OLEFIN AND ACETYLENE COMPLEXES OF TRANSITION METALS

MARTIN A. BENNETT

*Department of Chemistry, University of Southern California, Los Angeles 7, California**

Received November 16, 1961

CONTENTS

INTRODUCTION

"At present, the triangle of elements Cu(I), Pd(II), Ag(I), Pt(II), Hg(II) is known to form reasonably stable (olefin) complexes. There are also iron complexes of the type (butadiene)$Fe(CO)_3$, but their structures are unknown."

This statement is taken from a paper published at the end of 1957 (46). It is a measure of the pace of advance in the field of metal–olefin complexes that, four years later, their existence has been established for well over half the transition metals. Figure 1 shows that in the rectangle bounded by the Group VI transition metals and the coinage metals, respectively, only technetium and gold have so far defaulted in this respect.

The reasons for this rapid expansion, which forms part of a general expansion of interest in transition metal to carbon bonds, are threefold: (1) The recognition in 1952 of a new type of bond, the so-called "sandwich" bond, in ferrocene $Fe(C_5H_5)_2$, and the subsequent discovery of a host of compounds of other transition metals containing sandwich-bonded aromatic systems such as $(C_5H_5)^-$ and C_6H_6 (95, 198, 200, 244); (2) the increasing availability and use of chelating and conjugated olefins whose metal complexes are often very stable, whereas those of mono-olefins such as ethylene are either unstable or non-existent; (3) the re-examina-

* Dept. of Chemistry, University College, London, England.

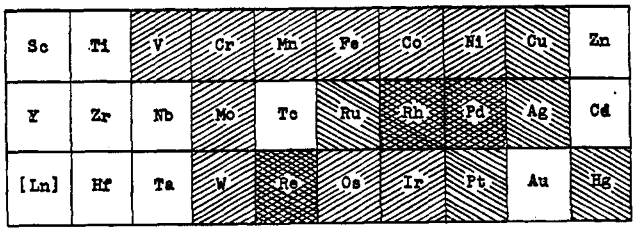


Fig. 1. Transition metals which form olefin complexes:

olefin complex formed by direct reaction of metal halide with olefin

olefin complexes usually formed when other strongly π-bonding ligands are present; olefin metal halide complexes may be formed indirectly

both possibilities occur

tion of metal carbonyl–acetylene reactions, stimulated by the advances in "sandwich" chemistry which, aside from their important organic synthetic applications, have yielded many new metal-olefin complexes, as well as metal-acetylene and other types of organometallic complex.

In a field which is developing as rapidly as this, it is almost impossible to present a balanced, coherent, unified treatment. This review, therefore, is an attempt to survey work, largely experimental, in the field of transition metal–olefin complexes, with the following limitations. First, the numerous complexes of platinum and palladium will not be dealt with, since they are surveyed by Doyle (81) in a recent review. Second, only occasional reference for purposes of comparison is made to the closely related field of π-cyclopentadienyl and π-arene metal complexes, since this has already been surveyed recently (95, 198, 200, 244). Third, no mention will be made of complexes formed by the acetylide ion with transition metals (190); we shall deal only with those acetylene complexes in which the acetylene–metal bonding is essentially similar to that existing in metal–olefin complexes.

The last review dealing specifically with metal–olefin complexes appeared in 1941 (157). Since then, the topic has received occasional mention in reviews on related subjects (91, 195, 225, 244). Mention must be made in particular of some very recent reviews on organo-transition metal complexes (43, 48, 49, 199, 250). In this review, an attempt has been made to cover the literature through March of 1961.

II. OLEFIN AND ACETYLENE COMPLEXES OF AG, CU, HG, RH, RU AND RE

These elements are characterized by the ability of solutions of their simple salts (usually halides, nitrates or perchlorates) to react directly with an olefin forming a metal–olefin complex. This reaction often is accompanied by a reduction in the valence state of the metal. The most stable complexes formed in this way are those of platinum(II) and palladium(II) (81) which are not decomposed readily to the parent olefin by water. The olefin complexes of silver, on the other hand, are considerably less stable in this respect, and much of the information about them has been derived from a comparison of the distribution of various olefins between aqueous silver nitrate and carbon tetrachloride with the distribution between aqueous potassium nitrate at the same ionic strength and carbon tetrachloride (87, 135, 170, 171, 231, 232, 233a, 248). Several general conclusions can be drawn: (1) in all cases, 1:1 complexes are formed, which may be written as [olefin Ag]$^+$. There is evidence in some cases for the additional formation of [olefin 2Ag]$^+$ and [2 olefin Ag$^+$] complexes. (2) The extent of complex formation is greater for *cis*- than for *trans*- isomers, and is reduced by the presence of substituents on the double bond. The effect of the substituents seems to be largely steric in nature. (3) In the case of cyclic olefins and bicyclic olefins, the formation constants are in essentially the same order as the estimated relative strains in the olefins. Thus, cyclopentene and cycloheptene are more strained than cyclohexene, and both form silver complexes more readily than does cyclohexene (231). Nevertheless, the cyclopentene complex is considerably more stable than the cycloheptene complex, even though these olefins are approximately equally strained; this effect probably is due to transannular hydrogen interference. Many olefins yield silver nitrate or perchlorate complexes which are sufficiently stable to be isolated, usually as white or yellow crystalline solids, which are decomposed into their components either on heating or on treatment with water, aqueous sodium chloride or aqueous ammonia (Table I). Table I shows that many of the olefins which form stable silver complexes are those which contain a pair of "chelate" double bond, *i.e.*, the olefins exist, or can be made to exist, in a conformation which allows the double bonds to occupy two coördination positions about the metal atom. Anhydrous silver nitrate has been reported (114) to form liquid complexes with propene and but-1-ene containing 1.3 moles of olefin per mole of salt, but these are stable only at low temperatures under a pressure near that of the vapor pressure of the olefin.

It may be noted that the stoichiometry of a solid silver–olefin complex does not necessarily correspond to that obtained from distribution studies for the main species present in solution. This is exemplified by the reaction of silver nitrate with bicyclo[2.2.1]hepta-2,5-diene (norbornadiene). Distribution studies on this system, employing 1 *M* silver nitrate, show that a 1:1 complex, and no other, is present in solution (232). It was claimed by the authors that the solid complex separating from solution also had this stoichiometry,

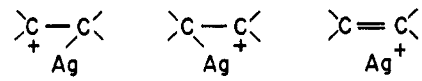
TABLE I

OLEFIN COMPLEXES OF SILVER

Olefin	Formula of complex	Physical properties	Reference
Propene	$1.3C_3H_6/AgNO_3$	Liquid	(114)
But-1-ene	$1.3C_4H_8/AgNO_3$	Liquid	(114)
Cyclohexene	$2C_6H_{10}\cdot AgClO_4$	White solid	(54)
Dicyclopentadiene	$C_{10}H_{12}\cdot AgNO_3$	White solid	(248)
Biallyl	$C_6H_8\cdot AgClO_4$	White solid	(248)
cis-Cycloöctene	$2C_8H_{14}\cdot AgNO_3$	Solid m.p. 51°	(150)
Cycloöcta-1,3-diene (conformation not stated)	$C_8H_{12}\cdot 2AgNO_3$	Solid d. 150°	(149)
Cycloöcta-1,3-diene (*cis–trans*)	$C_8H_{12}\cdot AgNO_3$	White needles m.p. 122–124°	(56)
Cycloöcta-1,4-diene	$C_8H_{12}\cdot 2AgNO_3$	White crystals m.p. 110–111°	(149)
Cyclo-öcta-1,5-diene	$C_8H_{12}\cdot AgNO_3$	White needles m.p. 128.5–131°	(62)(149)
Cycloöcta-1,3,5-triene	$C_8H_{10}\cdot AgNO_3$	Solid m.p. 125–126°	(58)
Cycloöcta-1,3,6-triene	$C_8H_{10}\cdot 3AgNO_3$	White needles m.p. 139°	(150)
Cycloöctatetraene	$2C_8H_8\cdot AgNO_3$	Pale yellow crystals m.p. 173–174°	(58)
	$C_8H_8\cdot AgNO_3$	Pale yellow crystals m.p. 173–174°	(58)
	$2C_8H_8\cdot 3AgNO_3$	Pale green crystals m.p. 173° d.	(58)
Methylcycloöctatetraene	$2C_9H_{10}\cdot 3AgNO_3$	Light yellow prisms m.p. 123–124.5°	(57)
Ethylcycloöctatetraene	$C_{10}H_{12}\cdot 2AgNO_3$	Gray-white crystals m.p. 124–125.5°	(57)
n-Propylcycloöctatetraene	$C_{11}H_{14}\cdot 2AgNO_3$	Faintly yellow crystals m.p. 141° d.	(57)
Phenylcycloöctatetraene	$C_{14}H_{12}\cdot AgNO_3$	Yellow-green m.p. 144–145°	(59)
Benzoylcycloöctatetraene	$C_{15}H_{12}O\cdot AgNO_3$	Pale yellow needles m.p. 38–39.5°	(60)
cis-Cyclononene	$2C_9H_{16}\cdot AgNO_3$	M.p. 67–69°	(61)
trans-Cyclononene	$2C_9H_{16}\cdot AgNO_3$	M.p. 90–94°	(61)
cis-Cyclodecene	$2C_{10}H_{18}\cdot AgNO_3$	D. 167–187° (softens 97–98°)	(61)
trans-Cyclodecene	$2C_{10}H_{18}\cdot AgNO_3$	M.p. 81–83.5°	(61)
α-Pinene	$2C_{10}H_{16}\cdot AgClO_4$	White solid	(54)
β-Pinene	$2C_{10}H_{16}\cdot AgClO_4$	White solid	(54)
Bicyclo[2.2.1]hepta-2,5-diene	$C_7H_8\cdot 2AgNO_3$	White crystals m.p. 155–160° der.	(5)(14)(232)
Dimers of cycloöctatetraene			
(i) M.p. 41.5°	$C_{16}H_{16}\cdot AgNO_3$	Prisms m.p. 153°	(148)
	$C_{16}H_{16}\cdot 2AgNO_3$	Crystals m.p. 176°	(148)
(ii) M.p. 38.5°	$C_{16}H_{16}\cdot AgNO_3$	White powder m.p. 196°	(148)
(iii) Liquid dimer from heating C_8H_8 in *o*-dichlorobenzene	$C_{16}H_{16}\cdot 2AgNO_3$	White plates m.p. 154°	(148)

