obtained by reaction of maleic anhydride with $Ni(CO)_4$ (*600*). With $Ni(CO)_4$, diphenylcyclopropenone yields, in addition to diphenylacetylene and tetraphenylcyclopentadienone, a pale green diamagnetic complex $[(C_6H_5)_2C_2CO]_3Ni(CO)$, melting at 188°C, which is presumably tris(π-diphenylcyclopropenone)-carbonylnickel (*66*). The infrared spectrum of the complex indicates coordination at the double bond.

B. Palladium

One of the most convenient methods of preparation of palladium(II)–olefin complexes has been (*268*, *341*) and continues to be (*175*, *370*, *438*) via the Kharash intermediate, dichlorobis(benzonitrile)palladium(II). However, successful preparation by direct interaction of the olefin with $PdCl_2$ suspended either in an inert solvent (*383*) or liquid olefin (*486*) has been achieved as well.

The complexes obtained with simple monoolefins (*305*, *438*, *486*) are crystalline, yellowish-brown compounds, melting with decomposition below 100°C. Complex formation results in a shift to lower frequencies of the infrared $C{=}C$ stretching vibration by about 100–150 cm^{-1} (*261*, *438*, *478*). The molecular structure most commonly encountered in these complexes is the bridged dimer (**198**). The far-infrared spectrum of the ethylene complex dimer has a band at 427 cm^{-1} assigned to the $Pt{-}C_2H_4$ stretching vibration (*261*).



(198)

Because of the ability of $PdCl_2$ in aqueous systems to catalyze the oxidation of simple olefins to the corresponding aldehyde or ketone (*268*), considerable attention has been devoted to the study of the nature of the complex in solution and of the kinetics of the oxidation reaction. This subject has been thoroughly reviewed (*4*, *556*). Moiseev and co-workers (*414*, *467*, *468*) have established that the complex equilibria in solution are as represented by Eqs. (6) and (7)

$$C_nH_{2n} + [PdCl_4]^{2-} \overset{K_1}{\rightleftharpoons} [(C_nH_{2n})PdCl_3]^- + Cl^- \tag{6}$$

$$C_nH_{2n} + [PdCl_4]^{2-} + H_2O \overset{K_2}{\rightleftharpoons} [(C_nH_{2n})PdCl_2(H_2O)] + 2Cl^- \tag{7}$$

and that there is no evidence for formation of the species $(C_nH_{2n})_2PdCl_2$.

While K_1 and K_2 both show some dependence upon the structure of the olefin, K_2, which is smaller in magnitude than K_1, is much more sensitive to changes in the ionic strength of the solution.

For the oxidation of ethylene, propylene, 1-butene, and *cis*- and *trans*-2-butene, Henry (*286*, *287*) has shown that the rate expression is

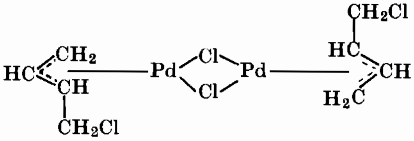
$$\frac{-d[C_nH_{2n}]}{dt} = \frac{k_1K_1[PdCl_4^{-2}][C_nH_{2n}]}{[Cl^-]^2[H^+]} \tag{8}$$

wherein K_1 is the equilibrium constant of Eq. (6) for the formation of the palladium(II)–olefin complex.

Both the $PdCl_2$-catalyzed isomerization (*552*) and dimerization (*337*) of alkenes have been reported and interpreted in terms of a Pd(II)–olefin π-complex intermediate.

Tsuji and co-workers (*586–589*) have shown that saturated or unsaturated esters can be easily obtained by carbonylation of $PdCl_2$–olefin complexes in an alcoholic solution.

Although it was originally considered that in the butadiene complex $[(C_4H_6)PdCl_2]_2$, the diene acted either as a bridging unit (*285*, *547*) or as a chelating ligand (*117*) the complex subsequently was shown by Shaw (*538*) to be the π-allylic compound (**199**).



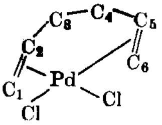
(**199**)

At a temperature below −20°C, a butadiene complex $[(C_4H_6)PdCl_2]_2$, in which only one of the double bonds of each diene molecule is complexed can be obtained by ligand exchange with the 1-pentene complex (*180*).

However, as the temperature rises this is rapidly converted to the π-allylic complex. Similar complexes of conjugated dienes involving complexing of only one double bond have been observed with *trans*-1,3-pentadiene, *cis,trans*-2,4-hexadiene, and 1,3-cyclooctadiene.

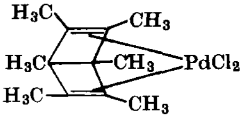
In 50% acetic acid solution, the 1,3-dienes such as cyclohexa-, cyclohepta-, and cyclooctadiene form π-allylic complexes at room temperature (*304*). With the corresponding cyclo- and 1-methylcyclo-olefin complexes, however, heating is required to effect the conversion (*302, 304*). Interestingly, the cyclooctene complex $[(C_8H_{14})PdCl_2]_2$, which melts with decomposition at 130°C (*371*), is not converted even by heating. Some of the simple alkene–palladium chloride complexes are also converted to the π-allyl complexes by treatment at 25°C with weak bases such as Na_2CO_3, $NaHCO_3$, or Na_2HPO_4 (*336*).

The formation of (1,5-hexadiene)dichloropalladium(II) by reaction of dry allyl chloride with bis(benzonitrile)dichloropalladium(II) at about 5°C has been reported (*627*). X-Ray analysis has shown the molecule to have the structure (**200**) in which carbon atoms C-1–C-2–C-3 and C-4–C-5–C-6 are in mutually perpendicular planes both of which are perpendicular to the square coordination plane about Pd(II). While the other bonds are of normal length, with the Pd–trigonal carbon distance at about 2.2 Å, the C-3–C-4 single bond at 1.46 Å is considered to be abnormally short. It has been suggested (*371*) that the greater stability of this complex than that prepared directly from 1,5-hexadiene (*283, 315*) may indicate a different molecular structure for the latter, perhaps having one double bond perpendicular to and one parallel to the co-ordination plane. The formation of structure (**200**) might be more difficult from the diene than from allyl chloride because of the energy required to compress the C-3–C-4 bond.



(**200**)

When reacted in chloroform with a deficiency of $PdCl_2$ as the bis(benzonitrile) complex, Dewar hexamethylbenzene (bicyclo[2.2.0]-hexa-2,5-diene) forms yellow platelets of the monomeric complex, with postulated structure (**201**), which decomposes sharply at 79°C (*175*).



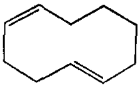
(201)

Complex formation results in a downfield change in the chemical shift of the methyl protons and a decrease in the double-bond infrared stretching frequency from 1680 to 1532 cm^{-1}. In the presence of a small excess of $PdCl_2$, the complex is rapidly converted to hexamethylbenzene and palladium chloride.

An X-ray analysis (*26, 32*) of the yellow, monomeric (norbornadiene)-dichloropalladium(II) (*1, 6*) has shown the diene molecule chelated to palladium with both double bonds perpendicular to the coordination plane. The distance from the Pd atom to the trigonal carbons is about 2.16 Å and the angle subtended at Pd(II) by the coordinate bonds is 71.8°. The bond lengths within the norbornadiene molecule appear to be changed very little by coordination.

In its very stable monomeric complex with PdX_2 ($X = Cl$ or Br), 1,5-cyclooctadiene is considered also to be chelated (*105, 284*). Frye and co-workers have observed that this is the product resulting also from an attempt to complex PdX_2 with either 1,3-cyclooctadiene (*233*) or 4-vinylcyclohexene (*234*) in benzene. With Pt(II) systems, 1,3-cyclooctadiene appears similarly to undergo a rearrangement to the 1,5-isomer (*233*); no rearrangement of 4-vinylcyclohexene is observed (*234*). (1,5-Cyclooctadiene)dibromopalladium(II) reacts with cyclopentadienyldicarbonyliron dimer or cyclopentadienyldicarbonyliron bromide to produce the complex salt (1,5-cyclooctadiene)cyclopentadienylpalladium(II) tetrabromoferrate (*389*), an air-stable paramagnetic crystalline solid. The magnetic susceptibility is that expected for the tetrahedral Fe(III) anion.

Rearrangement of *cis,trans*-1,5-cyclodecadiene (**202**), upon reaction with bis(benzonitrile)dichloropalladium(II) in benzene has also been reported (*581*). The product is (*cis*-1,2-divinylcyclohexane)dichloropalladium(II), a monomeric complex decomposing above 123°C. The



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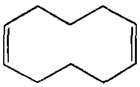


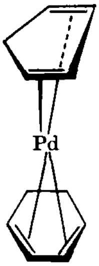
(203)

isomeric *cis,cis*-1,6-cyclodecadiene (**203**) does not rearrange, however, but produces the expected complex. It has been suggested (*581*) that the rearrangement of the 1,5-diene involves a π-allylic intermediate.

Spectroscopic investigation (*227*) of the cyclooctatetraene complex $(C_8H_8)PdCl_2$ indicates that all double bonds in the molecule are coordinated, but the structure of the complex has not been determined. When suspended in methanol, this complex is rapidly solvolyzed to produce μ-dichlorobis(2-methoxy-3,5,7-cyclooctatrienyl)dipalladium(II) (*501*). Similar complexes are formed by the reaction of 1,3-cyclohexadiene, 1,3-cycloheptadiene, or 1,3- or 1,5-cyclooctadiene with Na_2PdCl_4 in methanol at room temperature. The last species reacts with HCl to give (1,5-cyclooctadiene)dichloropalladium(II) (*501*). Pyrolysis of the complex $[(C_8H_{12}OCH_3)PdCl]_2$ obtained from 1,5-cyclooctadiene yields 1-methoxy- and 2-methoxy-1,3-cyclooctadiene (*535*).

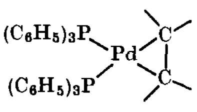
Interaction of bis(benzonitrile)dichloropalladium(II) with *all-trans*- and *cis,trans,trans*-1,5,9-cyclododecatriene (*370, 456*) produces yellow 1:1 complexes melting with decomposition at 170° and 190°C, respectively. The infrared spectra of the complexes indicate that coordination is at a trans double bond in both species.

Fischer and Werner (*218*) have reported the preparation of the Pd(0)–olefin complex (cyclopentadiene)(1,3-cyclohexadiene)palladium(0). Initially they prepared dimeric (1,3-cyclohexadiene)dichloropalladium(II) by reaction of the diene with $Pd(CO)Cl_2$, which was, in turn, reacted with cyclopentadienylpotassium. The red, air-stable, monomeric complex was diamagnetic, soluble in most organic solvents, and had a dipole moment of 2.11 *D* in agreement with the tetrahedral structure (**204**).



(**204**)

It has been reported (*221*) that a suspension of tetrakis(triphenylphosphine)palladium(0) reacts readily at room temperature with tetracyanoethylene, maleic anhydride, and diethyl fumarate to produce the complexes of structure (**205**), and at reflux temperature with tetra-



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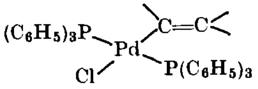


(206)

chloro-, trichloro-, and *cis*- and *trans*-1,2-dichloroethylene to yield complexes of structure (**206**). The structural assignments have been based on the proton NMR spectra. Bis(triphenylphosphine)(maleic anhydride)palladium in benzene, tetrahydrofuran, or acetone catalyzes the dimerization of butadiene to 1,3,7-octatriene (*568*).

C. PLATINUM

Although a variety of platinum(II)–ethylene complexes have been described (*268*), those most frequently encountered are Zeise's salt, $K[(C_2H_4)PtCl_3]\cdot H_2O$, and Zeise's dimer, $[(C_2H_4)PtCl_2]_2$. These have been employed for preparation of many other platinum(II)–olefin complexes and have been the subject of much research.

Although many infrared investigations of Zeise's salt, its homologs, and analogs concentrate on the changes in the olefin spectrum upon complexation (*101*, *478*, *479*), more recently the emphasis has been upon the far-infrared region in which the spectra contain bands associated with the metal–olefin and metal–chlorine vibrations (*2*, *3*, *8*, *232*, *246*, *247*, *259*, *261*, *485*). In Zeise's salt, the Pt–Cl stretching bands associated with the asymmetric and symmetric vibrations of Cl–Pt–Cl and with C_2H_4–Pt–Cl appear at 339, 331, and 310 cm^{-1}, respectively (*8*, *259*). The frequency of these vibrations are relatively insensitive to deuteration of the olefin (*259*) or substitution of another olefin for ethylene (*2*, *485*). In Zeise's dimer, the Pt–Cl stretching frequency for the terminal chlorine is at 364 cm^{-1}, while the stretching vibration of the bridging chlorine is coupled with several other vibrations producing bands at 321 and 293 cm^{-1} (*261*). In the Pd(II) analog, these vibrations occur at somewhat lower frequencies (*261*). In the dimer, the Pt–Cl (terminal) stretching force constant is slightly larger than those of Zeise's salt (2.17 *vs.* ~1.8 mdyne/Å), whereas the stretching force constant for Pt–Cl (bridging) is much smaller (0.69 mdyne/Å) (*261*).

In both Zeise's salt and the dimer, the frequency of the platinum–olefin stretching vibration is about 407 cm^{-1} (*232*, *259*, *261*). This is lowered somewhat by deuteration of the olefin, by substitution of another olefin for ethylene, or by substitution of bromine for chlorine (Table II) (*259*, *261*). The stretching force constant for this vibration has been calculated to be about 2.23 mdyne/Å (*259*, *261*, *485*). Despite the fact that the stretching force constant for the metal–olefin vibration in the palladium dimer $[(C_2H_4)PdCl_2]_2$ is lower (2.14 mdyne/Å), the frequency of the vibration is higher (427 cm^{-1}) than in the platinum analog owing to the lighter mass of the palladium atom (*261*).