but independent studies (5, 14) have shown that in fact the solid complex is $C_7H_82AgNO_3$. A similar situation seems to exist in the case of the silver nitrate–cyclohexene complexes (54, 231, 248). Another characteristic of these complexes is a tendency to change composition on standing in air, or on recrystallization, and this is well shown by the existence of three different silver nitrate–cycloöctatetraene complexes $C_8H_8\cdot AgNO_3$ $2C_8H_8\cdot AgNO_3$ and $2C_8H_8\cdot 3AgNO_3$ (58). It is therefore difficult to decide from the observed stoichiometry of the complexes in each case the number of double bonds associated with each silver ion, although the distribution studies clearly show that the predominant tendency is for one silver ion to be associated with each double bond.

The structure and bonding of these compounds has been a matter for some discussion. It was originally suggested (248) that the [olefin Ag]$^+$ species could be represented as a resonance hybrid of three forms



A somewhat more satisfying picture, which seems to be generally accepted, has been presented by Dewar (77).

(I) (II)

The bonding is believed to consist of a μ-bond formed by overlap of a vacant 5s orbital of silver with a filled π-2p orbital of the olefin, and a π-bond formed by overlap of a filled 4d-orbital of the metal with a vacant π*-2p antibonding orbital of the olefin(II). The π-bonding tends to remove negative charge from the metal which would otherwise accumulate owing to the μ-bonding. The Dewar concept explains why the majority of stable metal–olefin complexes of this type are formed by metals at or near the ends of the transition series, since it is these elements which have filled d-orbitals available for overlap with the antibonding orbitals of the olefin. It can also be extended (41) to explain the bonding in the square planar olefin complexes of Pt(II), Pd(II) and Rh(I) by assuming that the μ-bond is now formed by overlap of dsp^2 hybrid orbitals of the metal with the π-2p orbitals of the olefin, while the π-bond is formed by overlap of filled d- or dp-hybrid orbitals of the metal with the π*-2p antibonding orbitals of the olefin.

On the basis of the Dewar concept, the double bond of the olefin should not be changed greatly on complexing with silver. In agreement with this, studies of the Raman spectra of a number of olefins in silver nitrate solution show that the C=C stretching frequency is lowered by only 50–60 cm.$^{-1}$, and thus that the double bond remains almost intact in the silver–olefin complexes (227). This also is indicated by the proton resonance spectra of the complexes, which do not differ greatly from those of the free olefins (202). A detailed X-ray study of the cycloöctatetraene silver complex $C_8H_8AgNO_3$ shows that cycloöctatetraene in the complex retains its "tub" configuration with alternating single and double bond lengths of 1.46 and 1.37 Å., respectively (181, 182). The silver ion is placed unsymmetrically with respect to a pair of non-conjugate double bonds. Some evidence also was obtained for covalent bonding of the nitrato group to the metal atom. In the case of the silver nitrate complex of one of the dimers of cycloöctatetraene, the silver ion is found by

X-ray study to be associated with two double bonds, each from different dimer molecules (194). Similarly, in the silver perchlorate-benzene complex, the silver ion is associated equally with two carbon atoms from each of two benzene rings (209, 210).

From the values of the formation constants for the silver complexes of trimethylethylene and cyclohexene at 0 and 25°, it is possible to calculate a value of 6 kcal. for the enthalpy of the reaction

$$Ag^{+}(H_2O)_n + \text{olefin}(CCl_4) = [Ag\ \text{olefin}]^{+} + nH_2O \quad (248)$$

This gives a value of 20–30 kcal. for the silver–olefin bond energy, the uncertainty lying in the fact that n may be either 4 or 6 (88).

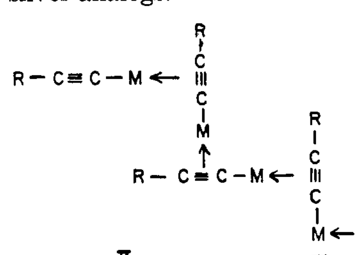
Attempts have been made to correlate the formation constants of silver-olefin complexes with the parameters of other chemical reactions of olefins which may involve a transition state closely resembling a π-complex. A good linear relationship has been observed between log K for the reaction

$$Ag^{+}(aq.) + \text{olefin}(aq.) \rightleftarrows [Ag\ \text{olefin}]^{+}aq.$$

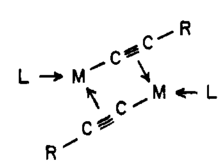
and heats of hydrogenation of the olefins (120). On the other hand, there is no obvious correlation between silver–olefin complex formation and iodine–olefin complex formation for a series of cyclic and bicyclic olefins (232).

The corresponding complexes of copper(I) are probably analogous to those of silver, but, on the whole, they have been less extensively studied. Solid cuprous chloride absorbs a number of mono-olefins, such as ethylene, propene and but-2-ene, under pressure, giving complexes of general formula CuCl(olefin) (122, 233). With butadiene and isoprene, complexes of formula 2CuCl(diolefin) are formed (121, 219, 236). Their structures are unknown, but the possibility of butadiene functioning either as a chelate or as a bridging ligand has been discussed (219). Cuprous chloride also dissolves readily in solutions of various unsaturated alcohols and acids, and extensive solubility studies (9, 9a, 154, 155, 156, 158) have been interpreted to show the existence of complexes such as $(H_2M)CuCl$, H_2MCu^{+}, $HMCuCl^{-}$ and HMCu (H_2M = dibasic olefinic acid). In the particular case of maleic acid, a solid compound of formula $CuC_4H_3O_4 \cdot H_2O$ can be isolated (9). The cuprous complexes of unsaturated alcohols are considerably more stable than the corresponding silver complexes (156), but whether this generalization holds for all the olefin complexes of the two metals, as has been suggested (16), is more doubtful. Experience with the norbornadiene complexes of Ag(I) and Cu(I) showed (5) that the latter lost its coördinated olefin (*e.g.*, *in vacuo*, or on prolonged washing with organic solvents) far more readily than the former. In the case of unsaturated alcohols and acids there is the possibility of bonding from both the double bond and oxygen, and the latter may be stronger in the case of copper(I) than in silver(I). The norbornadiene complex of cuprous bromide $C_7H_8 \cdot 2CuBr$ is of interest in that it is formed by direct reaction of the olefin with cupric bromide (5). Presumably some of the norbornadiene is oxidized simultaneously; the reaction indicates clearly the powerful complexing properties of the olefin, of which mention is made in later sections of this review.