TABLE II

C═C AND PT–OLEFIN STRETCHING FREQUENCIES OF VARIOUS MONOOLEFIN COMPLEXES[a]

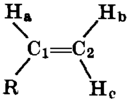
Complex	ν(C═C) free olefin	ν(C═C) complexed olefin	Δν	ν(metal–olefin)
$K[(C_2H_4)PtCl_3]\cdot H_2O$	1623	1526	97	407
$K[(C_2D_4)PtCl_3]\cdot H_2O$	1515	1428	87	387
$K[(C_2H_4)PtBr_3]\cdot H_2O$	1623	1511	112	395
$K[(C_3H_6)PtCl_3]$	1649	1505	144	393
K[(*trans*-C_4H_8)$PtCl_3$]	1681	1522	159	387
K[(*cis*-C_4H_8)$PtCl_3$]	1672	1505	167	405

[a] From (*261*).

Some investigators have assigned additional infrared bands at 480–500 (*232*, *485*) and 360–370 cm^{-1} (*485*) to platinum–olefin vibrations as well. Grogan and Nakamoto suggest (*259*, *261*), however, that these are probably due either to overtones or combination bands or to metal–chlorine vibrations.

The low frequency shift of $\nu_{C=C}$ ($\Delta\nu$, Table II) has often been considered to be a measure of the strength of the coordinate bond. It is evident from Table II, however, that the magnitude of the shift does not parallel the Pt–olefin stretching frequency. It has been pointed out by Grogan and Nakamoto (*259*, *261*) that the C═C stretching mode of an olefin often couples with the CH_2 scissoring mode thus rendering unreliable the use of $\Delta\nu_{C=C}$ for determination of coordinate bond strength. A much better measure would be the metal–olefin stretching force constant (*261*).

In the NMR spectra the magnitude of the increased magnetic shielding experienced by the olefinic protons when complexed with platinum(II) decreases in the order ethylene > propene > *cis*-2-butene > styrene (*231*). The observed net increase in shielding suggests that in the coordinate bond the π component is more significant than the σ component. The inductive effect of the methyl group in propene and *cis*-2-butene and the conjugative effect of the phenyl group in styrene render the π^* orbitals of the olefin less effective *d*-electron acceptors than are those of ethylene. In an asymmetrically substituted ethylene (**207**), a smaller increase of shielding of H_a than of H_b and H_c indicates



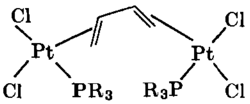
(**207**)

that the platinum atom is closer to C-2 than to C-1. This is not surprising since an electron-releasing substituent R will result in some displacement of π-electron density toward C_2. Further, a larger coupling of platinum with H_b than with H_c suggests that the olefin molecule is oriented so that H_b is closer to the platinum (*231*). This orientation may be the result of the steric effect of the substituent group.

Broad line NMR studies of Zeise's salt crystals (*397*) indicate that the ethylene molecule experiences large-amplitude rotational oscillations about both the double bond axis and the metal–olefin axis with relatively little distortion of the molecule being apparent. An analogous study of Zeise's dimer (*497*) shows similar oscillations with some moleular distortion evident.

Proton magnetic resonance at low temperature has been employed by Cramer (*150*) to evaluate the rapid rate of exchange ($k > 70\ \text{sec}^{-1}$) of ethylene in the Zeise's anion in methanolic HCl.

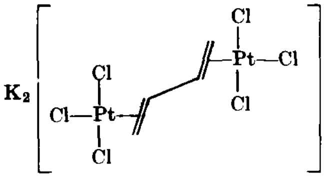
The complexes $(C_8H_{12})PtCl_2$ and $(C_8H_{14})_2PtCl_2$ have been obtained from 4-vinylcyclohexene and cyclooctene, respectively (*371*). The latter loses one molecule of olefin at about 100°C presumably to yield the dimer. similarly, 1-octene forms a white crystalline complex $(C_8H_{16})_2PtCl_2$ which on standing loses olefin to produce the dimer (*275*). The color and insolubility of this complex suggest a cis structure. Treatment of $[(R_3P)PtCl_2]_2$ with an olefin, R'—CH═CH_2 ($R' = H$, CH_3, or C_2H_5), at 20°C produces the cis complex (olefin)$PtCl_2(R_3P)$ (*130*) which loses olefin above 100°C. If the olefin is 1,3-butadiene, the pale yellow, insoluble product obtained has been postulated to have structure (**208**) in which the butadiene molecule is bridged between two platinum atoms (*102*).



(**208**)

A somewhat similar butadiene complex has been obtained with ammonia as a ligand (*285*) by addition of dilute aqueous ammonia to an aqueous solution of $K_2[(C_4H_6)Pt_2Cl_6]$.

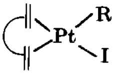
Because of the similarities between the infrared spectra of free 1,3-butadiene, Zeise's salt, and the complex $K_2[(C_4H_6)Pt_2Cl_6]$, Grogan and Nakamoto (*260*) have concluded that the complex has the structure (**209**) in which the butadiene molecule has the trans configuration which predominates in the free olefin. It seems not unlikely then that in the other Pt(II)–butadiene complexes (*102*, *285*) also the diene molecule has the trans configuration.



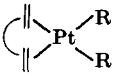
(**209**)

With 1,5-hexadiene, the compound $K_2[(C_6H_{10})Pt_2Cl_6]$ with a bridging diene molecule can be obtained (*283*); this diene will form the complex $(C_6H_{10})PtCl_2$ as well in which it is chelated, probably with a gauche configuration (*283*) and which is less stable than the analogous complex with chelated 1,5-cyclooctadiene (*284*).

The reaction of Grignard compounds with *cis*-(olefin)–diiodoplatinum(II) (*6*) yields the product (**210**) if the olefin is norbornadiene or dicyclopentadiene and the product (**211**) if the olefin is 1,5-cyclooctadiene (*360*). If the olefin is cyclooctatetraene, the binuclear compound $R_2Pt(C_8H_8)PtR_2$ is sometimes obtained (*181*, *360*), in addition to the mononuclear species (**211**); the infrared spectrum of the latter shows the presence of uncomplexed double bonds.



(**210**)



(**211**)

1,3,5-Cycloheptatriene reacts with platinum(IV) bromide in acetic acid to produce a mixture of tropylium hexabromoplatinate $(C_7H_7)_2PtBr_6$ and (1,3,5-cycloheptatriene)*cis*-dibromoplatinum(II) in a ratio of about 1 : 2 (*359*). It has been suggested (*359*) that the initial step involves hydride ion abstraction from the olefin and a concomitant reduction of platinum. This observation is in conflict with an earlier report (*198*) that the product of the reaction is the tropylium complex $[(C_7H_7)PtBr_2]_2$.

Both *cis*, *trans*, *trans*- and *all-trans*-1,5,9-cyclododecatriene yield upon reaction with Zeise's dimer in acetone, the compounds bis(olefin)-*trans*-dichloroplatinum(II) as yellow-orange plates melting at about 130°C (*456*). Dissolution of the *all-trans* product in an organic solvent results in loss of olefin to produce the polymeric species $(C_{12}H_{18})_4(PtCl_2)_6$ (*456*). An attempted preparation of the platinum(II) complex of *cis,trans*-1,5-cyclodecadiene resulted in slow rearrangement of the olefin to produce *cis*-(1,2-divinylcyclohexane)dichloroplatinum(II) (*581*).

A crystal structure analysis (*30*) of the complex (dipentene)dichloroplatinum(II) (*104*) has shown (Fig. 6) that although the double bond in the ring is perpendicular to the dsp^2 plane of platinum(II), that in the propenyl side chain is tilted to make an angle of 62° with the plane. The platinum–trigonal carbon atom distances vary between 2.11 and 2.25 Å and are greater for the carbon atoms of the ring double bond. The

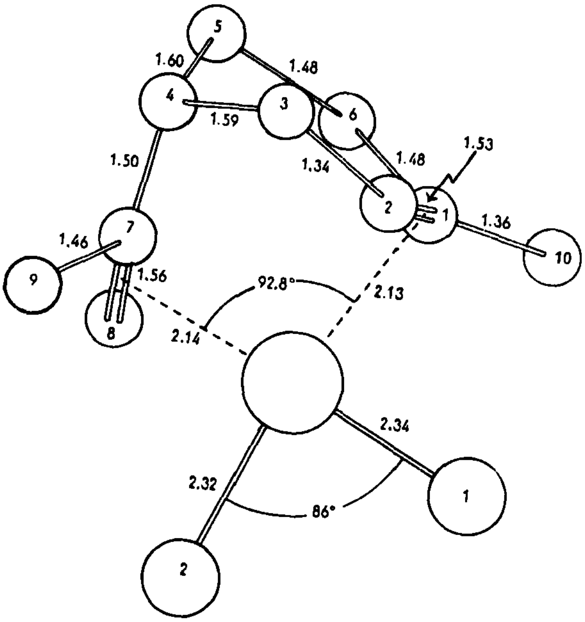


FIG. 6. Molecular structure of (dipentene)dichloroplatinum(II) (*30*).

interatomic distances indicate that the platinum atom is not symmetrically positioned with respect to the trigonal carbon atoms of the propenyl group, but is closer to the terminal carbon. The nonperpendicular inclination of this double bond to the platinum(II) coordination plane would be expected to reduce considerably the *d*–π^* back-bonding, thereby producing a weaker coordinate bond.

An X-ray analysis (*27*) of the dicyclopentadiene complex $C_{10}H_{12}PtCl_2$ (*104*, *182*) has shown that the olefin has an endo configuration with both double bonds coordinated to platinum. The platinum–trigonal carbon atom distances are much the same as in the dipentene complex, but no indication is given of the orientation of the double bonds with respect to the platinum coordination plane.

The complex μ-dichlorobis(methoxydicyclopentadiene)diplatinum (*104*, *558*) prepared by reaction of methanol with $(C_{10}H_{12})PtCl_2$, has been shown by X-ray diffraction (*603*) to have a structure (Fig. 7) in which the platinum is π-bonded to the double bond of the cyclopentene ring and σ-bonded to one of the carbon atoms of the norbornene ring, while the methoxy group is attached to a neighboring carbon of the same ring. This structure is that proposed earlier by Chatt and coworkers (*104*). Obviously, it is the double bond of the norbornene ring that is opened when the reaction with alcohol occurs. The platinum–

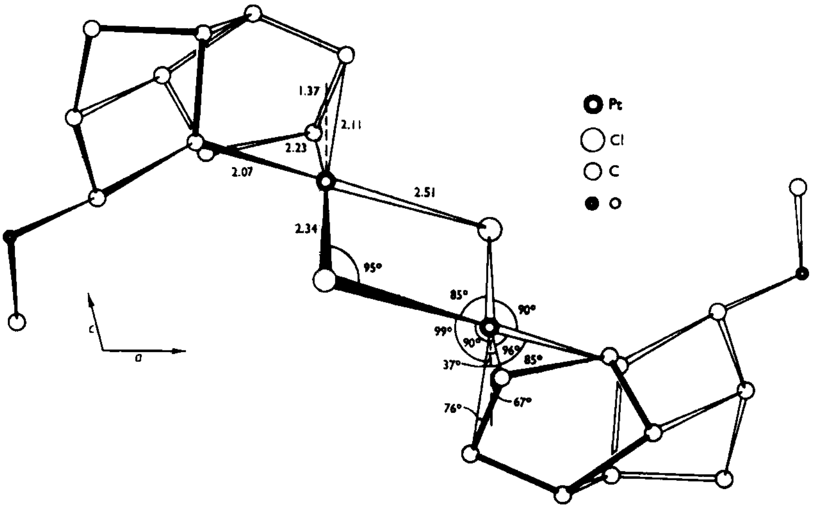
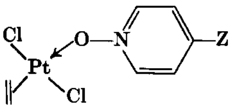


FIG. 7. Molecular structure of μ-dichlorobis(methoxydicyclopentadiene)diplatinum (*603*).

chlorine distances indicate that the σ-bonded carbon atom exerts a stronger trans effect than does the π-bonded olefin.

Orchin and colleagues have studied (*239*, *325*, *326*, *514*, *543–545*) extensively the platinum complexes *trans*-(olefin)(4-ZC_5H_4NO)$PtCl_2$ (**212**) in which the 4-substituent, Z, on pyridine-*N*-oxide is OCH_3, CH_3, H, Cl, CO_2CH_3, CN, or NO_2. The olefins have included ethylene (*239*), styrene, and 3- or 4-substituted styrenes (*239*, *544*), 1-dodecene (*544*), propene (*326*), vinyl butyrate (*326*), vinyl benzoate (*326*), and *cis*-2-butene (*514*). The ethylene complexes are readily prepared by reaction of either Zeise's salt or dimer with the pyridine-*N*-oxide (*239*). The ethylene can then be displaced by another olefin if desired. Although it was initially reported (*543*) that, for a series of the ethylene complexes, there was a dependence of the infrared stretching frequencies $\nu_{N\rightarrow O}$ and $\nu_{C=C}$ upon the substituent Z, a subsequent study (*514*) of the corresponding *cis*-2-butene complexes showed no dependence of $\nu_{C=C}$ on Z. Similarly there is little sensitivity of $\nu_{Pt\leftarrow O}$ to change in Z (*545*).



(**212**)

A spectrophotometric study (*544*) of the competition of 1-dodecene with a series or 3- or 4-substituted styrenes in these complexes has shown that the equilibrium is affected not only by changing the substituents on styrene but to an even greater extent by change of Z.

The magnitude of the increase in magnetic shielding of the ethylene protons in $(C_2H_4)(4\text{-}ZC_5H_4NO)PtCl_2$ is dependent upon Z, being larger when Z is an electron-releasing and smaller when Z is an electron-withdrawing substituent (*325*). This dependence has been attributed to the effect of Z on the π interaction between Pt(II) and ethylene. The dependence upon Z of the coupling constant $J_{^{195}Pt-C_2H_4}$ (67–71 cps), which increases with increasing electron-withdrawing character of Z, has been suggested by Kaplan and Orchin (*325*) to reflect the platinum–ethylene distance. Braterman (*78*) argues, however, that it more likely reflects the change in the σ-bonding component of the platinum–olefin bond with change of Z.

When the olefin has the configuration (**207**) and $Z = CH_3$, complex formation results in an upfield change in the olefinic proton shielding in the order $\Delta H_c > \Delta H_b > \Delta H_a$, the values for propene being 0.69, 0.64, and 0.63 ppm, respectively (*326*). The ^{195}Pt coupling constants with

H_a, H_b, and H_c are 79.0, 77.0, and 67.2 cps, respectively, suggesting again (*231*) that in the complex with an asymmetrically substituted olefin the platinum atom is not in the plane of the π orbital and is closer to H_a and H_b than to H_c.

Because replacement of 4-substituted pyridine-*N*-oxide by the corresponding pyridine results in a higher frequency for $\nu_{C=C}$, Schmidt and Orchin suggest (*514*) that complexing is weakened by competition of the π^* orbitals of pyridine with the olefin π^* orbital for the metal *d*-electrons. The coupling of the olefinic protons with platinum indicates also that the olefin is less strongly bonded in the pyridine complex (*327*). Fritz and Sellmann (*232*) contend, however, that, since $\nu_{Pt-C_2H_4}$ does not vary with change of the pyridine substituent, whereas $\nu_{Pt \leftarrow N}$ shows marked variation, there is predominantly σ bonding of pyridine to platinum and probably relatively little participation of the π^* orbitals of the pyridine ligand. They conclude that in the platinum(II)–ethylene complex, on the other hand, the major bonding component is the d–π^* back-bonding.

Platinum complexes incorporating an optically active amine have been employed for resolution of racemic mixtures of optically active olefins by reaction of the olefin with *trans*-(ethylene)(amine)dichloroplatinum(II). The differing solubility of the diastereoisomers permits separation by fractional crystallization and the olefin can be recovered by reaction of the complex with aqueous alkali cyanide. Using either (+)-1-phenyl-2-aminopropane (Dexedrine) or (+)- or (−)-α-phenylethylamine, Cope and co-workers have resolved the optical isomers of *trans*-cyclooctene (*129*, *130*), *trans*-cyclononene (*126*), and *cis,trans*-1,5-cyclooctadiene (*131*). With (+)-*trans*-(ethylene)(α-phenylethylamine)dichloroplatinum(II), the diene forms a complex having only the trans double bond coordinated and, with (−)-*trans*-(ethylene)(α-phenylethylamine)dichloroplatinum(II), a bridged complex with each double bond coordinated to a different platinum atom.

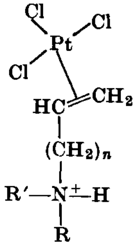
Employing a somewhat similar approach. Paiaro and Panunzi and co-workers (*137*, *455*, *458*, *459*, *462*) have shown that diastereoisomeric pairs are produced when an olefin which does not contain symmetry planes perpendicular to the plane of the double bond and an optically active ligand such as α-phenylethylamine are coordinated to platinum(II). When a double bond is coordinated to the metal atom, each of the trigonal carbon atoms, if already linked to two different substituent groups, becomes an asymmetric center. One would thus expect to obtain two diastereoisomers from propylene, styrene, or *trans*-2-butene, but from *cis*-2-butene a meso compound would be expected since the two asymmetric carbon atoms have opposite configuration.

By displacement of ethylene from (−)-*trans*-(ethylene)-(*S*)-(α-phenylethylamine)dichloroplatinum(II) with propylene, styrene, or *trans*-2-butene followed by fractional crystallization from a suitable solvent or solvent mixture these investigators (*455*, *458*) have obtained with each olefin one diastereoisomer in almost quantitative yield. In solution, the pure diastereoisomer undergoes mutarotation attaining at equilibrium a rotational value corresponding to that of the initial diastereoisomeric mixture which is about the same as that of the original ethylene complex. The rate of mutarotation is much greater for the complexes having one asymmetric carbon atom than for that having two. The rotational values indicate that the contribution to the molecular rotation by each asymmetric center in the complexed olefin molecule is about 125°.

Similar diastereoisomeric complexes have been obtained (*459*, *462*) from (−)-*cis*-(ethylene)-(*S*)-(α-phenylethylamine)dichloroplatinum(II). However, in solution these undergo mutarotation much more slowly than do the corresponding trans complexes; furthermore, the equilibrium constant for mutarotation deviates quite notably from unity indicating an induced asymmetry probably due to steric interaction between the amine and olefin. This effect is most marked for the *trans*-disubstituted olefins. Circular dichroism spectra (*137*) of the complex with *trans*-2-butene show that, in the equilibrium mixture in ethanol at 25°C, the (−)-diastereoisomer predominates to the extent of 40%.

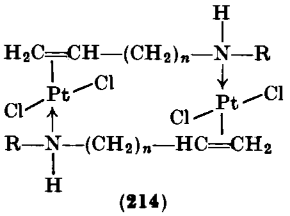
The optically active isomers of *endo*-dicyclopentadiene have been obtained (*460*) by reaction of α-phenylethylamine with (methoxydicyclopentadiene)chloroplatinum(II) dimer, separation of the diastereoisomers of the monomeric $(C_{10}H_{12}OCH_3)Pt(amine)Cl$, and treatment of these with KCN.

Unsaturated amines interact with K_2PtCl_4 in hydrochloric acid to produce a zwitterion (**213**) (R or R′ = H, C_2H_5, allyl, or *n*-octyl, $n = 1$–3) in which the double bond is coordinated at Pt(II) (*114*, *164*). With diallylamine, there is coordination at only one double bond. With



(213)

secondary amines, treatment of the zwitterion with base yields either a dimer (**214**) (R = *n*-octyl), in which there is bridging through the



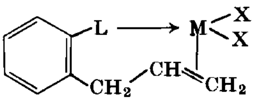
(214)

nitrogen atom, or an insoluble, polymeric product. The visible and ultraviolet spectrum of the dimer with *n*-octylallylamine indicates some platinum–platinum interaction (*164*).

The stability constants for some platinum(II)–olefin complexes $[H_2C{=}CH(CH_2)_n{-}LR_2R']^+PtX_3^-$, (L = N, P, or As, X = Cl or Br), in aqueous solution have been spectrophotometrically determined (*162*, *163*, *125*, *276*). The enthalpy and entropy changes upon complexation indicate that, for formation of a stable Pt(II)–olefin bond, the π-acceptor capacity of the olefin is more important than its σ-donor capacity (*162*). A similar study involving C-substituted allyl ammonium cations (*163*) has shown that both steric and electronic effects are important in determining the strength of the coordinate bond. Although the stability constants for the bromo systems are lower than those for the corresponding chloro systems, an analyses of the enthalpy data indicates that the Pt(II)–olefin bond is stronger in the bromo complexes (*165*). This conclusion appears to be supported by infrared spectral data (*165*).

The stability constants of the complexes of unsaturated alcohols are higher than those of the corresponding complexes with unsaturated ammonium ions (*276*). The difference is due largely to the difference in enthalpy change for complex formation in the two systems and this has been attributed to the difference in solvation energies between the free ligands and the complexes.

When the ligands are *o*-allylphenyldimethylarsine or *o*-allylphenyldiphenylphosphine (*52*), the diamagnetic, monomeric complexes involve coordination of both the double bond and the group V metal atom at the transition metal (**215**). A similar complex is formed with the 4-pentenyl-



M = Pd or Pt

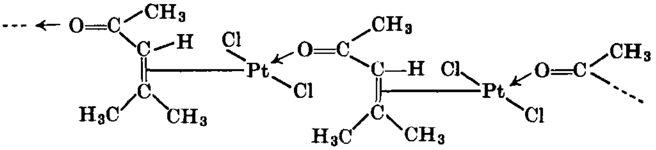
L = $As(CH_3)_2$ or $P(C_6H_5)_2$

X = Cl or Br

(215)

dimethyl-, 4-pentenyldiphenyl-, di-4-pentenylphenylarsines (*53*), and 4-butenyldialkylphosphine (*313*).

With mesityl oxide, the Pt(II) complex involves coordination of both the double bond and the carbonyl oxygen (*464*). The product is, however, polymeric in nature (**216**). With palladium(II), the π-allylic dimer is formed (*464*).



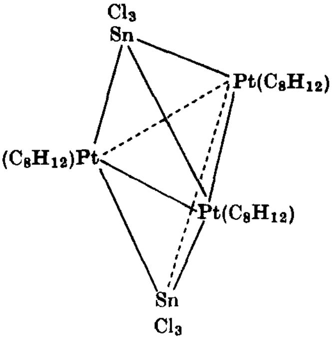
(**216**)

With acrylonitrile, coordination appears to occur only at the double bond to produce $(CH_2{=}CH{-}CN)_2PtCl_2$ (*369*).

In addition to the complexes of platinum(II), a number of olefin complexes of platinum(0) have been prepared. Chatt, Shaw, and Williams (*103*) have described the complex (olefin)bis(triphenylphosphine)-platinum(0) prepared by reaction of the olefin at 60°C with *cis*-dichloro-bis(triphenylphosphine)platinum(II) in ethyl alcohol containing hydrazine hydrate. The complex was formed only with *trans*-stilbene, *trans*-4,4-dinitrostilbene, and acenaphthene. The ethylene complex $(C_2H_4)Pt[P(C_6H_5)_3]_2$ has been prepared (*121*) by reduction of the corresponding oxygen complex with sodium borohydride in the presence of the olefin.

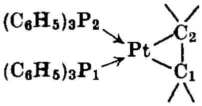
Colorless diamagnetic crystals of bis(1,5-cyclooctadiene)platinum(0) (m.p. 110°C decomposes) have been obtained (*419*) by treatment of (1,5-cyclooctadiene)dichloroplatinum(II) with an excess of isopropylmagnesium bromide in ether at –40°C in the presence of the diene followed by ultraviolet irradiation at room temperature. This represents the first purely olefinic complex of zero-valent platinum. Another 1,5-cyclooctadiene complex of platinum(0) involving a platinum–tin metal cluster with a trigonal-bipyramidal structure (**217**) has been reported (*263*, *378*). This compound was prepared by reaction of the diene with the anion $[Pt_3Sn_8Cl_{20}]^{4-}$ which, in turn, was obtained by reaction of stannous chloride with either $PtCl_2$ or $[Cl_2Pt(SnCl_3)_2]^{2-}$ in acetone.

Chloro- (*69*, *70*) and fluoroolefins (*69*, *250*, *511*) also have been observed to form stable complexes upon reaction with tetrakis(triphenylphosphine)platinum(0). These show no C=C stretching band in the



(217)

infrared and have been postulated to have a structure (**218**) suggesting σ bonding of the olefinic carbon atoms to the metal.



(218)

Tetracyanoethylene forms a similar very stable complex (*25*) when reacted with (phenylacetylene)bis(triphenylphosphine)platinum(0) in benzene. An X-ray analysis of this complex (*461*) has shown that the olefin molecule is somewhat distorted from planarity and that the dihedral angle between the planes P-1–Pt–P-2 and C-1–Pt–C-2 is about 10° [similar to that observed in the analogous (ethylene)nickel(0) complex (*122*)]. The C-1–C-2 bond length is 1.52 Å and the platinum–carbon distance 2.10 Å. In view of the small angle (42°) subtended at platinum by the olefin it is difficult to rationalize σ bonding of C-1 and C-2 to platinum. It has been suggested (*461*) that, since the donor character of the double bond in tetracyanoethylene is negligible, there may be an essentially pure π bonding involved. This same argument may apply for the halogenated ethylenes since the electron-withdrawing character of the substituent groups would also render these olefins poorer π donors and better π acceptors.

IX. Group Ib: Copper, Silver, and Gold

A. COPPER

Early workers (*244, 585*) have established that 1:1 complexes, unstable under ambient conditions, could be obtained by reaction of solid CuCl with ethylene, propylene, or isobutylene and of solid CuBr with ethylene. With the exception of mention of the 1:1 complex (*cis*-cyclooctene)CuCl (*269*) the literature does not describe other complexes with monoolefinic hydrocarbons.

Reaction of liquid 1,3-butadiene with solid CuCl (*285*) produces the complex $(C_4H_6)(CuCl)_2$. The infrared spectrum of this complex has bands at 1570 and 1507 cm^{-1} which are considered to represent the C=C stretching frequencies of free and coordinated double bonds, respectively. Addition of 1,5-hexadiene to a solution of CuCl in concentrated HCl yields a white, rather unstable complex $(C_6H_{10})(CuCl)_2$ (*283*). Complex formation results in a shift in the double-bond stretching frequency from 1640 to 1545 cm^{-1} and the overall simplicity of the infrared spectrum suggests a trans configuration for the diene.

Haight and co-workers (*269*) have found that crystalline complexes can be readily obtained by reduction of $CuCl_2 \cdot 2H_2O$ or $CuBr_2$ dissolved in ethanol with sulfur dioxide in the presence of the di- or oligoolefin. By this method they have prepared 1:1 complexes with norbornadiene, 1,5-cyclooctadiene, cyclooctatetraene, and dicyclopentadiene, 1:2 complexes with *cis,trans,trans*- and *all-trans*-1,5,9-cyclododecatriene, and a 1:3 complex with 1,3-cyclooctadiene. It was noted that rapid addition of SO_2 to the system produced 1:2 complexes with norbornadiene and cyclooctatetraene.

The 1:2 complexes with the cyclododecatrienes have also been produced (*456*) by reaction of the olefin with an ethanolic suspension of CuCl.