Much less work has been carried out on acetylene complexes of silver and copper. Distribution (80) and solubility studies (134) have been made of the interaction of hex-3-yne, methyl-substituted hex-3-ynes and hept-2-yne with silver nitrate, and evidence for the formation of complexes containing one and two molecules of acetylene per silver ion was obtained. As found in the olefin complexes, the general effect of substituents on the triple bond is to hinder complex formation. In some cases, solid complexes can be isolated; for example, pent-2-yne gives white crystals of formula $AgNO_3 \cdot 3C_5H_8$ (55), which lose the acetylene on exposure to air, with hex-3-yne with powdered silver nitrate gives a colorless solid $AgNO_3 \cdot C_6H_{10}$ in the course of three weeks (55). Nothing is known about the structures of these compounds, nor have any spectroscopic studies been undertaken to discover how the triple bond is affected by complexing. X-ray studies on some cuprous chloride acetylene complexes suggest a geometry very similar to the silver- and platinum–olefin complexes, but no details of carbon–carbon bond lengths were given (37). It has been suggested (21a) that the complexes of copper and silver of general formula RC≡CM (R = alkyl, aryl, M = Cu, Ag) are not simple acetylides, but coördination polymers in which the triple bond is bound to the metal atom(IIa). The polymeric structure is broken down by reaction with phosphines and arsines giving crystalline complexes of formula LMC≡CR (L = $(C_2H_5)_3P$, $(C_2H_5)_3As$, M = Cu, Ag, R = alkyl, aryl), which show degrees of association varying between two and four in various organic solvents. Structure IIb, in which copper and silver attain coördination number 3, is suggested. It may be noted that in this series the copper complexes are considerably more stable to air and light than their silver analogs.



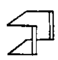
II a

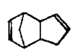


II b

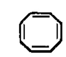
We shall not discuss in any detail in this review the olefin complexes of mercury(II). The available chemical evidence (39), allied with proton resonance measurements (66), suggests that in these complexes, the double bond is not preserved, and that addition of the elements HgX and X across the double bond occurs instead.

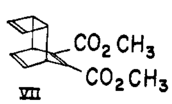
The extension of the Dewar concept to explain the bonding in olefin complexes of Pt(II), Pd(II) and Rh(I) has been noted. It is clear that olefin–metal bonding is closely similar in type to metal-carbon monoxide bonding in metal carbonyl derivatives, and this undoubtedly explains the frequently noted resemblance in stoichiometry and chemical properties between olefin metal halides and metal carbonyl halides, especially of Pt(II) and Pd(II). The same point is brought out in the olefin complexes of rhodium(I), which are remarkably similar both to those of the isoelectronic palladium(II) (81), and to the carbonyl halide complexes of rhodium(I). By reaction of rhodium trichloride or rhodium carbonyl chloride $Rh_2(CO)_4Cl_2$ with excess of the chelating diolefin cycloöcta-1,5-diene (III), Chatt and Venanzi (45, 46)


III

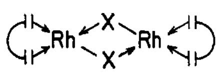

IV


V


VI



VII



VIII

obtained a stable, orange, dimeric complex $C_8H_{12}RhCl$, to which structure VIII (X = Cl) was assigned on the basis of the chemical reactions and diamagnetism of the complex. Presumably reduction in the valence of the metal occurs at the expense of the olefin. The corresponding dimeric compounds with X = Br, I and OAc were prepared by carrying out displacement reactions on the chloro-complex, and an order of stability Cl > Br > I was noted. Chatt and Venanzi (46) also were able to prepare the corresponding chloro-complex with dicyclopentadiene (IV), but could not obtain pure complexes from cycloöctatetraene (VI), hexa-1,5-diene or styrene. More recently, by using less vigorous reaction conditions, the reaction has been extended to give stable complexes of rhodium(I) of the same general formula with norbornadiene (V), cycloöctatetraene (VI) and some of its Diels–Alder adducts, *e.g.* (VII) (5). The presence of bridging halogen groups in the complexes (diene $RhCl)_2$ is shown by the "bridge-splitting" reaction well-known in platinous chemistry. Thus, the rhodium complexes of norbornadiene and cycloöcta-1,5-diene have been shown (19, 46) to react with a number of ligands, such as amines and tertiary phosphines, to give monomeric square-planar complexes according to the equation

$$[\text{diene RhCl}]_2 + 2\text{L} \rightarrow \text{diene RhClL} \quad (\text{L} = \text{ligand})$$

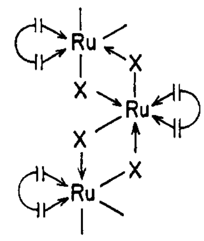
Evidence also has been obtained for the existence of unstable cationic and anionic rhodium–olefin species (46). The rhodium complex of cycloöcta-1,5-diene $(C_8H_{12}RhCl)_2$ is soluble in warm concentrated hydrochloric acid and in chelating diamines, and it is probable that equilibria such as

$$[\text{diene RhCl}]_2 + 2\,\text{Cl}^- \rightleftarrows 2[\text{diene RhCl}_2]$$

$$[\text{diene RhCl}]_2 + 2\text{ diamine} \rightleftarrows 2[\text{diene Rh(diamine)}]^+ + 2\text{Cl}^-$$

are established. The corresponding reaction with α,α'-dipyridyl gives a red, insoluble salt which may be formulated as [(diene)Rh(dipy)][diene $RhCl_2$]. The anionic species (diene $RhCl_2)^-$ is of course iso-electronic with the well-known palladous complexes (diene $PdCl_2$) (81). The cycloöctatetraene-rhodium complex $(C_8H_8RhCl)_2$ is of interest in showing two peaks in its proton resonance spectrum, suggesting that cyclooctatetraene has the "tub" configuration in this complex as in the silver complex (19).

The existence of stable square planar olefin complexes of Pt(II), Pd(II) and Rh(I) led Chatt and Venanzi (46) to suggest that the presence of a vacant p_z orbital on the metal was a prerequisite for the formation of olefin complexes, since this could form hybrid orbitals with the filled d_{xz} and d_{yz} orbitals suitable for forming strong π-bonds with the antibonding orbitals of the olefin. It was suggested that d-orbitals alone do not always give sufficiently good overlap, and that some p-character is always necessary. In agreement with this is the failure to isolate six-coördinate olefin complexes of Pt(IV) and Rh(III) by halogen addition to the corresponding Pt(II) and Rh(I) complexes (19, 46). That the criterion of p-character is not valid for all the transition metals is shown by the isolation of stable, six-coördinate olefin complexes of ruthenium(II). They have the general formula diene RuX_2 (X = Cl, Br, I) and are isolated from prolonged reaction of ruthenium halides with the chelating diolefins norbornadiene and cycloöcta-1,5-diene (5, 18). In contrast to the rhodium complexes, they are almost completely insoluble in organic solvents, and a polymeric structure involving six-coördinate Ru(II) has been suggested to explain these properties and the observed diamagnetism



(IX)

The presence of halogen bridges in IX is indicated by the typical bridge-splitting reaction with *p*-toluidine, which gives yellow complexes, probably monomeric, of general formula (diene) $Ru(p\text{-tol})_2X_2$ (X = Cl, Br). Reaction of diene $RuCl_2$ with pyridine not only breaks the halogen bridges, but displaces the olefin as well, giving monomeric Ru py_4Cl_2. It may be noted that the analogy between olefin metal halides and metal carbonyl halides is continued in these ruthenium compounds, since the corresponding carbonyl iodide $Ru(CO)_2I_2$ is likewise reddish-brown and insoluble, and probably possesses a polymeric structure (5, 144). Evidence has been reported recently that ruthenium(II) forms 1:1 complexes with ethylene and propylene, and the corresponding maleic acid complex probably is intermediate in the homogeneous hydrogenation of maleic acid to succinic acid in the presence of ruthenium(II) (131). The failure to obtain olefin complexes of rhodium(III), which is isoelectronic with ruthenium(II), must be attributed to the increased positive charge and decreased size of the cation, which presumably contract the metal orbitals sufficiently to prevent good overlap with the orbitals on the olefin (19, 46). No acetylene complexes of rhodium are known.

Recently, a number of olefin and acetylene complexes of rhenium have been described (53). The complex $ReCl[(C_6H_5)_3P](C_{10}H_{12})_2$ obtained from $ReCl_3$-$[(C_6H_5)_3P]$ and dicyclopentadiene is presumably a monomeric six-coördinate complex of Re(I), and the complex $ReCl_2(C_{10}H_{12})_2$ obtained from rhenium trichloride and dicyclopentadiene is insoluble, black and probably polymeric; its stoichiometry is surprising, since, by analogy with the bridged carbonyl halide $[Re(CO)_4Cl]_2$ (6), a complex $[ReCl(C_{10}H_{12})_2]$ would have been expected. A phenylacetylene complex $ReCl(C_6H_5$-$C_2H)_2$ also is reported from the reaction of phenylacetylene with rhenium trichloride. In this complex, the C≡C bond is reduced effectively to a C=C bond by complexing, as shown by a C—C stretching frequency of 1700 cm.$^{-1}$, so the acetylene presumably is bonded to the metal by two σ-bonds, as in some analogous platinum complexes (81). In similar complexes formed from some acetylenic alcohols, it is thought that the acetylene acts as a bidentate ligand with bonding from C≡C and from hydroxyl oxygen (53).