On the basis of the infrared spectrum, it was suggested by Hendra and Powell (*284*) that in the complex $(C_8H_{12})CuCl$, 1,5-cyclooctadiene assumes the chair form; to the contrary, on a similar basis, Schrauzer and Eichler (*523*) have concluded that it assumes the tub form. The question has been resolved by the structural analysis of van den Hende and Baird (*594*) which shows a centrosymmetric dimeric complex (Fig. 8) having the copper atoms quasitetrahedrally bonded to two chlorine atoms and the two double bonds of the 1,5-cyclooctadiene molecule, which assumes a slightly staggered tub form. Complex formation involves an enthalpy change of 23.5 kcal/mole and a lowering of the C=C stretching frequency from 1660 to 1612 cm^{-1}.

Electrolysis at copper electrodes of cupric perchlorate with 1,5-cyclooctadiene in methanol yields well-defined crystals of an air-stable cuprous complex $(C_8H_{12})_2CuClO_4$ (*390*). The C=C stretching band at 1660 cm^{-1} in the diene is replaced by two bands at 1638 and 1595 cm^{-1} in the complex, suggesting nonequivalent coordination of the double bonds. As with the silver–olefin complexes (*492*) there is a dependence

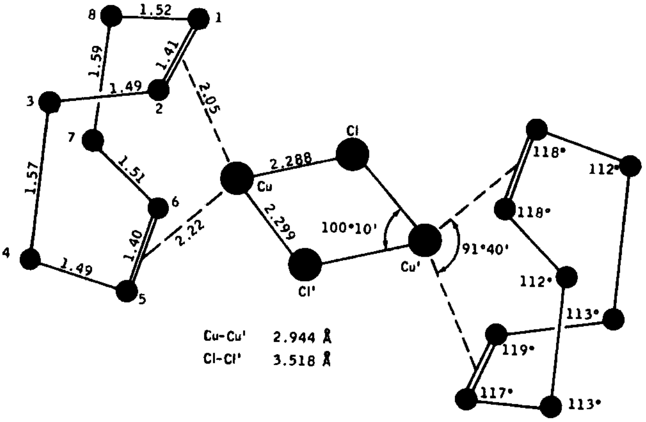
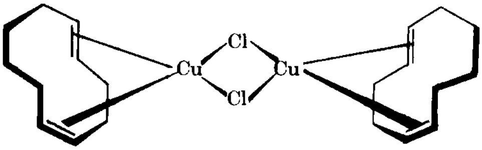


FIG. 8. Molecular structure of μ-dichlorobis(1,5-cyclooctadiene)dicopper(I) (*594*).

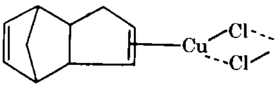
of the complex stoichiometry upon the anion associated with Cu(I), i.e., 1:1 for CuCl and 2:1 for $CuClO_4$.

The complexes $(C_{10}H_{16})CuCl$ and $(C_{10}H_{16})(CuCl)_2$ are formed with *cis,trans*-1,5-cyclodecadiene and *cis,cis*-1,6-cyclodecadiene, respectively (*580*). With CuBr, both olefins form the 1:2 complex. The infrared spectra indicate complexing of all double bonds and structure (**219**) has been postulated for $(C_{10}H_{16})CuCl$. A polymeric structure has been suggested for the 1:2 CuBr complex with the same olefin.



(**219**)

With dicyclopentadiene, both cuprous chloride and cuprous bromide form a 1:1 complex which decomposes above about 110°C (*523*). The infrared spectra indicate complexing of only one double bond of the olefin and Schrauzer and Eichler (*523*) have suggested the structure (**220**) in which complexing takes place at the cyclopentene side of the molecule.



(**220**)

Subsequent investigation of the corresponding complex with aurous chloride (*307*) placed the point of coordination at the norbornene side. Recent investigations (*584*) of the CuCl-catalyzed photochemical dimerization of norbornene and *exo*-dicyclopentadiene have established that dimerization occurs similarly with both molecules, i.e., through the double bonds of the norbornene rings. Since it is considered that the reaction intermediate involves complexing of the olefin molecules at the Cu(I) atom it is almost a certainty that the coordination of dicyclopentadiene to Cu(I) is through the norbornene unsaturation.

The cuprous halide complexes which have been most thoroughly investigated are those with norbornadiene and cyclooctatetraene. While with CuBr, the most common norbornadiene complex is $(C_7H_8)(CuBr)_2$ (*1, 269, 523*), that with CuCl is usually $(C_7H_8)CuCl$ (*269, 523*). It has been observed, however, that rapid addition of SO_2 to $CuCl_2$ and C_7H_8 in methanol yields $(C_7H_8)(CuCl)_2$ (*269*). The infrared spectra (*523*) indicate complexing of both double bonds in $(C_7H_8)(CuBr)_2$, but of only one in $(C_7H_8)CuCl$.

Baenziger and co-workers (*29*) have observed that the structure of $(C_7H_8)CuCl$ consists of the tetrameric unit $[(C_7H_8)CuCl]_4$ in which the Cu and Cl atoms form an 8-membered tub-shaped ring (Fig. 9). The complexed double bond of norbornadiene lies approximately in the plane of the Cu atom and its two adjacent Cl atoms producing a distorted trigonal configuration about the copper. The shortest Cu–C distance is 2.05 Å and the plane of the norbornadiene molecule containing the coordinated double bond makes an angle of 109.1° with the trigonal coordination plane of the copper. The deviation of that angle from 90° may be attributable to the proximity of the copper atom to a hydrogen atom on the bridging carbon.

With cyclooctatetraene, the complexes $(C_8H_8)CuCl$ (*269*), $(C_8H_8)(CuCl)_2$ (*523*), and $(C_8H_8)CuBr$ (*523*), which decompose at about 150°C, have been obtained. The infrared spectra of these indicate the presence of both free and complexed double bonds. Baenziger, Richards, and Doyle (*31*) have found that the structure (Fig. 10) of $(C_8H_8)CuCl$ consists of continuous chains of copper and chlorine atoms extending in the direction of the shortest axis of the orthorhombic unit cell. There is one double bond of the olefin bound to each copper atom with a shortest Cu–C distance of 2.07 Å. As with $(C_7H_8)CuCl$, there is a distorted trigonal coordination about the Cu atom and the plane of the coordinated double bond makes an angle of 110° with the trigonal coordination plane. Two other double bonds, one in the olefin molecule complexed to Cu(I) and the other in an adjacent molecule, are located in directions approximately perpendicular to the trigonal plane, i.e., at the apices of a distorted tri-

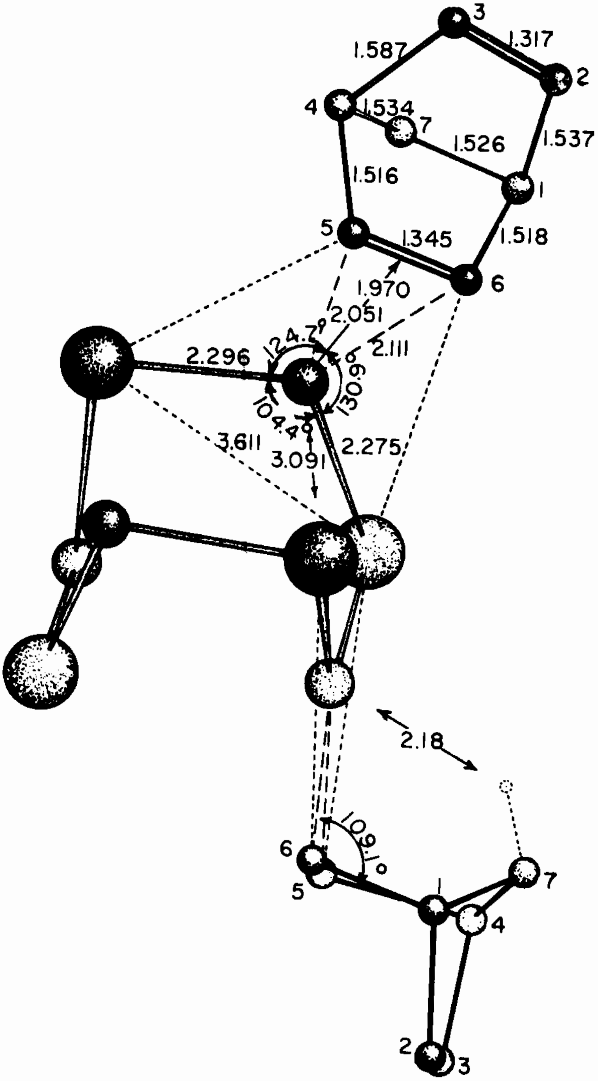


FIG. 9. Structure of cyclic tetramer of (nor-C_7H_8)CuCl (*29*). (Two C_7H_8 molecules have been omitted.)

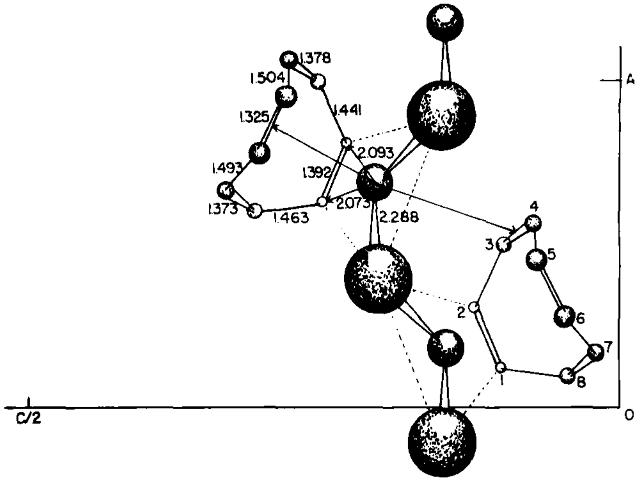


FIG. 10. Crystal and molecular structure of $(C_8H_8)CuCl$ (*31*).

gonal bipyramid; however, the distances from the copper atom, 2.76 and 3.5 Å, indicate little participation in bonding.

In both $(C_7H_8)CuCl$ and $(C_8H_8)CuCl$, the copper is asymmetrically located with respect to the double bond, but the asymmetry is almost identical in the two species. This is rather surprising (*29*) in view of the quite different packing arrangements of the complexes.

Cuprous halide complexes have also been obtained with acrolein (*330*) and various unsaturated nitriles (*519, 523*). In general, the infrared spectra of the 1:1 complexes indicate a primary coordination through the double bond with some evidence for participation of the other donor group in the molecule. With acrolein and acrylonitrile the enthalpy change for complexing of the gaseous molecule with solid CuCl was found to be −11.8 and −14.9 kcal/mole, respectively.

B. SILVER

The interaction of olefins with silver salts in solution has been thoroughly investigated and frequently reviewed (*47, 268*). Distribution (*237, 288, 578, 621*) and solubility (*40, 77, 193, 235, 237*) data from aqueous systems, as well as retention data obtained from glycol solutions of $AgNO_3$ on gas chromatographic columns (*154, 236, 240, 243, 296, 416, 548*), have been employed for determination of stability constants for silver ion–olefin complexes. Although, in general, there is good correspondence between the stability constants determined by gas chromatography and the distribution or solubility methods, some very definite exceptions have been noted (*296*, *416*).

These studies have indicated that (*i*) there is usually only one olefin molecule coordinated at each silver ion (*621*), (*ii*) alkyl substitution at the double bond decreases the stability of the complex (*288*, *416*, *621*), (*iii*) with *endo*-cycloolefins, the stability constant increases with increasing ring strain (*578*), (*iv*) more stable complexes are formed with *cis*- than with *trans*-olefins (*236*, *288*, *416*, *442*), (*v*) the most stable diene complexes are formed by the 1,5-diene systems (*416*), and (*vi*) deuteration of an olefin increases the complex stability (*154*).

The effect of alkyl substitution at the double bond on complex stability has been attributed to steric factors (*288*, *416*, *621*). However, the question as to whether the steric effects of the alkyl substituent result in a weaker metal–olefin bond or only in a larger entropy change (and thus a smaller free energy change) for the system upon complex formation has not been adequately discussed by the earlier investigators. Almost intuitively one would expect that the more basic olefin would form a stronger bond with the silver ion which might, in turn, result in a larger entropy change for the system. More recent studies (*154*, *235*, *237*) indicate that increasing the basicity of the olefin probably results in a stronger silver ion–olefin interaction and can result even in a more stable complex. Thus, for a series of *m*- and *p*-substituted styrenes (*235*) and a series of unsaturated ethers, esters, and ketones (*237*) the logarithm of the complex stability constant increases linearly with decreasing Hammett σ and σ_m values, respectively, for the olefin. Deuteration, which produces a more basic olefin, results also in formation of a more stable complex (*154*).

While it has been suggested (*167*) that there may be a weakening of the π component of the σ,π bond of the complex concurrent with the strengthening of the σ component by the electron-donating alkyl substituent, it is not known how significant the effect would be since a qualitative estimate (*403*) indicates that with silver the σ component should predominate.

Shopov and Andreev (*542*), using a molecular orbital approach, have found for a series of olefins and diolefins a fairly linear relationship between the logarithm of the stability constant and the difference between the energy of the bonding and antibonding π orbitals. Since, however, they have related the stability constant to the bonding energy only and have not considered at all the effect of entropy change upon complex stability, the straight line relationship may be fortuitous.

There are factors other than olefin basicity and the steric effects of substituent groups on the olefin which can affect the stability of the silver ion complex. These include the energy required to displace solvate molecules from the coordination sphere of the metal ion and the degree of association between the cations and anions, especially in concentrated solutions or in solid salts.

A calculation (*296*) taking into account the charge number, the ionization potential, the electron affinity, the ionic radius, the solvation (hydration) energy, and the various atomic excitation energies of the ions has demonstrated that the metal ions with closed *d* shells which form the most stable olefin complexes are those which show the smallest difference between the destabilization introduced by replacement of part of the water of hydration with an olefin molecule and the stabilization introduced by charge delocalization from olefin to metal.