A number of ill-characterized compounds which may be olefin complexes of iridium have been described, and are summarized by Keller (157). An allyl alcohol complex of iridium of unstated formula has been mentioned briefly (44). It is surprising that, as yet, very few olefin complexes of iridium and osmium analogous to those of rhodium and ruthenium have been obtained although a monomeric cycloöcta-1,5-diene complex of osmium(II), $C_8H_{12}Os[(C_6H_5)_2PC_2H_5]_2Cl_2$ has been described very briefly in a recent paper (42).

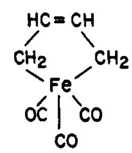
In most of the olefin complexes described in this section infrared bands are observed in the 1500 cm.$^{-1}$ region which may be assigned to carbon–carbon stretching frequencies modified by coördination to the metal atoms. This assignment has been made definite in the case of some mono-olefin complexes of platinum(II) (7, 41, 202). In these complexes, therefore, the C=C stretching frequency is lowered by some 150 cm.$^{-1}$ on coördination, which suggests, in agreement with chemical evidence, that the metal–olefin bond is stronger in the platinum, rhodium, and ruthenium complexes than in the silver and copper complexes. There is, however, no quantitative information on this point.

To summarize, in the reactions of olefins with transition metal salts, the most stable complexes are formed by elements principally of the Second and Third Rows with chelating diolefins. Very few complexes of this type are known with conjugated olefins. At present, relatively few acetylene complexes analogous to these olefin complexes are known. The prediction of Chatt and Venanzi (46) that, with decreasing nuclear size (and valence), a point to the left of Group VIII will be reached where the d_{xz} orbital will reach out sufficiently to stabilize olefin complexes without the addition of p-character has been amply justified, not only by the isolation of olefin complexes of ruthenium and rhenium, but also by the isolation of olefin complexes of the Group VI metals in their zerovalent state (stabilized by the presence of carbon monoxide groups). These complexes are described in Section IV.

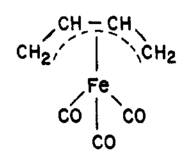
III. OLEFIN IRON CARBONYLS

A. BUTADIENE IRON TRICARBONYL AND RELATED COMPOUNDS

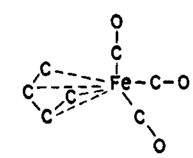
Butadiene iron tricarbonyl, the precursor of all the organo-metal carbonyls, was first obtained in 1930 by Reihlen and co-workers by the reaction of iron pentacarbonyl with butadiene under pressure (206). It is a pale yellow, diamagnetic, low-melting solid of considerable thermal stability, and it is readily soluble in organic solvents.



X



XI



XII

In a thorough re-investigation in 1958, Hallam and Pauson (129) pointed out that the structure X suggested by Reihlen was untenable, since (a) it would lead to paramagnetism, being a 34-electron molecule, (b) the thermal and oxidative stability observed would not be expected for a complex containing two σ-bonds to iron, and (c) there was no evidence of a free double bond, since the compound is unaffected by catalytic hydrogenation and maleic anhydride. The complex also shows a band at 1464 cm.$^{-1}$ in its infrared spectrum which is probably a C=C stretching frequency lowered by about 150 cm.$^{-1}$ through coordination to the metal. Although structure X can be modified by coördinating the double bond to iron so as to meet these objections (124), Hallam and Pauson

(129) made the significant suggestion that the butadiene–iron bond resulted from overlap of a suitable metal orbital with a π-orbital of butadiene overlapping all four carbon atoms, more like a "sandwich" bond than the conventional olefin–metal bond considered in Section II, and they advanced structure XI. That the butadiene must be *cis*-oid in this complex was shown by the isolation of the first of the cycloölefin iron carbonyl complexes, *viz.*, (cyclohexa-1,3-diene)$Fe(CO)_3$ from the reaction of iron carbonyl with cyclohexa-1,3-diene. The structure of the butadiene complex, as determined by X-ray study (185), shows that the butadiene is indeed planar and *cis*-oid, although it is not coplanar with the $Fe(CO)_3$ grouping (structure XII). In agreement with the suggestion of delocalized bonding, the carbon–carbon bond lengths are almost equal (1.45 Å.), this value being almost that expected for a single bond formed between two sp^2-hybridized carbon atoms. Further, the C–C–C angles of the butadiene moiety are about 118°. The coördination about the iron atom is of interest; a square pyramid is formed from the three carbonyl groups and the two terminal carbon atoms of the butadiene chain, while the other two carbon atoms do not occupy normal coördination positions.

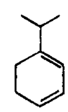
In their original work, Reihlen and co-workers (206) also investigated the reaction of isoprene with iron pentacarbonyl, and obtained compounds of surprising stoichiometry, *e.g.*, $(C_5H_8)_2Fe(CO)_3$. This and other reactions involving substituted butadienes and cyclohexa-1,3-dienes have been reinvestigated recently (160), and the results of this work show very clearly the importance of conjugation to the stability of diolefin iron tricarbonyl complexes. Isoprene reacts with $Fe(CO)_5$ under irradiation with ultraviolet light, or with $Fe_3(CO)_{12}$ in refluxing benzene, to form the orange oil isoprene iron tricarbonyl $C_5H_8Fe(CO)_3$, analogous to the butadiene compound. Reihlen's $(C_5H_8)_2Fe(CO)_3$ is probably a mixture of $C_5H_8Fe(CO)_3$, (α-terpinene)$Fe(CO)_3$ (XIII) and dipentene (XIV), the latter two compounds arising from dimerization of the isoprene under the vigorous reaction conditions used. The unconjugated diolefins penta-1,4-diene and 1,3,5-trimethyl-cyclohexa-2,5-diene, however, react with $Fe_3(CO)_{12}$ giving iron tricarbonyl complexes of the corresponding isomeric conjugated diolefins penta-1,3-diene and 1,3,5-trimethyl-cyclohexa-2,4-diene, whose properties and thermal stability closely resemble those of butadiene iron tricarbonyl (160).

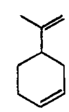
Examination of Table II also shows clearly that the vast majority of diolefin iron tricarbonyls are formed by conjugated diolefins. This is in complete contrast to the situation with olefin complexes of Pt, Pd, Rh, Ru, *etc.* considered in Section II, in which the dominant factor seems to be the steric configuration of the double bonds, so that the most stable complexes are formed by "chelate" diolefins, such as cycloöcta-1,5-diene.

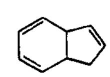
The most stable iron tricarbonyl complex of a formally unconjugated diene is the orange liquid $C_7H_8Fe(CO)_3$ obtained from the thermal or photochemical reaction of $Fe(CO)_5$ with norbornadiene (V) (32, 124, 201). The reaction is considerably more complex than is represented by the simple equation

$$Fe(CO)_5 + C_7H_8 \rightarrow C_7H_8Fe(CO)_3 + 2CO$$

since a number of ketones and dimers derived from the olefin are also obtained (20, 201), while at higher temperatures $Fe(C_5H_5)_2$ and $[C_5H_5Fe(CO)_2]_2$ also are formed, presumably from the breakdown of norbornadiene to cyclopentadiene and acetylene. Although norbornadiene is a powerful chelating diolefin, it does also undergo Diels–Alder addition reactions with some difficulty (234). This suggests that the double bonds may be pulled together sufficiently for overlap to occur between the π-orbitals, so that, in the reaction with $Fe(CO)_5$, it may be behaving as a kind of "conjugated" diolefin. By contrast, (cycloöcta-1,5-diene)$Fe(CO)_3$, obtained from $Fe_3(CO)_{12}$ and the olefin in refluxing benzene, is a volatile orange liquid which is very unstable compared both with its butadiene and norbornadiene analogs (160). Even under nitrogen, it decomposes in a few hours at room temperature. A complex described as (dipentene)$Fe(CO)_3$ (175) subsequently has been identified as (α-terpinene)$Fe(CO)_3$ (160), the α-terpinene being an impurity in commercial dipentene. However, the iron tricarbonyl complex of 8,9-dihydroindene (XV) is so unstable thermally as to suggest coördination from nonconjugate double bonds (162).