The solubility of olefins in aqueous silver ion solutions is dependent upon the anion of the silver salt (*40*, *193*). In dilute solutions, solubility decreases in the order $ClO_4^- > BF_4^- \simeq NO_3^-$, whereas in concentrated solutions the decreasing order is $BF_4^- > ClO_4^- \gg NO_3^-$. The latter order parallels that of the strength of the corresponding acids and has been attributed (*193*) to protonation of the olefins as a result of hydrolysis of the silver salts. It seems more reasonable, however, to relate this order to the degree of association of the ions in the concentrated solution. Accordingly, Baker (*40*) has observed, with increasing salt concentration, an increasing solubility of ethylene in $AgBF_4$ solutions, but a decreasing solubility in $AgNO_3$ solutions, and has correlated the solubility data with the values of the activity coefficient for each salt. Further, he has reported that the addition of other fluoroborates (including fluoroboric acid) increases the solubility of C_2H_4 in aqueous $AgBF_4$ to an extent proportional to the tendency (related to the charge : radius ratio) of the added cation to decrease the hydration of the silver ion and thus make it more readily available for olefin complexing.

It has been independently observed (*296*) that the different stabilities of the silver complexes seem to depend upon the strength of the interaction between the cations and anions and suggested that the inability of silver chloride and sulfate to form olefin complexes may be explained by assuming that in these compounds the anions have a very strong affinity for the silver ions.

Spectroscopic studies of aqueous solutions of silver ion–olefin complexes have not yielded much useful data. Electronic spectra have been obtained for the aqueous systems $AgClO_4$–styrene (*426*) and $AgClO_4$–cyclohexene (*296*). The latter shows a charge-transfer band at 220–230 mμ which has been observed to have the mixing character of the charge transfer from olefin to metal and of the Rydberg transition within the olefin molecule. Infrared (*296*) and Raman (*574*) spectra indicate a shift to lower frequencies by 60–75 cm^{-1} for the olefinic C=C stretching vibration frequency, and NMR spectra (*480, 534*) show a deshielding of the olefinic protons by about 0.6–0.7 ppm upon complexing.

Additional information has been obtained by investigation of the crystalline complexes of monoolefins. With anhydrous $AgNO_3$, propylene and 1-butene form only rather unstable liquid complexes containing about 1.3 moles of olefin per mole of salt (*223*), whereas ethylene forms the solid complex $(C_2H_4)(AgNO_3)_2$ (*569*). At 0°C, this complex has an equilibrium dissociation pressure of about 150–160 mm Hg and the heat of dissociation is about 10.6 kcal/mole, considerably higher than that of the complex $(C_2H_4)AgNO_3$ in aqueous solution (5.8 kcal/mole). With anhydrous $AgBF_4$, ethylene forms four complexes $(C_2H_4)AgBF_4$, $(C_2H_4)_3(AgBF_4)_2$, $(C_2H_4)_2AgBF_4$, and $(C_2H_4)_3AgBF_4$ (*492*). It is unique in its ability to form stable 1:1 and 3:2 complexes with this salt since the most stable complex with the other monoolefins studied has a 2:1 stoichiometry (*492, 493*). This uniqueness may be due to the small size and the symmetry of the ethylene molecule which permits it to penetrate readily the $AgBF_4$ lattice with minimum lattice disruption. It is interesting to note (Table III) that although the 1:1 complex is much more stable than $(C_2H_4)(AgNO_3)_2$ (*569*), the heats of dissociation are identical.

The 2:1 ethylene complex is much less stable than the corresponding complexes with the other hydrocarbon olefins. This is certainly indicative of a weaker coordinate bonding of the silver ion with ethylene than with the more basic olefins since one must think in terms of steric effects being larger with the latter. The 2:1 complex with vinyl chloride is, on the other hand, much less stable (*495*) than that with ethylene because of the lowering of olefin basicity by the electron-withdrawing substituent. This effect contrasts with that of electron-withdrawing substituents on the stability of rhodium–olefin complexes (*152*). At the 3:1 stoichiometry the ethylene complex is again more stable than the propylene complex suggesting that here steric factors are beginning to predominate as indicated by the larger changes in ΔS° than in ΔH° for propylene upon going from the 2:1 to 3:1 ratio. The relatively unstable 3:1 complex is not produced with all olefins; for example, in the butene series, it forms with 1-butene and *cis*-2-butene, but not with isobutene or *trans*-2-butene, probably due to steric hindrance (*492*).

In this system also the 2:1 complex with *cis*-2-butene is significantly more stable than that of *trans*-2-butene. The thermodynamic data (Table III) show that the stability difference is almost completely due to differences in the entropy change contrary to that observed with alkenyl

TABLE III

THERMODYNAMIC DATA FOR SILVER SALT–MONOOLEFIN COMPLEXES[a]

Olefin	Complex	ΔH_D[b] (kcal/mole)	ΔS_D[b] (cal/mole degree)	Dissociation pressure (mm Hg) (25°C)
Ethylene	$(C_2H_4)AgBF_4$	10.61	27.47	12.8
	$(C_2H_4)_3(AgBF_4)_2(\beta)$[c]	10.38	27.45	41.1
	$(C_2H_4)_2AgBF_4(\beta)$[c]	9.49	25.67	205.4
Propylene	$(C_3H_6)_2AgBF_4$	10.97	29.10	15.7
	$(C_3H_6)_2AgClO_4$	7.10	20.69	157.8
1-Butene	$(C_4H_8)_2AgBF_4$	12.03	31.61	9.4
Isobutene	$(C_4H_8)_2AgBF_4$	11.14	28.51	8.8
cis-2-Butene	$(C_4H_8)_2AgBF_4$	12.90	32.85	4.1
trans-2-Butene	$(C_4H_8)_2AgBF_4$	12.76	35.64	20.8
1-Pentene	$(C_5H_{10})_2AgBF_4$	13.3	35.0	5.2
3-Methyl-1-butene	$(C_5H_{10})_2AgBF_4$	13.3	36.1	10.0
Ethylene	$(C_2H_4)_3AgBF_4$	9.08	27.00	2032
Propylene	$(C_3H_6)_3AgBF_4$	10.62	31.29	2538
	$(C_3H_6)_3AgSbF_6$	11.22[d]	35.92[d]	320
1-Butene	$(C_4H_8)_3AgBF_4$	11.29	33.80	888
cis-2-butene	$(C_4H_8)_3AgBF_4$	11.89	35.14	707

[a] From (*492, 495*).

[b] Values for complete dissociation of complex.

[c] Higher temperature modification (*492*).

[d] Dissociation to produce lower complex.

alkyl ethers (*236*). While part of this difference may be due to relief of strain caused by bond oppositions between adjacent methyl groups in the *cis*-olefin (*416*), the absence of the 1:3 complex with the *trans*-olefin suggests that other steric factors also may be involved.

A phase diagram investigation (*494*) of the 1-pentene-$AgBF_4$ system has shown the 2:1 and 3:1 complexes with congruent melting points at 43.3 and –30.3°C, respectively. In addition, evidence is provided for the existence of a 1:1 complex stable only in the solid state at temperatures below about –10°C. It appears to be formed by a solid state reaction between the 2:1 complex and $AgBF_4$.

The stability of the propylene complexes of various silver salts is very dependent upon the nature of the anion. The data of Table III in conjunction with the recorded (*223*) stability of the propylene complex of $AgNO_3$ establish that the order of increasing stability is $NO_3^- < ClO_4^- <$

$BF_4^- < SbF_6^-$. This order parallels that observed for olefin solubility in concentrated silver salt solutions (*40, 193*). Structural investigations of crystalline silver–olefin complexes have shown a nearly covalent bond between the silver and the nitrate ions (*28, 399*), but an electrostatic bond only between silver and fluoroborate ions (*537*). Consequently, the differing complex stability may be largely attributable to the differences in the energy required for the expansion which permits incorporation of the olefin molecule into the salt lattice. These differences will depend upon the anion composition (*537*), geometry, and size. Similarly, the degree of silver ion–anion association in concentrated solutions will vary with the anion and a similar explanation can account for the dependence of olefin solubility on the anion. In dilute solutions, however, the silver ion environment and thus the olefin solubility may be essentially independent of the anion (*193*).

Infrared and NMR spectra of deuterochloroform solutions of the $AgBF_4$ complexes have shown that the 2:1 stoichiometry prevails in solution (*493*). Also, the infrared spectra of solutions and of mulls of the solid are essentially identical (*296, 493*). The shift to lower frequency of the double-bond stretching vibrations $\nu_{C=C}$ is very dependent upon the number of substituent alkyl groups at the trigonal carbons, but essentially independent of their configuration. For olefins with zero, one, two, and three alkyl substitutents at the double bond, the shifts of $\nu_{C=C}$ are about 38, 55, 63, and 70 cm^{-1}, respectively, paralleling the olefin basicity. Although $\Delta\nu_{C=C}$ may not be a direct measure of the strength of the coordinate bond (*261*), it is reasonable to assume that increased bond strength would result in more perturbation of the olefin molecule and thus larger values of $\Delta\nu_{C=C}$ (as indicated by the difference between $\Delta\nu_{C=C}$ for $PtCl_3^-$ and Ag^+). For a number of olefins an approximately linear relationship between $\Delta\nu_{C=C}$ and both the ionization potential of the olefin and the enthalpy change ΔH°_D for complex dissociation has been observed (*492*). Whether increasing π basicity of the olefin leads then to increasing complex stability is dependent upon the value of ΔS°_D which, in turn, reflects the steric effects introduced by substituent groups.

In the crystalline complexes of straight-chain 1-olefins with 13 or more carbon atoms, the C=C stretching band has a splitting of about 10 cm^{-1} which disappears upon melting or dissolution. The only olefin showing this effect in a solution of the complex is 3,3-dimethyl-1-butene. The splittings have been attributed (*493*) to intermolecular interactions between the complexed molecules, probably due to lattice restrictions with the long straight-chain olefins and to the bulky tertiary butyl group of 3,3-dimethyl-1-butene.

Although complexation markedly reduces the intensity of the C–H stretching bands for the olefinic protons, there is no evidence for a significant frequency shift (*493*). This suggests decreased polarity in the C–H bond with little loss of sp^2 character by the trigonal carbon atom. The only other shifts are those of the out-of-plane deformation bands which move about 30–45 cm^{-1} toward higher frequencies (*296*, *493*).

In the NMR spectra, complex formation results in a deshielding of all the protons in the olefin (*493*). The deshielding is greatest (0.2 to 1 ppm) for the protons at the trigonal carbons and amounts to about 0.2 ppm for the protons of methyl groups similarly attached. On the basis of its dependence upon the number and configuration of alkyl substituents at the double bond, the deshielding has been interpreted (*493*) in terms of both the electronic and steric effects of the substituent group upon the positioning of the silver ion with respect to the trigonal carbons and the effect of this positioning upon the σ and π bonding in the complex. Since with silver a deshielding is always observed [as opposed to the shielding effect found with many other transition metal ions (*384*)], it has been suggested (*493*) again (*403*) that the σ component predominates and that the variation of the magnitude of deshielding with the alkyl substituent is primarily a reflection of the effect of the substituent upon the π component.

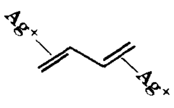
Although complex formation has relatively little effect upon the proton-proton coupling constants for the olefin, it was observed (*493*) that with certain branched-chain 1-olefins, there was a decrease in the coupling between the protons at the C-2 and C-3 positions; this was interpreted as evidence for an effect of complexing upon the relative populations of the trans and gauche rotational conformers.

Endocyclic monoolefins produce, in general, more stable silver complexes than do the corresponding aliphatic *cis*-2-olefins (*416*, *578*). The difference has been attributed to the effect of ring strain upon the π basicity of the olefin and thus upon the strength of the coordinate bond (*578*). The more strained bicyclic olefins form even more stable complexes (*416*, *578*). Distribution studies with aqueous $AgNO_3$ (*578*) have produced the order of increasing complex stability: cyclopentene > cycloheptene > cyclohexene > *cis*-cyclooctene. By contrast, the order obtained by the gas chromatographic technique (*416*) is *cis*-cyclooctene > cycloheptene > cyclopentene > cyclohexene. The difference may be attributable, in part, to differences in the physical state of the system or to the different solvents employed (*416*). As a result of steric effects, the 1-alkyl-substituted cycloolefins all form less stable complexes than do the corresponding unsubstituted olefins (*243*, *416*, *578*). When the substituent is in the 3- or 4-position, the stability constant is not much different from that of the unsubstituted olefin, although the 3-alkylcycloolefin forms a more stable complex than does its 4-alkyl-substituted analog (*243*, *488*).

Crystalline complexes with a 2:1 cycloolefin:Ag^+ ratio have been obtained with $AgNO_3$ (*120*, *135*, *318*), $AgClO_4$ (*120*, *296*) and $AgBF_4$ (*322*, *495*). A 3:1 $AgBF_4$ complex also has been obtained with cyclopentene (*495*). Although no data are available to establish the relative stability of the $AgBF_4$ complexes, the values of $\Delta\nu_{C=C}$ which range from about 65–75 cm^{-1}, indicate that the order of decreasing strength of the coordinate bond is cyclopentene > cyclohexene > *cis*-cyclooctene ≃ cycloheptene (*495*). Furthermore, the effect of a 1-methyl substituent is to increase $\Delta\nu_{C=C}$ by about 10 cm^{-1} (*495*) as a result of the increase in π basicity. Also $\Delta\nu_{C=C}$ is greater for 4-methyl- than for 3-methylcyclohexene as would be predicted (*488*). The difference between the order based on $\Delta\nu_{C=C}$ and that based on the stability constant (*416*, *578*) suggests that steric effects, perhaps dependent upon the conformation of the ring, are again markedly influencing the stability constant.

The complexes formed by aliphatic and alicyclic di- and oligoolefins are often much more stable and more easily isolated as crystalline solids than those of the corresponding monoolefins. In many instances, the silver nitrate complex has been employed for isolation of the hydrocarbon from its synthesis mixture and sometimes for determination of the ring conformation (*9*, *225*, *238*, *408*, *446*).

Kraus and Stern (*364*) have prepared from aqueous $AgNO_3$ a mixture of 1:2 and 1:1 complexes of 1,3-butadiene. From dissociation pressure measurements, they have calculated $\Delta H°$ values of 13.0 and 10.8 kcal/mole for $(C_4H_6)(AgNO_3)_2$ and $(C_4H_6)AgNO_3$, respectively, and have suggested that the complexes might best be represented by the structures (**221**) and (**222**).



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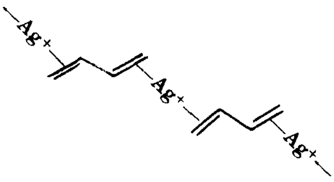

(222)

From nonaqueous solutions of $AgBF_4$, the very stable, relatively insoluble complexes $(C_4H_6)AgBF_4$ and $(C_4H_6)_3(AgBF_4)_2$ have been prepared (*490*). In these, the coordination number of the silver is analogous to that in the 2:1 and 3:1 monoolefin complexes. The infrared spectra indicate that in both complexes all double bonds are coordinated and coordination results in a low frequency shift of $\nu_{C=C}$ of 43 cm^{-1}, significantly smaller than that observed with monoolefins and suggestive of weaker bonding probably as a result of the conjugation in the diene molecule (*416*). The greater stability of the diene complex than that of the corresponding monoolefin is largely due to the presence of two coordinate bonds per hydrocarbon molecule (*490*). The 3:2 complex appears to contain two somewhat nonequivalent butadiene molecules, one identical to that of the 1:1 complex and the other less strongly coordinated. Consequently, it has been suggested that the 1:1 complex is probably a coordination polymer (**222**) and that the 3:2 complex is produced by cross-linking of the polymer chains with additional diene molecules (*490*).

With $AgBF_4$, a 3:2 complex has also been obtained with 2-methyl-1,3-butadiene, whereas only a 1:1 complex forms with 1,3-and 1,4-pentadiene (*490*) and with 1,4-diphenylbutadiene (*91*).

Within a series of α,ω-dienes, the 1,5-diene forms the most stable $AgNO_3$ complex (*416*), perhaps because it possesses the optimum configuration for chelation. As with monoolefins, the presence of alkyl substituents decreases the stability of the diene complexes (*416*).

With $AgClO_4$, 1,5-hexadiene, 1,7-octadiene, and 1,9-decadiene form 3:2, 1:1, and 1:1 complexes, respectively (*85a*). The 1:1 complexes are considered (*85a*) to be coordination polymers while the 3:2 complex of 1,5-hexadiene has been shown (*45a*) to have chelated diene–silver ion entities connected through a bridging diene molecule to produce a distorted trigonal coordination about the metal.

In addition to the $AgNO_3$ complexes of cyclic di- and oligoolefins listed in Table IV, the following complexes of $AgClO_4$ and $AgBF_4$ have been prepared: cyclopentadiene $(C_5H_6)AgClO_4$ (*591*), $(C_5H_6)AgBF_4$ (*219*), $(C_5H_6)_3(AgBF_4)_2$ (*495*); 1,3-cyclohexadiene $(C_6H_8)AgBF_4$ (*219*); 1,4-cyclohexadiene $(C_6H_8)AgBF_4$ (*495*); 1,3,5-cycloheptatriene $(C_7H_8)AgBF_4$ (*495*), $(C_7H_8)_2AgBF_4$ (*409*); norbornadiene $(C_7H_8)AgBF_4$ (*491*), $(C_7H_8)_3(AgBF_4)_2$ (*491*); cyclooctatetraene $(C_8H_8)AgBF_4$ (*495*); 1,3,5-cyclooctatriene $(C_8H_{10})_2AgBF_4$ (*495*); 1,5-cyclooctadiene $(C_8H_{12})_2AgBF_4$ (*495*); bullvalene $(C_{10}H_{10})AgBF_4\ (H_2O)$ (*406*), $(C_{10}H_{10})_2AgBF_4$ (*10*), $(C_{10}H_{10})_3AgBF_4$ (*404*); dicyclopentadiene $(C_{10}H_{12})AgClO_4$ (*621*), $(C_{10}H_{12})AgBF_4$ (*495*).

In those cyclic olefins, having both cis and trans double bonds, complexing with silver ion occurs preferentially at the trans (*372*), undoubtedly as a result of the higher strain energy associated with the trans endocyclic double bond (*416*). The 2:1 and 3:1 stoichiometry of the complexes formed by some of the cyclic di- (*495*) and triolefins (*290, 404, 495*) suggest the presence of both free and coordinated double bonds in the complex. The infrared spectra of the $AgBF_4$ complexes of 1,5-cyclooctadiene (*495*) and bullvalene (*404*) have shown this to be the case. This situation has been revealed also by structural investigation of some 1:1 complexes (*9, 278, 399, 408*).

The norbornadiene complexes of $AgNO_3$ (*577*) and $AgBF_4$ (*491*) are quite analogous in stoichiometry to those of 1,3-butadiene with the same salts. A structural analysis (*28*) of the 1:2 complex $(C_7H_8)(AgNO_3)_2$ has shown chains of silver nitrate molecules cross-linked by norbornadiene molecules (Fig. 11). In this complex, each silver ion is coordinated to one double bond and to an oxygen atom in each of two different nitrate ions, the arrangement being approximately triangular-planar. It is probable that the 1:1 norbornadiene complexes consist of chains of silver ions and norbornadiene molecules with two double bonds at each silver ion (*577*). Such a structure has been observed for the Ag^+ 1:1 complexes of bullvalene (*406*), cyclooctatetraene dimer (*446*), and germacratriene (*9*). In $(C_7H_8)AgNO_3$, the chains are probably linked by nitrate ions as in the germacratriene complex (*9*) and in $(C_7H_8)_3(AgBF_4)_2$,

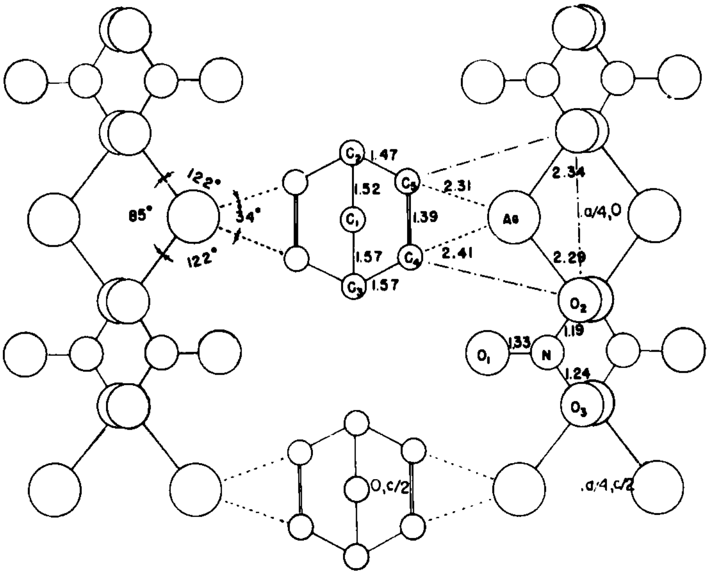

FIG. 11. Crystal and molecular structure of (norbornadiene)$(AgNO_3)_2$ (*28*).

TABLE IV

COMPLEXES OF CYCLOOLEFINS WITH SILVER NITRATE

Olefin	Complex	Melting point (°C)	Ref.
Cyclohexene	$(C_6H_{10})_2AgNO_3$	24–32	(*120*)
Norbornadiene	$(C_7H_8)(AgNO_3)_2$	153–154.5	(*1, 22, 577*)
	$(C_7H_8)AgNO_3$	—	(*577*)
cis-Cyclooctene	$(C_8H_{14})_2AgNO_3$	51	(*318*)
cis,trans-1,3-Cyclooctadiene	$(C_8H_{12})AgNO_3$	126–127.5	(*127*)
1,4-Cyclooctadiene	$(C_8H_{12})(AgNO_3)_2$	110–111	(*317*)
1,5-Cyclooctadiene	$(C_8H_{12})AgNO_3$	128.5–131	(*136*)
		135–136	(*317*)
1,3,5-Cyclooctatriene	$(C_8H_{10})AgNO_3$	125–126	(*132*)
1,3,6-Cyclooctatriene	$(C_8H_{10})(AgNO_3)_3$	138–139	(*318*)
Cyclooctatetraene	$(C_8H_8)_2AgNO_3$	173[a]	(*132*)
	$(C_8H_8)AgNO_3$	173[a]	(*132*)
	$(C_8H_8)_2(AgNO_3)_3$	173–174	(*132*)
cis-Cyclononene	$(C_9H_{16})_2AgNO_3$	67–69	(*135*)
trans-Cyclononene	$(C_9H_{16})_2AgNO_3$	90–94	(*135*)
cis,cis,cis-1,4,7-Cyclononatriene	$(C_9H_{12})(AgNO_3)_3$	243 d[b]	(*592*)
Methylcyclooctatetraene	$(C_9H_{10})_2(AgNO_3)_3$	123–124.5	(*128*)
cis-Cyclodecene	$(C_{10}H_{18})_2AgNO_3$	97–98	(*135*)
trans-Cyclodecene	$(C_{10}H_{18})_2AgNO_3$	81–83.5	(*135*)
1,3-Cyclodecadiene		176–178	(*192*)
cis,trans-1.5-Cyclodecadiene	$(C_{10}H_{16})AgNO_3$	138–139	(*580*)

cis,cis-1,6-Cyclodecadiene	$(C_{10}H_{16})AgNO_3$	213	(*580*)
Dicyclopentadiene	$(C_{10}H_{12})AgNO_3$	—	(*621*)
1,2-Dimethylcyclooctatetraene	$(C_{10}H_{12})(AgNO_3)_2$	142.5–144.5	(*128*)
Ethylcyclooctatetraene	$(C_{10}H_{12})(AgNO_3)_2$	124–125.5	(*128*)
Tricyclo[4.2.2.$0^{2,5}$]-3,7,9-decatriene	$(C_{10}H_{10})(AgNO_3)_2$	95–100 d	(*22*)
Bullvalene	$(C_{10}H_{10})(AgNO_3)_2$	140 d	(*10*)
3,7-Dimethylenebicyclo[3.3.1]nonane	$(C_{11}H_{16})AgNO_3$	198–204 d	(*557*)
n-Propylcyclooctatetraene	$(C_{11}H_{14})(AgNO_3)_2$	141 d	(*128*)
trans,trans,trans-1,5,9-Cyclododecatriene	$(C_{12}H_{18})AgNO_3$	198–199 d	(*626*)
	$(C_{12}H_{18})(AgNO_3)_2$	—	(*83*)
cis,trans,trans-1,5,9-Cyclododecatriene	$(C_{12}H_{18})AgNO_3$	166–167	(*83, 372, 626*)
	$(C_{12}H_{18})_2AgNO_3$	149	(*372*)
cis,cis,trans-1,5,9-Cyclododecatriene	$(C_{12}H_{18})(AgNO_3)_2$	—	(*83*)
cis,cis,cis-1,5,9-Cyclododecatriene	$(C_{12}H_{18})(AgNO_3)_3$	150 d	(*593*)
7,8-Dimethyltricyclo[4.2.2.$0^{2,5}$]deca-3,9-diene(*endo-cis-anti*)	$(C_{12}H_{16})AgNO_3$	175	(*22*)
1,2-benzo-1,3,7-Cyclooctatriene	$(C_{12}H_{12})AgNO_3$	163–165 d	(*623*)
Phenylcyclooctatetraene	$(C_{14}H_{12})AgNO_3$	144.5 d	(*133*)
7,8-Dicarbomethoxytricyclo[4.2.2.$0^{2,5}$]deca-3,9-diene(*endo-cis-anti*)	$(C_{14}H_{16}O_2)AgNO_3$	212 d	(*22*)
Humulene	$(C_{15}H_{24})(AgNO_3)_2$	175 d	(*290*)
Germacratriene	$(C_{15}H_{24})AgNO_3$	—	(*9*)
Benzoylcyclooctatetraene	$(C_{15}H_{12}O)AgNO_3$	121.4–122	(*134*)
1,2; 5,6-Dibenzocyclooctatetraene	$(C_{16}H_{12})AgNO_3$	222	(*21*)

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[a] Complexes lose olefin upon heating.

[b] d, Decomposes.

in which all double bonds are complexed (*491*), the cross-linking is probably through the additional norbornadiene molecules.

From aqueous solutions of $AgBF_4$, one obtains the crystalline 1 : 1 and 3 : 2 norbornadiene complexes, but each contains water of crystallization (*491*). The similarity between the infrared spectra of the anhydrous and hydrated complexes has led to the suggestion (*491*) that in the latter, the water molecules do not strongly interact with the silver ions, but are probably held in the lattice through hydrogen bonding to the fluoroborate ions. In the hydrated bullvalene complex, $(C_{10}H_{10})AgBF_4(H_2O)$, it was found, however, that the water molecules were simultaneously coordinated with the silver ion and hydrogen-bonded to the fluoroborate ion (*406*).