XIII


(XIV)


XV

B. CYCLOÖCTATETRAENE IRON CARBONYLS

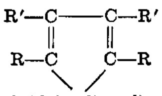
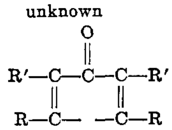
Cycloöctatetraene iron carbonyls were discovered independently by three groups, whose published results are in essential agreement (173, 176, 188, 205). The thermal reaction of equimolar quantities of cyclooctatetraene and iron pentacarbonyl in an inert solvent gives as the main product cycloöctatetraene iron tricarbonyl $C_8H_8Fe(CO)_3$ in 60% yield, together with lower yields of two binuclear complexes $C_8H_8Fe_2(CO)_6$ and $C_8H_8Fe_2(CO)_7$. The same results are obtained if equimolar quantities of the same reactants are irradiated with sunlight, or, better, ultraviolet light, and a high yield of $C_8H_8Fe_2(CO)_6$ is obtained either by starting with a large excess of $Fe(CO)_5$, or by irradiating a mixture of $Fe(CO)_5$ and $C_8H_8Fe(CO)_3$.

The complex $C_8H_8Fe(CO)_3$ is a red, crystalline, diamagnetic solid which is very stable to air, sublimes readily *in vacuo*, and dissolves in most organic solvents.

TABLE II
OLEFIN CARBONYL COMPLEXES OF IRON

Organic ligand	Formula of complex	Physical properties	References: Prepn.	References: Infra-red	Dipole moment (solvent)	N.m.r. ref.
Butadiene	$C_4H_6Fe(CO)_3$	Pale yellow crystals m.p. 19° b.p. 48° (0.06 mm.)	(129) (206)	(129)	—	(123)
Isoprene	$C_5H_8Fe(CO)_3$	Yellow liquid	(160)	(160)	—	(160)
Penta-1,3-diene	$C_5H_8Fe(CO)_3$	Yellow liquid	(160)	(160)	—	—
1,2,3,4-Tetraphenylbutadiene	$C_{28}H_{22}Fe(CO)_3$	Yellow needles m.p. 230–232° d.	(139) (213)	(139) (213)	—	(123)
$CH_3(CH{=}CH)_2CO_2C_2H_5$ (ethyl sorbate)	$C_8H_{12}O_2Fe(CO)_3$	Yellow solid m.p. 49–51°	(160)	(160)	—	—
$CH_3(CH{=}CH)_2CONH_2$ (sorbamide)	$C_6H_9NOFe(CO)_3$	Yellow solid m.p. 132–134°	(160)	(160)	—	—
$CH_3(CH{=}CH)_2COCH_3$	$C_7H_{10}OFe(CO)_3$	Yellow solid m.p. 31–33°	(160)	(160)	—	—
$CH_3(CH{=}CH)_2CN$	$C_6H_7NFe(CO)_3$	Yellow liquid	(160)	(160)	—	—
$CH_3(CH{=}CH)_2CHO$	$C_6H_8OFe(CO)_3$	Orange liquid	(160)	(160)	—	—
Cyclohexa-1,3-diene	$C_6H_8Fe(CO)_3$	Yellow liquid m.p. 8–9°	(129)	(129)	—	(34)
1,3-Dihydromesitylene	$C_9H_{14}Fe(CO)_3$	Yellow oil	(160)	(160)	—	(160)
Perfluorocyclohexa-1,3-diene	$C_6F_8Fe(CO)_3$	Pale yellow crystals m.p. 45°	(138) (236)	(138) (236)	—	(138) (236)
Allo-ocimene (2,6-dimethylocta-2,4,6-triene)	$C_{10}H_{16}Fe(CO)_3$	Golden crystals m.p. 47–48°	(160)	(160)	—	(160)
α-Terpinene	$C_{10}H_{16}Fe(CO)_3$	Orange oil	(160)	(160)	—	—
Hexa-1,3,5-triene	$(C_6H_8)_2Fe(CO)_3$	Orange red oil m.p. ∼ −70°	(249)	(249)	—	—
Cyclohepta-1,3-diene	$C_7H_{10}Fe(CO)_3$	Yellow liquid b.p. 60° (0.5 mm.) m.p. ∼ 5° (73) m.p. 23° b.p. 74° (0.4 mm.) (34)	(34) (73)	(34) (73)	—	(34) (73)
Cycloheptatriene	$C_7H_8Fe(CO)_3$	Orange-yellow liquid m.p. −2° b.p. 60° (0.5 mm.) (73) m.p. 5° b.p. 70° (0.4 mm.) (34)	(34) (73)	(34) (73)	2.43 ± 0.04*D* (benzene) (34)	(34) (73)
	$(C_7H_8)_2Fe_3(CO)_9$	Yellow crystals	(34)	(34)	—	—
Bicyclo[4.2.0]octa-2,4-diene ("cyclooctatriene")	$C_8H_{10}Fe(CO)_3$	Orange oil	(105) (176) (177)	(105) (176) (177)	2.37 ± 0.03*D* (cyclohexane) (105)	(34) (177)
Cycloöcta-1,3,5-triene (or 1,3,6-isomer)	$C_8H_{10}Fe(CO)_3$	Yellow solid m.p. 24°	(177)	(177)	—	(177)
	$C_{16}H_{12}O_6Fe_2$	Orange solid m.p. 72–74°	(105)	(105)	3.66 ± 0.03*D* (cyclohexane) (105)	—
Cycloöctatetraene	$C_8H_8Fe(CO)_3$	Red crystals m.p. 92–93.5°	(173) (176) (188) (205)	(173) (176) (188) (205)	—	(173) (176) (205)
	$C_8H_8Fe_2(CO)_6$	Yellow solid dec. 190°	(173) (176) (188) (205)	(173) (176) (188) (205)	—	(78)
	$C_8H_8Fe_2(CO)_7$	Black solid	(173) (176)	(173) (176)	—	—
Cycloöctatetraene	$C_8H_8Fe(CO)_2\text{-}As(C_6H_5)_3$	Red oil	(176)	(176)	—	(176)
	$C_8H_8Fe(CO)_2\text{-}Sb(C_6H_5)_3$	Red oil	(176)	(176)	—	(176)
Cycloöcta-1,5-diene	$C_8H_{12}Fe(CO)_3$	Orange liquid	(160) (175)	(160)	—	—
Bicyclo[2.2.1]hepta-2,5-diene	$C_7H_8Fe(CO)_3$	Golden liquid m.p. −2°	(32) (124) (201)	(124) (201)	—	(124)
Acrylonitrile	$C_3H_3NFe(CO)_4$	Yellow crystals m.p. 47–48°	(159)	(159)	—	—
	$(C_3H_3N)_2Fe(CO)_3$	Yellow solid	(216)	—	—	—
8,9-Dihydro-indene	$C_9H_{10}Fe(CO)_3$	Pale yellow crystals m.p. ∼ 25°	(162)	(162)	—	—
Thianaphthene	$C_8H_6SFe_2(CO)_5$	Red-orange solid m.p. 100–101°	(162)	(162)	—	(162)
Acenaphthylene	$C_{12}H_8Fe_2(CO)_6$	Red-violet crystals m.p. 158°	(162)	(162)	—	—
Cyclopentadienone	$(C_5H_4O)Fe(CO)_3$	Yellow crystals m.p. 114–115° d.	(124) (207) (239)	(124) (239)	—	(124)
Cyclopentadienone	$(C_5H_4O)Fe(CO)_2$	Orange crystals d. 160°	(124) (207) (239)	(124) (239)	—	(124)
Cyclopentadienone	$(C_5H_4O)Fe(CO)_3 \cdot HI$	Yellow solid m.p. 163–165° d.	(239)	(239)	—	—
Cyclopentadienone	$[(C_5H_4O)Fe(CO)_3]_2 \cdot$ hydroquinone	Pale yellow solid m.p. 126–127° d.	(124) (207) (239)	(124) (239)	—	(124)
Cyclopentadienone	$(C_5H_4O)Fe(CO)_2[P(C_6H_5)_3]$	Yellow solid d. 176–177°	(239)	(239)	—	—
Tetraphenylcyclopentadienone	$(C_{29}H_{20}O)Fe(CO)_3$	Yellow solid d. ∼ 180°	(139) (140) (211) (213) (238)	(139) (213) (238)	—	—
Tetraphenylcyclopentadienone	$(C_{29}H_{20}O)Fe(CO)_2[P(C_6H_5)_3]$	Yellow crystals d. 170–230°	(238)	(238)	—	—
Tetraphenylcyclopentadienone	$(C_{29}H_{20}O)Fe(CO)_2[P(OC_6H_5)_3]$	Yellow needles m.p. 216–217°	(238)	(238)	—	—
2,5-Dimethyl-3,4-diphenylcyclopentadienone	$(C_{19}H_{16}O)Fe(CO)_3$	Yellow needles d. ∼ 150°	(238)	(238)	—	—
2,5-Diphenyl-3,4-dimethylcyclopentadienone	$(C_{19}H_{16}O)Fe(CO)_3$	Yellow solid d. 206–207°	(238)	(238)	—	—