The only complex having olefinic double bonds alone in the coordination sphere of the silver ion which has been subjected to a complete structural analyses (*404*) is the bullvalene (*532*) complex $(C_{10}H_{10})_3AgBF_4$. The structure consists of discrete $(C_{10}H_{10})_3Ag^+$ cations and BF_4^- anions (Fig. 12). The three bullvalene molecules in the complex cation are

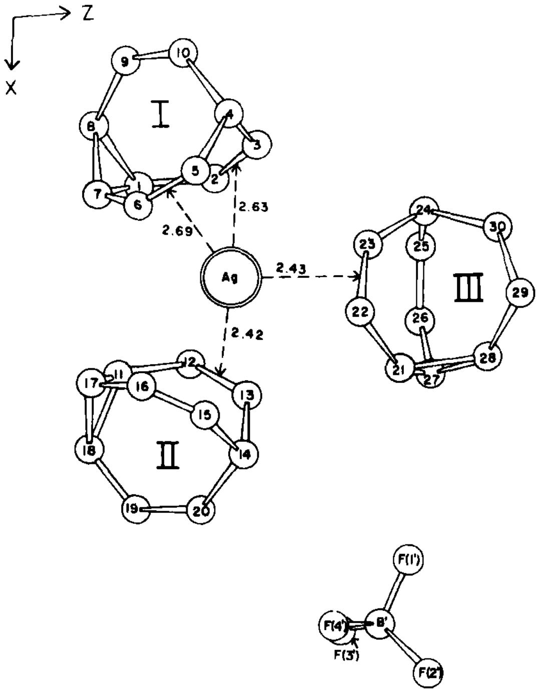


FIG. 12. Molecular structure of $(bullvalene)_3AgBF_4$ (*404*).

approximately trigonally positioned about the silver atom, two of these (II and III) having essentially equivalent orientations with one double bond directed toward the silver, while the third (I) is oriented so that two of its double bonds are equidistant from the silver. Although the silver ion is further from the nearest double bond of molecule I (Fig. 12) than from that of molecules II and III, it is less displaced from the plane of the π orbital (about 1° with molecule I versus about 13–14° with molecules II and III) (*404*). This might suggest weaker σ bonding but more effective π bonding for molecule I. It has been pointed out, however, (*407*) that the shortest Ag^+-carbon distances are accompanied, in general, by the largest dihedral angles between the plane containing the silver ion and double bond and that containing the double bond and its two cis substituents, perhaps indicating that in cis-substituted double bonds the π orbitals are twisted out of their normal 90° position.

In the various complexes which have been crystallographically characterized, the ligands have been reported to have a trigonal planar (*28*, *404*, *406*), distorted trigonal-bipyramidal (*399*, *408*), or distorted tetrahedral (*9*, *314*) arrangement about the silver ion. The silver ion–trigonal carbon distance for the coordinated double bond varies from about 2.3 to about 2.6 Å, increasing with the number of olefinic ligands (Table V). Almost invariably, the silver ion is asymmetrically positioned with respect to the double bond and in those complexes having a trigonal arrangement the silver is often displaced from the plane by about 0.1–0.2 Å (*407*). Interestingly, in the $AgNO_3$ complexes the shortest Ag–O distances (Table V) are shorter than in the $AgNO_3$ lattice itself (2.51 Å) (*377*) indicating a greater degree of covalency in the cation-anion bonding of the complex. Although some of the longer Ag–C or Ag–O contacts may be short enough to represent weak interaction of double bonds or nitrate ions with Ag^+, it must be borne in mind that these contacts may be more dependent upon the configuration of the olefin or the positioning of the olefin or anion with respect to another silver ion in the lattice than upon the strength of the interaction with the silver ion in question. Thus, one must accept with reservation the suggestion that some of the complexes have, for example, a trigonal-bipyramidal arrangement if the distances from the silver ion to the apices of the bipyramid are relatively long.

Although there is little recorded evidence that silver ion acts as a catalyst for the reactions of olefins, it has been reported that it decreases the rate of tautomerism of bullvalene (*10*) and catalyzes the isomerization of tricyclooctadienes to cyclooctatetraenes (*410*).

Among the nonhydrocarbon olefins vinyldiphenylphosphine forms with $AgNO_3$ 1:1 (**223**), m.p. 124°C, and 2:1 (**224**), m.p. 109°C, complexes

TABLE V

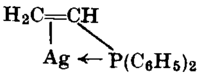
STRUCTURAL DATA FOR SILVER–OLEFIN COMPLEXES

Olefin	Complex	Configuration	No. of C=C per Ag^+	Shortest silver contacts		Ref.
				Ag–C[a]	Ag–O[b]	
Norbornadiene	$(C_7H_8)(AgNO_3)_2$	Trigonal planar	1	2.31, 2.41	2.27, 2.34	(*28*)
cis,cis,cis-1,4,7-Cyclononatriene	$(C_9H_{12})(AgNO_3)_3$	Distorted tetrahedral	1	2.38, 2.41	2.44–2.48	(*314*)
Humulene	$(C_{15}H_{24})(AgNO_3)_2$	Trigonal-bipyramidal	1	2.33, 2.42	2.31, 2.38	(*408*)
Cyclooctatetraene	$(C_8H_8)AgNO_3$	Trigonal-bipyramidal	1	2.46, 2.51	2.36, 2.43	(*399*)
			(2 or 3)	2.78, 2.84	—	(*399*)
				3.21, 3.29	—	(*399*)
trans-Cyclodecene	$(C_{10}H_{18})_2AgNO_3$	—	2	2.42, 2.46	2.49	(*238*)
Germacratriene	$(C_{15}H_{24})AgNO_3$	Distorted tetrahedral	2	2.49–2.59	2.37	(*9*)
Bullvalene	$(C_{10}H_{10})AgBF_4(H_2O)$	Trigonal planar	2	2.40–2.60	—	(*407*)
	$(C_{10}H_{10})_3AgBF_4$	Trigonal planar	3–4	2.45, 2.58	—	(*404*)
				2.48, 2.55		
				2.66, 2.78		
				2.69, 2.84		

[a] Silver ion–trigonal carbon distance.

[b] Silver ion–nitrate oxygen distance.

which involve coordination both at the double bond and at the phosphorus atom (*624*). With *o*-allylphenyldimethylarsine, $AgNO_3$ forms a



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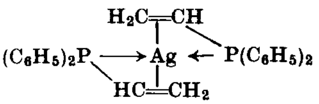


(224)

1:1 complex involving also coordination of the double bond and of the arsenic atom (*51*). Although *o*-allylphenyldiphenylphosphine forms complexes with both silver nitrate and the silver halides, in neither instance is coordination at the double bond involved (*51*).

As is the case with the $PtCl_3^-$ complexes (*276*), unsaturated alcohols form more stable complexes than do the corresponding unsaturated ammonium ions (*277*). The stability constants are, however, two or three orders of magnitude smaller with Ag^+ than with $PtCl_3^-$ and the difference is greater with the ammonium ions than with the alcohols, probably as a result of the difference in charge on the metallic species (*277*). This charge difference may be also an important factor in determining whether the σ or π component predominates in the coordinate bond.

C. GOLD

The first gold(I)–olefin complex to be isolated was reported by Chalk (*99*) in 1964. Irradiation with ultraviolet light of a mixture of 1,5-cyclooctadiene and $HAuCl_4$ in ether or isopropyl alcohol reduced the gold(III) and yielded colorless crystals of $(C_8H_{12})(AuCl)_2$. The same complex was produced by warming 1,5-cyclooctadiene with AuCl in ethanol. Warming of the diene with $HAuCl_4$ in ethers produced a mixture of $(C_8H_{12})(AuCl)_2$ and $(C_8H_{12})AuCl_3$.

Subsequently, Hüttel and co-workers (*303*, *306*, *307*) have described a series of gold(I)–olefin complexes involving both cyclic and acyclic mono- and oligoolefins (Table VI). The 1:1 monoolefin complexes, prepared in almost quantitative yield by reaction of excess olefin with AuCl in ether, are monomolecular and are obtained as colorless crystals. The cyclic olefins, which react as well with aqueous $HAuCl_4$ or $NaAuCl_4$, form complexes which are more stable than those of the corresponding straight-chain olefins. Formation of the complex results in a low infrared frequency shift in the C=C stretching vibration of 115 cm^{-1} for the

TABLE VI

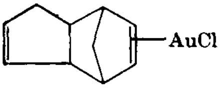
Gold(I) Chloride–Olefin Complexes

			Frequency of C=C stretching vibration (cm^{-1})		
Olefin	Complex	Decomposition temperature (°C)	Olefin	Complex	Ref.
Cyclopentene	$(C_5H_8)AuCl$	55–60	—	—	(*307*)
Cyclohexene	$(C_6H_{10})AuCl$	60	—	—	(*307*)
Cycloheptene	$(C_7H_{12})AuCl$	93–98	1651	1526	(*307*)
cis-Cyclooctene	$(C_8H_{14})AuCl$	93–96	1648	1512	(*307*)
trans-Cyclodecene	$(C_{10}H_{18})AuCl$	90–93	1657	1532	(*307*)
1,5-Cyclooctadiene	$(C_8H_{12})(AuCl)_2$	110–114	1655	1520	(*99*)
cis,trans-1,5-Cyclodecadiene	$(C_{10}H_{16})AuCl$	73–75	1674 (*trans*)	1544	(*307*)
			1644 (*cis*)	1644	(*307*)
Norbornadiene	$(C_7H_8)AuCl$	75–78	1550	1434	(*307*)
Dicyclopentadiene	$(C_{10}H_{12})AuCl$	90–95	—	—	(*307*)
cis,cis,trans-1,5,9-Cyclododecatriene	$(C_{12}H_{18})(AuCl)_2$	102–103	—	1630	(*307*)
			—	1525	(*307*)
all-trans-1,5,9-Cyclododecatriene	$(C_{12}H_{18})(AuCl)_2$	98–100	—	1622	(*307*)
			—	1528	(*307*)
1-Octene	—	0	—	—	(*306*)
1-Decene	—	0	—	—	(*306*)
1-Dodecene	$(C_{12}H_{24})AuCl$	23–24	—	—	(*306*)
1-Tetradecene	$(C_{14}H_{28})AuCl$	33–35	—	—	(*306*)
1-Hexadecene	$(C_{16}H_{32})AuCl$	43–45	1640	1525	(*306*)
1-Octadecene	$(C_{18}H_{36})AuCl$	49–51	1640	1525	(*306*)
1,4-Hexadiene	$(C_6H_{10})(AuCl)_2$	50	1636	1519	(*306*)
1,5-Hexadiene	$(C_6H_{10})(AuCl)_2$	50	1645	1515	(*306*)
1,4,9-*trans*-Decatriene	$(C_{10}H_{16})(AuCl)_2$	58–60	1640	1638	(*306*)
			—	1517	(*306*)

1-olefins and of about 125–135 cm^{-1} for the cyclic monoolefins. The NMR spectra indicate a very small increased shielding for the protons at C-1 and a corresponding deshielding for the C-2 proton of 1-olefins when complexed. The effect of complexing on the shielding of the olefinic protons of the cyclic olefins varies regularly from a deshielding of 0.30 ppm for cyclohexene to an increased shielding of 0.23 ppm for *trans*-cyclodecene. It is of interest that, over this same series, there is a rather marked deshielding of the methylene protons adjacent to the double bond.

The straight-chain oligoolefins, 1,4-hexadiene, 1,5-hexadiene, and *trans*-1,4,9-decatriene all yield complexes of 1:2 olefin:AuCl stoichiometry. Infrared and NMR spectra indicate that in *trans*-1,4,9-decatriene the terminal double bonds are complexed, while the internal double bond is free.

The stoichiometry of the crystalline complex obtained by reaction of cyclic oligoolefins with AuCl in absolute ether at room temperature (0°C for norbornadiene) depends upon the olefin. 1,5-Cyclooctadiene and both *cis,cis,trans*- and *all-trans*-1,5,9-cyclododecatriene form 1:2 complexes. The infrared spectra of the trienes indicate the presence of both complexed and free double bonds, the *cis,cis,trans*-1,5,9-cyclododecatriene showing one free cis unsaturation. *Cis,trans*-1,5-cyclodecadiene and dicyclopentadiene form, on the other hand, only 1:1 complexes. The former olefin is complexed only at the trans double bond, whereas the latter is complexed only at the double bond in the norbornene part of the molecule (**225**).



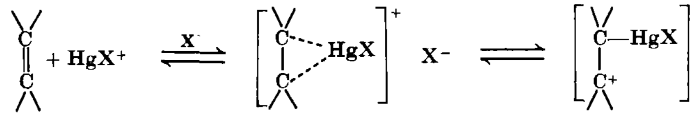
(225)

Norbornadiene appears to form a mixture of 1:1 and 1:2 complexes from which the 1:1 complex can be isolated. The infrared spectrum indicates complexing of both double bonds in the molecule, but, because of low solubility, it is not possible to establish whether the complex is a coordination polymer or a chelated compound.

X. Group IIb: Mercury

Mercury(II) salts form addition compounds with olefins, particularly in the presence of active-hydrogen solvents such as alcohols. Although a π-complex intermediate has not been isolated from these systems, it is considered that its formation plays an important role in the mechanism of the addition reaction. A mercurinium ion mechanism (Eqs. 9–11) has

$$HgX_2 \rightleftharpoons HgX^+ + X^- \qquad (9)$$



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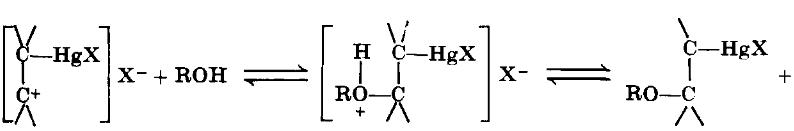


(11)

been proposed (*100*, *554*) as that which best explains the behavior of the system. Addition of acid reverses the reaction and releases the olefin isomerically unchanged. With 1-olefins the addition proceeds 10 and 100 times more rapidly than with 2- and 3-olefins, respectively (*553*), and the mercury atom always occupies the terminal carbon (*554*). With most olefins, trans addition is encountered (*365*), but with certain bicycloolefins, cis addition, perhaps due to steric factors, is observed (*576*). The rate of addition is dependent upon the anion of the salt, being much slower for the chloride than for the more ionic nitrate or acetate.

Recent NMR studies (*512*) of the aqueous mercuric nitrate–ethylene system have been reported to show, in addition to the σ complex 2-hydroxyethylmercury(II), a species considered to be the ethylene-mercury(II) π complex. The interpretation of these spectra has been questioned however (*361*). Reutov and co-workers (*551*) also have reported NMR evidence for the cyclohexylmercury(II) π complex.

For the hydroxymercuration of olefins in aqueous perchloric acid, Halpern and Tinker (*273*) have obtained a rate expression first-order in Hg^{2+} and in olefin and have observed an excellent correlation between the logarithm of the rate constant and Taft's σ^* value for substituted olefins. This they interpret as suggestive of a transition state with considerable carbonium ion character. Although they have found no evidence for mercury(II)-olefin π-complex intermediates, they do not exclude the possibility of their existence.

XI. Discussion

The nature of the transition metal–olefin coordinate bonding has been the subject of much discussion. It is quite generally accepted that the σ,π bonding suggested by Dewar (*167*) and Chatt and Duncanson (*101*) for silver(I) and platinum(II), respectively, holds for most of the transition series. This bonding involves overlapping of the occupied bonding π orbital of the olefin with a vacant metal orbital (σ component) and an overlapping of the vacant antibonding π^* orbital of the olefin with an occupied metal *d*-orbital (π component). The importance of the π component for stability of the complexes may be indicated by the very few known complexes of the metals with fewer *d*-electrons, i.e., group IIIB–VB metals.

Whether, for a given metal, the σ and π component of the coordinate bond predominates will depend upon the energy levels of its acceptor and donor orbitals relative to those of the olefin. The energy levels of the metal orbitals will depend upon its oxidation state, which will often define the *d*-electron density, and upon the number and nature of other ligands, while the energy levels of the olefin will be affected by the substituent groups at the double bond. Furthermore, the efficiency of overlap may be detrimentally affected by the steric influence of substituent groups on the olefin or of other ligands at the metal.

In the transition metal carbonyls, there is a dependence of the carbonyl infrared stretching frequency ν_{CO} upon the amount of d–π^* overlapping between the metal and carbonyl carbon atoms (*470*, *562–564*). In general, an increase in d–π^* overlap results in a decrease in ν_{CO}, although the magnitude of that decrease for a given carbonyl group will depend upon the geometry of the molecule. Consequently, for a given metal, an increase in the oxidation state increases ν_{CO}, while substitution of carbonyl ligands by another, such as cyclopentadienyl, tends to decrease ν_{CO}. In the latter case, the magnitude of the change of ν_{CO} will depend also upon the amount of d–π^* overlap between the metal and the cyclopentadienyl ring.

In Table VII are recorded mean values for ν_{CO} in a number of ethylene–metal carbonyl complexes and parent metal carbonyls as well as values for the double-bond infrared stretching frequency $\nu_{C=C}$ and the magnetic shielding parameter τ for ethylene in those transition metal complexes for which data are available. Although with the metal carbonyl complexes, differences of geometry, oxidation state, etc., do not permit a correlation to be drawn between the absolute values of ν_{CO} and $\nu_{C=C}$ for the various complexes, it is quite apparent from the tabulated data for the Mo, Mn, and Fe complexes that for a given metal,

TABLE VII

INFRARED AND NMR DATA FOR ETHYLENE COMPLEXES OF TRANSITION METALS

Metal	Complex	τ (ppm)	Mean $\nu_{C=C}$ (cm^{-1})	ν_{CO} (cm^{-1})	Ref.
Mo	$Mo(CO)_6$	—	—	1990	(*86a*)
	$(C_2H_4)Mo(CO)_5$	—	—	2008	(*559*)
	trans-$(C_2H_4)_2Mo(CO)_4$	—	—	1964	(*559*)
	$[(C_2H_4)Mo(CO)_3(C_5H_5)]^+$	—	1511	2055	(*195*)
		—	1514	—	(*148*)
W	$(C_2H_4)W(CO)_5$	—	—	2005	(*559*)
	trans-$(C_2H_4)_2W(CO)_4$	—	—	1964	(*559*)
	$[(C_2H_4)W(CO)_3(C_5H_5)]^+$	—	1510	2054	(*195*)
Mn	$[Mn(CO)_6]^+$	—	—	2090	(*86a*)
	$[(C_2H_4)Mn(CO)_5]^+$	—	1541	2103	(*209*)
	$(C_2H_4)Mn(CO)_2(C_5H_5)$	8.5	1508	1946	(*200*)
Re	$[Re(CO)_6]^+$	—	—	2078	(*86a*)
	cis-$[(C_2H_4)_2Re(CO)_4]^+$	6.6	1539	2072	(*209*)
Fe	$Fe(CO)_5$	—	—	2011	(*191a*)
	$(C_2H_4)Fe(CO)_4$	—	1511	2024	(*425*)
	$[(C_2H_4)Fe(CO)_2(C_5H_5)]^+$	—	1527	2066	(*195*)
Rh	$[(C_2H_4)_2RhCl]_2$	—	1520	—	(*148a*)
	$[(C_2H_4)Rh(CO)Cl]_2$	6.1	—	2000	(*480*)
	$(C_2H_4)_2Rh(C_5H_5)$	8.1	1493	—	(*149*)
	$(C_2H_4)_2Rh(acac)$	6.9	1524	—	(*149*)
	$(C_2H_4)(C_2F_4)Rh(acac)$	5.8	—	—	(*463*)
	trans-$(C_2H_4)RhCl[P(C_6H_5)_3]_2$	5.6	—	—	(*450*)
Pd	$[(C_2H_4)PdCl_2]_2$	—	1527	—	(*261*)
Pt	$[(C_2H_4)PtCl_2]_2$	—	1516	—	(*261*)
	$[(C_2H_4)PtCl_3]^-$	5.3	—	—	(*484*)
		—	1526	—	(*261*)
	trans-$(C_2H_4)PtCl_2(ONC_5H_5)$	5.6	1510	—	(*543*)
Ag	$[(C_2H_4)Ag]^+$	4.3	—	—	(*493*)
		—	1583	—	(*492*)
	C_2H_4	4.6	1623[a]	—	(*259*)

[a] Raman value.

or perhaps a given group in the periodic table, there is a parallelism between the direction of change of ν_{CO} and $\nu_{C=C}$ when a change occurs in the complex. Since a decrease in ν_{CO} infers greater d–π^* overlap of metal with CO, a concomitant decrease in $\nu_{C=C}$ should also imply greater d–π^* overlap of metal with olefin. In other words, a change of d-electron donor character of the metal should be felt by both olefinic and carbonyl ligands. The different $\nu_{C=C}$ values for the various ethylene complexes may then reflect the relative amounts of *d*-electron donation from metal to olefin.

It is interesting to note that, when ethylene replaces a carbonyl group with no change of oxidation state of the metal or geometry of the complex, i.e., in $Mo(CO)_6$, $[Mn(CO)_6]^+$ or $Fe(CO)_5$, ν_{CO} is increased somewhat. This may indicate a poorer σ-donor character for C_2H_4 than for CO thus rendering the metal a somewhat poorer *d*-electron donor.

There appears to be also a parallelism between $\nu_{C=C}$ and τ for the complexed ethylene molecule, lower $\nu_{C=C}$ values accompanying higher τ values. Higher τ values reflect an increased magnetic shielding of the olefinic protons, which appears then to result at least in part from the increased d–π^* overlap with the olefin. From these considerations, the conclusion to be drawn is that a greater π component in the coordinate bond results in a decrease in $\nu_{C=C}$ and an increase in τ for ethylene. Although this statement might be valid for other olefins, the introduction of substituent groups at the double bond may complicate the picture.

The effect of change of other ligands at the metal upon the metal–olefin bond is best demonstrated by the rhodium complexes. It is quite evident that the cyclopentadienyl ligand renders rhodium a much better *d*-electron donor than does the acetylacetonate ligand. Further, the greater π acidity of C_2F_4 results in a decrease of the π component of the metal–ethylene bond when one C_2H_4 molecule in $(C_2H_4)_2Rh(acac)$ is replaced by C_2F_4. In addition, the study by Orchin and colleagues (*325*) of the effect of the substituent group Z on the pyridine-*N*-oxide complexes of platinum, *trans*-$(C_2H_4)PtCl_2(ONC_5H_4Z)$, on the shielding of the ethylenic protons has shown a greater shielding when Z is an electron-releasing group than when it is an electron-withdrawing group. If, on the other hand, the electron-releasing substituent is on the olefin, the effect is in the opposite direction since now the olefin is a poorer *d*-electron acceptor resulting in a weakening of the π component. Thus, in Zeise's salt and its homologs, the magnetic shielding experienced by the olefinic protons upon complexation decreases in the order ethylene > propylene > *cis*-2-butene (*231*).

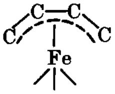
The marked difference between $\nu_{C=C}$ and τ for ethylene in the silver ion complex and in complexes with the other transition metals suggests either a much weaker coordinate bonding to silver or at least a smaller π component in the coordinate bond. In this instance the τ value is somewhat below that of free ethylene indicating a net transfer of charge from olefin to metal as opposed to the apparent net charge transfer from metal to olefin with the other metals. As has been suggested previously (*152*, *232*, *403*) the σ component of the coordinate bond may predominate in the silver, or indeed in group IB, complexes whereas the π component predominates in the others.

The relative stabilities of some $(\text{olefin})_2\text{AgBF}_4$ complexes, i.e., propylene > ethylene > vinyl chloride (*492*, *495*), as well as the greater deshielding of the olefinic protons upon complexing of the alkyl-substituted olefins than of ethylene (*493*), are indicative of a greater dependence of the silver–olefin bond upon the electron donor property of the olefin, and thus of a predominate σ component in the coordinate bond. By contrast, electron-releasing alkyl substituents decrease and electron-withdrawing fluorine substituents increase the stability of rhodium(I) complexes (*152*, *450*) indicating a predominate π component. The markedly greater low-frequency shift for nor-$C_7H_2Cl_6$ than for nor-C_7H_8 upon complexing with rhodium(I) or iridium(I) illustrates also the strengthening of the metal–olefin bond by introduction of the electron-withdrawing chlorine substituents.

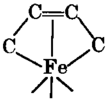
A molecular orbital assessment (*24*) of the coordinate bonding in the iridium complexes $(\text{olefin})\text{IrX(CO)L}_2$ shows that successive introduction of electron-withdrawing cyano groups, i.e., from acrylonitrile to tetracyanoethylene, into the ethylene molecule results in a progressive strengthening of the π component and corresponding weakening of the σ component. The coordination of tetracyanoethylene with iridium and perhaps with a number of other metals may involve then an almost pure π bonding as may also the coordination of other olefins with a number of electron-withdrawing substituents, such as C_2F_4. Although the molecular structure of such complexes as $[C_2(CN)_4]IrBr(CO)[P(C_6H_5)_3]_2$ (*402*) and $[C(CN)_4]Pt[P(C_6H_5)_3]_2$ (*461*) suggests the possibility of σ-covalent bonding between the metal and olefin to form a three-membered ring structure, it is equally likely that the bonding is coordinate with a predominate d–π^* overlap since on the basis of geometry alone one cannot distinguish between the two bonding types.

The same reasoning can be applied to explain the difference between the structures (**162**) and (**163**) of the cyclopentadienylcobalt complexes of tetrakis(trifluoromethyl)cyclopentadienone (*241*) and tetramethylcyclopentadienone (*268*, reference 58), respectively. The lesser bending of the diene ring in the latter than in the former suggests fairly normal σ,π-coordinate bonding through the delocalized π system in structure (**163**) and more localized bonding in structure (**162**). The localization of bonding results from the better d-electron acceptor properties of the trigonal carbon atoms in the olefin with trifluoromethyl substituents and involves overlapping of a metal d-orbital with π^* orbitals on the carbon atoms adjacent to the carbonyl group (*108*, *339*). This d–π^* overlapping is facilitated by bending of the ring.

The iron atom is almost unique in its desire to coordinate strongly with a planar *cis*-1,3-diene system. The bonding which may vary from essentially delocalized (**226**) to markedly localized (**227**) can be accomplished (*113*) by introduction into the olefin of electron-withdrawing substituents or by attachment of other ligands at the metal which render it a poorer *d*-electron donor.



(**226**)



(**227**)

The strong tendency of iron to form stable complexes with 1,3-dienes may account for the isomerization of 1,5-cyclooctadiene in the presence of $Fe(CO)_5$ to yield $(1,3\text{-}C_8H_{12})Fe(CO)_3$ (*17*). Similarly, the isomerization of 1,3-cyclooctadiene to give the 1,5-diene complexes with Mo(0) or W(0) (*375*), Rh(I) (*499*), Pd(II), or Pt(II) (*375*) may be a consequence of the tendency for these metals to chelate the 1,5-diene in the tub conformation.

Using low-temperature NMR spectroscopy, one of the recent interesting discoveries in this field has been that of the valence tautomerism occurring in a number of transition metal complexes of cyclooctatetraene and its derivatives $(\text{olefin})M(CO)_3$. With chromium, molybdenum, and tungsten, the metal is coordinated to C_8H_8 through a planar six-carbon segment of the ring, whereas with iron and ruthenium the coordination involves a planar 1,3-diene segment, producing in all cases an inert gas electronic configuration about the metal. With the metals of both groups, the bond-breaking and bond-remaking tautomerism involves the 1,2-shift mechanism shown in structure (**119**). Further advances in synthetic and spectroscopic techniques may well lead to the discovery of more such complexes, which will, in turn, provide us with a better understanding of this phenomenon.

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