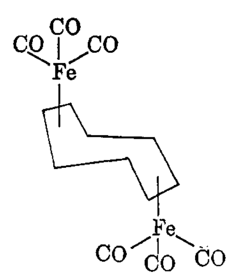
TABLE II (*Concluded*)

Organic ligand	Formula of complex	Physical properties	References: Prepn.	References: Infrared	Dipole moment (solvent)	N.m.r. ref.
2,5-Diphenylcyclopentadienone	$(C_{17}H_{12}O)Fe(CO)_3$	Yellow needles d. ~ 230°	(68) (139) (140) (167) (212) (213) (238)	(139) (167) (213) (238)	$3.1 \pm 0.2D$ (benzene) (68) (167)	(167)
Tetra-(*p*-chlorophenyl)cyclopentadienone	$(C_{29}H_{16}Cl_4O)Fe(CO)_3$	Yellow needles d. 175–180°	(238)	(238)	—	—
2,5-Diphenyl-3,4-di-(*p*-chlorophenyl)-cyclopentadienone	$(C_{29}H_{18}Cl_2O)Fe(CO)_3$	Yellow crystals d. 173–175°	(238)	(238)	—	—
2,5-(*p*-Bromophenyl)cyclopentadienone	$(C_{17}H_{10}Br_2O)Fe(CO)_3$	Yellow solid d. 250°	(238)	(238)	—	—
2,5-Trimethylsilylcyclopentadienone	$(C_{11}H_{20}OSi_2)Fe(CO)_3$	Yellow solid d. 167–168°	(238)	(238)	—	—
2,5-Trimethylsilyl-3,4-diphenyl-cyclopentadienone	$(C_{23}H_{28}OSi_2)Fe(CO)_3$	Yellow solid d. 174–175°	(238)	(238)	—	—
Tetraphenylcyclopentadienone-(*p*-dimethylamino-anil)	$(C_{37}H_{30}N_2)Fe(CO)_3$	Yellow prisms d. 233–235°	(238)	(238)	—	—
3,4-Dimethylthiophendioxide	$(C_6H_8O_2S)Fe(CO)_3$	Yellow crystals d. 150°	(238)	(238)	—	—
Pentaphenylphosphole	$(C_{34}H_{25}P)Fe(CO)_3$	Yellow solid m.p. 205–215°	(23)	(23)	—	—
Pentaphenylphosphole oxide	$(C_{34}H_{25}PO)Fe(CO)_3$	Yellow prisms m.p. 226–235° d.	(23)	(23)	—	—
Tetraphenylcyclobutadiene	$(C_{28}H_{20})Fe(CO)_3$	Yellow crystals m.p. 234°	(139)	(139)	—	—
Duroquinone	$(C_{10}H_{12}O_2)Fe(CO)_3$	Orange crystals d. ~ 50°	(223)	(223)	—	—
Cycloheptatrienone	$(C_7H_6O)Fe(CO)_3$	Two modifications: (a) red prisms m.p. 63.5–64.5°; (b) red prisms m.p. 78–79°	(142)	(142)	—	—
 (bridging ligand) R = R′ = H	$C_4H_4Fe_2(CO)_6$	Orange crystals m.p. 53° (124) m.p. 54–55° (142)	(124) (142)	(124)	—	(124)
RR = R′ = C_6H_5	$C_{28}H_{20}Fe_2(CO)_6$	Orange crystals m.p. 200° d. (139) m.p. 174–178° (213)	(139) (213)	(139) (213)	$3.3 \pm 0.2D$ (in benzene) (139)	—
R = H, R′ = C_6H_5	$C_{16}H_{12}Fe_2(CO)_6$	Yellow-orange crystals d. ~ 180°	(139)	(139)	—	—
R = H, R′ = OH	$(C_4H_4O_2)Fe_2(CO)_6$	Light yellow needles m.p. 80–85° d. (+ $1H_2O$) m.p. 104–110° d.	(47) (207) (221) (240)	47) (221) (240)	—	—
R = CH_3, R′ = OH	$(C_6H_8O_2)Fe_2(CO)_6$	Yellow crystals m.p. 100–105° d.	(47) (221) (240)	—	—	—
R = H, R′ = OCH_3	$(C_6H_8O_2)Fe_2(CO)_6$	Orange crystals m.p. 155.2–156.4°	—	—	—	—
R = H, R′ = $OCOC_6H_5$	$(C_{18}H_{12}O_4)Fe_2(CO)_6$	Yellow crystals m.p. 155–160°	—	—	—	—
unknown	$Fe_3(CO)_8C_{14}H_{10}$	Black needles m.p. 208–210° d.	(139)	(139)	—	—
 (Bridging ligand) R = R′ = C_6H_5	$(C_{29}H_{20}O)Fe_2(CO)_6$	Red crystals m.p. ~ 160° d.	(139)	(139)	—	—
ω,ω-Diphenylfulvene	$C_{18}H_{14}Fe\ CO)_3$	Dark-brown solid m.p. 93–95° d.	(143)	—	—	—
ω,ω-Diphenylfulvene	$C_{18}H_{14}Fe_2(CO)_5$	Dark violet solid m.p. 157–164° d.	(143)	—	—	—
ω,ω-Diphenylfulvene	$C_{18}H_{14}Fe_2(CO)_8$	Red solid m.p. 106–108° d.	(143)	—	—	—
Cyclopentamethylenefulvene	$C_{11}H_{14}Fe(CO)_3$	Yellow solid m.p. 170–175° d.	(143)	—	—	—
Cyclopentamethylenefulvene	$C_{11}H_{14}Fe_2(CO)_6$	Dark-red solid m.p. 126–131° d.	(143)	—	—	—
Fulvene	$C_6H_6Fe_2(CO)_6$	Dark-red solid d. ~ 140°	(143)	—	—	—
Dimer of ω,ω-dimethylfulvene	$C_{16}H_{20}Fe(CO)_2$	Yellow solid m.p. 92–95°	(143)	—	—	—
Dimer of ω,ω-dimethylfulvene	$C_{16}H_{20}Fe_2(CO)_5$	Red solid d. ~ 130°	(143)	—	—	—

Since 4 π-electrons are required from the eight-membered ring, we expect to find chemical and physical evidence for the existence of two free double bonds in the complex. Such evidence is almost completely lacking (176, 188, 205). The complex is only slowly decomposed by bromine, with release of carbon monoxide, it is unaffected by catalytic hydrogenation, and it does not react with dienophiles such as maleic anhydride. The infrared spectrum shows no bands in the 1600 cm.$^{-1}$ region attributable to free double bonds, although there is a band at 1416 cm.$^{-1}$ which can be assigned to an olefinic C═C stretching frequency modified by coördination to the metal. The C–H stretching region shows only two bands, even under high resolution. There is only one peak in the proton resonance spectrum. This evidence, taken together, suggests that $C_8H_8Fe(CO)_3$ contains a planar, or almost planar, eight-membered ring, and that bonding to the metal involves overlap of suitable metal orbitals with a symmetrical π-orbital encompassing all eight carbon atoms (176, 205).

It is true that free cycloöctatetraene itself, which has a "tub" D_{2d} configuration, also shows only one proton resonance. Nevertheless, three complexes of cyclooctatetraene in which the "tub" configuration is almost certainly retained, *viz.*, $C_8H_8PtI_2$ (144c), $[C_8H_8RhCl]_2$ (19) and π-$C_5H_5CoC_8H_8$ (189), are hydrogenated readily catalytically, show bands due to uncomplexed C=C in the infrared, and the latter two show two proton resonances assignable to different protons of the eight-membered ring. Whether all the carbon–carbon bond lengths in $C_8H_8Fe(CO)_3$ are equal can be decided only by an X-ray study presently in progress (168). Attempts to carry out aromatic-type substitution reactions on the eight-membered ring, in a manner similar to that described for π-$C_5H_5Mn(CO)_3$ (67, 106) and π-C_6H_6-$Cr(CO)_3$ (89, 208), have not yielded stable products so far, though there is reported to be indirect evidence for an acylation reaction (176). If this is correct, it would indicate the presence of π-electron density spread evenly on the eight-membered ring attached to the metal, and provide further evidence for delocalized bonding. It is interesting that triphenylphosphine displaces cyclooctatetraene in $C_8H_8Fe(CO)_3$, giving $[\{(C_6H_5)_3P\}_2Fe(CO)_3]$ whereas triphenylarsine and triphenylstibine preferentially displace a CO ligand, giving $C_8H_8Fe(CO)_2[(C_6H_5)_3As]$ and $C_8H_8Fe(CO)_2$-$[(C_6H_5)_3Sb]$, respectively (176).

The binuclear complex $C_8H_8Fe_2(CO)_6$ is a yellow, air-stable, diamagnetic solid which is only sparingly soluble in organic solvents (173, 176, 188, 205). The infrared spectrum shows three terminal CO stretching frequencies, no frequencies due to bridging CO groups or to uncomplexed C=C, and one frequency (at 1414 cm.$^{-1}$) probably due to complexed C=C. Suggestions (65, 176) that the cyclooctatetraene ring is located between the two iron atoms, with each iron atom receiving four π-electrons from a pair of double bonds, are supported by the results of the recently published X-ray study (78), which shows the structure XVI.



XVI

The unexpected features of the structure of $C_8H_8Fe_2$-$(CO)_6$ are the chair-conformation and the bond-lengths of the ring, which show no resemblance to those found in $C_8H_8AgNO_3$ (181) (182). Each $Fe(CO)_3$ group is associated with a planar four-carbon grouping, similar to the situation in (butadiene)$Fe(CO)_3$, although in this case the C–C bond lengths in each four-carbon chain are not equal, being 1.44, 1.39 and 1.44 Å. The two halves of the cyclooctatetraene unit are joined by C–C single bonds 1.49 Å in length, and there is about 10° distortion from the 120° angle expected for sp^2 hybridization in the central four C–C–C angles. Each iron atom is stated to be octahedrally coördinated, the three C–C bonds being staggered with respect to the three carbonyls. It is of interest that this complex also shows only one proton resonance in solution, although the structure in the solid state does not indicate proton equivalence. This suggests either that the structure changes in solution, perhaps giving rise to a planar cyclooctatetraene ring, or that there is some dynamic effect, as in C_8H_8 itself (78).

The binuclear complex $C_8H_8Fe_2(CO)_7$, which is a black non-volatile solid, is believed to be a derivative of $Fe_2(CO)_9$, in which a C_8H_8 group has replaced two terminal CO groups, since the infrared spectrum shows not only three terminal carbonyl frequencies, but also a bridging carbonyl frequency at 1802 cm.$^{-1}$ (173, 176).

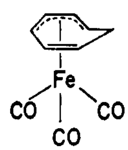
It may be noted finally that qualitative molecular-orbital treatments of $C_8H_8Fe(CO)_3$ and $C_8H_8Fe_2(CO)_6$ have been given (65), which are discussed in Section XV.

C. CYCLOHEPTATRIENE IRON CARBONYLS

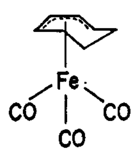
Since cycloheptatriene contains potentially six π-electrons available for donation to transition metals, reaction with iron carbonyls might be expected to give a diamagnetic dicarbonyl $C_7H_8Fe(CO)_2$, and an orange liquid of this composition was in fact described in a preliminary paper (32). Further investigation (34, 73) has shown that the thermal reaction of iron pentacarbonyl with cycloheptatriene gives a mixture of three organometallic complexes, the relative amounts of which vary with reaction conditions; none is the expected dicarbonyl. The complexes are: (a) cycloheptatriene iron tricarbonyl, $C_7H_8Fe(CO)_3$, an orange-yellow diamagnetic liquid; (b) cyclohepta-1,3-diene iron tricarbonyl, $C_7H_{10}Fe(CO)_3$, an orange-yellow diamagnetic liquid; (c) bis-(cycloheptatriene)-tri-iron nonacarbonyl $(C_7H_8)_2Fe_3(CO)_9$, a yellow crystalline diamagnetic solid.

If the reaction mixture of $Fe(CO)_5$ and cycloheptatriene is held at 110° for seven days (34), or at 135° for one day (73), cycloheptatriene iron tricarbonyl is the main product; at 135° for five days, however, the cycloheptadiene complex predominates over the cycloheptatriene complex (34, 73), and a small yield of the trinuclear complex is obtained. The two liquid products can be separated either by liquid phase chromatography (34), or by repeated fractional crystallization at low temperatures (73). It may be noted that although the proton resonance spectra described by the two independent groups (34, 73) for the two liquid products are in reasonable agreement, and support the respective formulations, there is some discrepancy in the quoted melting points, particularly in the cycloheptatriene complex (Table II). The cycloheptatriene complex is less stable to aerial decomposition than the cycloheptadiene complex.

There is good evidence that one of the double bonds of cycloheptatriene in $C_7H_8Fe(CO)_3$ is either not involved in bonding to iron, or at least is not so strongly as the other two (34, 73). The infrared spectrum shows a band at 1660 cm.$^{-1}$ which is not present in the spectra of the corresponding cyclohexa-1,3-diene or cyclohepta-1,3-diene complexes, and which is assignable as an uncomplexed C=C stretching frequency. The proton resonance spectrum shows peaks assignable to protons attached to a free double bond. The complex can be reduced by hydrogen at room temperature in the presence of Raney nickel to give the cycloheptadiene complex; under more vigorous conditions, cycloheptane is obtained. However, the free double bond does not respond to most of the usual olefin reactions, *e.g.*, with OsO_4, probably owing to complete decomposition of the complex, although some evidence for the transient formation of silver nitrate adduct was obtained (34). The simplest and most reasonable structure for (cycloheptatriene)$Fe(CO)_3$ therefore involves bonding to iron from conjugate double bonds, as in (butadiene)$Fe(CO)_3$



XVII



XVIII

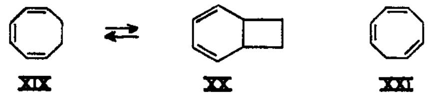
The cyclohepta-1,3-diene complex XVIII, which can also be prepared by heating $Fe(CO)_5$ with the diolefin, presumably arises in the cycloheptatriene reaction by hydrogen transfer to the coördinated triene by excess of the triene under the reaction conditions.

In Section XI, further reactions of these two complexes are surveyed, with special reference to addition reactions to the coördinated cycloheptatriene system.

Little is known about the trinuclear complex, although a structure has been suggested (34) in which the two originally uncomplexed double bonds of two cycloheptatriene rings are attached to a third $Fe(CO)_3$ group.

D. CYCLOÖCTATRIENE IRON CARBONYLS

The reactions of cycloöctatrienes are complicated by the existence of three isomers



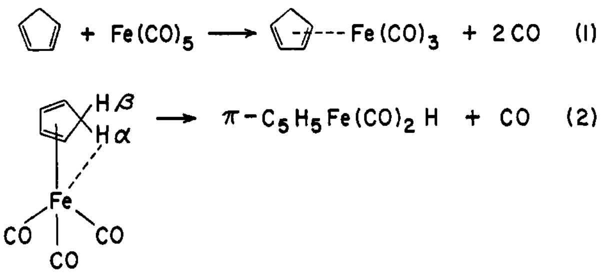
XIX XX XXI

Cycloöcta-1,3,5-triene (XIX) is in thermal equilibrium with its bicyclic isomer bicyclo[4.2.0]octa-2,4-diene (XX), and the proportion of the latter increases with temperature. A mixture of the 1,3,5- and 1,3,6-isomers is obtained by partial reduction of cyclooctatetraene.

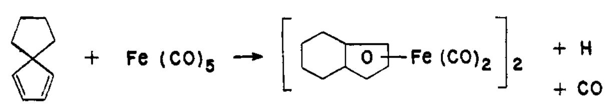
Fischer, Palm and Fritz (105) reported that thermal reaction of an isomeric mixture of the trienes with any of the iron carbonyls gave two products: (a) a golden yellow liquid $C_8H_{10}Fe(CO)_3$, m.p. 8°, which was thought to contain the 1,3,6-isomer (XXI) bonded to iron by its conjugate double bonds; this formulation was based on a comparison of its infrared spectrum with those of the pure isomers, (b) a red crystalline solid $Fe_2C_{25}H_{12}O_6$, for which no structure was suggested. It was noted, however, that the fairly large dipole moment (3.66 *D* in cyclohexane) made unlikely a structure as symmetrical as that found for $C_8H_8Fe_2(CO)_6$. Independently, Manuel and Stone (176) obtained the same complex $C_8H_{10}Fe(CO)_3$ by the same reaction, and concluded on the basis of degradative studies, that the bicyclic isomer (XX) was involved. This conflict has been satisfactorily resolved in favor of the latter formulation by the discovery that, under mild conditions, two isomeric complexes $C_8H_{10}Fe(CO)_3$ are obtained from the reaction of pure cycloöcta-1,3,5-triene with $Fe_3(CO)_{12}$ in benzene (177). The first, isolated in 24% yield, is identical in all respects with the compound obtained previously. It is unaffected by catalytic hydrogenation, and on treatment with maleic anhydride, it gives the adduct of bicyclo[4.2.0]octa-2,4-diene. Treatment with triphenylphosphine, which displaces the hydrocarbon, affords cycloöcta-1,3,5-triene containing an equilibrium amount of the bicyclic isomer. These experiments indicate that the first complex is (bicyclo[4.2.0]octa-2,4-diene)$Fe(CO)_3$, and n.m.r. evidence is in agreement with this (34). The second isomer of $C_8H_{10}Fe(CO)_3$ is much less stable than the first, and is converted to it on heating with $Fe(CO)_5$ in refluxing solvents. Its infrared spectrum differs from the more stable isomer in having an uncomplexed C=C stretching frequency, and its proton resonance spectrum has a peak which can be assigned to protons on a free CH_2 group in either the 1,3,5- or 1,3,6-isomer of cycloöctatriene. Since the 1,3,6-isomer requires strong base for its isomerization to the 1,3,5-isomer-bicyclic isomer equilibrium mixture, it seems more likely that the second, unstable isomer of $C_8H_{10}Fe(CO)_3$ is (cycloöcta-1,3,5-triene) $Fe(CO)_3$, although the matter is not completely settled. It is also not clear whether cycloöcta-1,3,6-triene can form a distinct iron tricarbonyl complex.

E. CYCLOPENTADIENE IRON TRICARBONYL

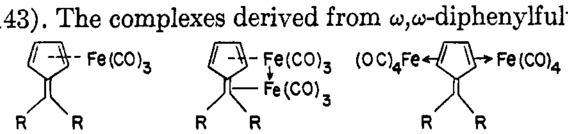
In view of the marked stability of iron tricarbonyl complexes of conjugated dienes, it is at first sight surprising that the complex $C_5H_6Fe(CO)_3$, containing cyclopentadiene behaving as a 4 π-electron donor, has never been reported, particularly since cyclopentadiene complexes of other metals have been characterized, *e.g.*, π-$C_5H_5RhC_5H_6$ (Section VI). Reaction of cyclopentadiene in refluxing inert solvents with $Fe(CO)_5$ gives the binuclear π-cyclopentadienyl carbonyl [π-$C_5H_5Fe(CO)_2]_2$, with loss of hydrogen (95, 244). It has been shown, however, that this hydrogen is not evolved in the reaction, but is transferred to cyclopentadiene, giving cyclopentene and cyclopentane (225) (*cf.* reaction of (π-$C_5H_5)_2ReH$) with CO, Section VII). This observation can be explained (199) by assuming that $C_5H_6Fe(CO)_3$ is the initial product, and that this decomposes to the carbonyl hydride π-$C_5H_5Fe(CO)_2H$, which has been isolated recently as a thermally unstable yellow liquid (125). This then transfers its hydrogen to cyclopentadiene forming cyclopentene and the binuclear complex.



There is evidence in the π-$C_5H_5MC_5H_6$ compounds (Section VI) for considerable interaction between the methylene hydrogen Hα and the metal atom, and this would obviously facilitate the decomposition of C_5H_6-$Fe(CO)_3$. Attempts to stop the reaction at stage (1) by using a spiran, *i.e.*, a cyclopentadiene whose methylene position is blocked, result in the formation of a substituted π-cyclopentadienyl carbonyl and loss of hydrogen (130)



Nevertheless, it is conceivable that if sufficiently mild conditions could be found for the reaction, $C_5H_6Fe(CO)_3$ might be isolated as a reasonably stable entity. In agreement with this is the recent preparation of fulvene iron carbonyls by reaction of the appropriate fulvene with $Fe_2(CO)_9$ under mild thermal conditions (143). The complexes derived from ω,ω-diphenylfulvene

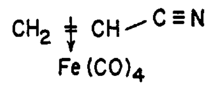


XXI A XXI B XXI C

and cyclopentamethylene-fulvene are believed to have the structures shown in XXI (A, B, and C); diphenylfulvene also gives a complex (fulvene)$Fe_2(CO)_5$ whose structure is unknown, but it is apparently analogous to complexes of similar stoichiometry derived from azulene and thianaphthene (Section IX). ω,ω-Dimethylfulvene forms complexes of the type (fulvene)$_2Fe(CO)_2$ and (fulvene)$_2Fe_2(CO)_5$, which are thought to contain a dimer of the fulvene coördinated to iron. It may be noted that, under more vigorous thermal conditions, fulvenes react with iron carbonyls (143) and Group VIb metal carbonyls (1) forming substituted π-cyclopentadienyl metal carbonyls; in this case, hydrogen is abstracted, either from the solvent or the fulvene itself.

F. MONOÖLEFIN IRON CARBONYLS

The only complex of this class which is well characterized is (acrylonitrile)$Fe(CO)_4$, which is obtained in low yield from $Fe(CO)_5$ and acrylonitrile in sunlight, or thermally from $Fe_2(CO)_9$ and acrylonitrile (159). It is a yellow diamagnetic solid of low thermal and oxidative stability, which can be sublimed *in vacuo*. Structure XXII was suggested. Very recently, a complex (acrylonitrile)$_2Fe(CO)_3$ has also been mentioned briefly (216).



XXII

The reaction of *trans*-hexa-1,3,5-triene with Fe_3-$(CO)_{12}$ is reported to give an orange red, thermally stable liquid $(C_6H_8)_2Fe(CO)_3$, among other products (249). If one double bond of each triene unit is coördinated to iron, the complex should contain four free double bonds; no infrared spectroscopic or chemical tests of this prediction were made. It is possible also that a dimer of the triene may be coördinated to iron, and this would explain the remarkable thermal stability of the compound.

IV. OLEFIN CARBONYL COMPLEXES OF THE GROUP VI METALS

In 1958, three groups discovered independently that Group VI metal hexacarbonyls react thermally with a variety of aromatic compounds to give arene metal tricarbonyls, no catalyst being required (101, 102, 191, 192, 193).

$$M(CO)_6 + \text{arene} \rightarrow (\text{arene})M(CO)_3 + 3CO \quad [M = Cr, Mo, W]$$

This discovery stimulated an investigation of the reaction of these carbonyls with cyclic olefinic systems, and revealed the existence of a new series of metal–olefin complexes similar in many ways to those of iron. Table III shows the olefin complexes of the Group VI transition metals known at present.

The first of these complexes to be discovered was cycloheptatriene molybdenum tricarbonyl, obtained from the reaction of molybdenum hexacarbonyl with cycloheptatriene according to the equation (2, 3)

$$Mo(CO)_6 + C_7H_8 \rightarrow C_7H_8Mo(CO)_3 + 3CO$$

This reaction has subsequently been extended to chromium and tungsten (2), and to a number of substituted cycloheptatrienes (2, 17); the reaction with tungsten carbonyl requires the use of solvents boiling above about 150°. The complexes are red or orange-red

TABLE III

OLEFIN CARBONYL COMPLEXES OF GROUP VIB METALS

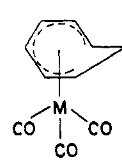
Organic ligand	Formula of complex	Physical properties	Preparation	Infrared	Dipole moment (solvent)	N.m.r.
Cycloheptatriene	$C_7H_8Cr(CO)_3$	Red crystals m.p. 128–130°	(2)	(2)	4.52*D* (benzene) (203)	(17)
Cycloheptatriene	$C_7H_8Mo(CO)_3$	Orange-red crystals m.p. 100°	(2)(3)	(2)	—	(17)
Cycloheptatriene	$C_7H_8W(CO)_3$	Red crystals m.p. 117°	(17)(175)	(17)	—	(17)
1-Methylcycloheptatriene	$C_8H_{10}Cr(CO)_3$	Red crystals m.p. 72–73	(2)	(2)	—	—
	$C_8H_{10}Mo(CO)_3$	d. > 150°	(2)	(2)	—	—
1-Phenylcycloheptatriene	$C_{13}H_{12}Cr(CO)_3$[b]	—	(2)	(2)	—	—
	$C_{13}H_{12}Mo(CO)_3$	Red solid d. >150°	(2)	(2)	—	—
Dicycloheptatrienyl	$C_{14}H_{12}Cr(CO)_3$[b]	Red	(2)	(2)	—	—
	$C_{14}H_{12}Mo(CO)_3$	Red solid d. >150°	(2)	(2)	—	—
	$C_{14}H_{12}Mo_2(CO)_6$	Red solid d. >150°	(2)	(2)	—	—
Dicycloheptatrienyl ether	$C_{14}H_{12}OMo_2(CO)_6$	d. >150°	(2)	(2)	—	—
1,1,4-Trimethylcycloheptatriene	$C_{10}H_{14}Mo(CO)_3$	Red crystals m.p. 86–87°	(17)	(17)	—	(17)
1,1,3,4-Tetramethylcycloheptatriene	$C_{11}H_{16}Mo(CO)_3$	Red crystals m.p. 119–120°	(17)	(17)	—	(17)
Cycloöcta-1,3,5-triene	$C_8H_{10}Cr(CO)_3$	Red crystals d. >96°	(103) (105) (105)	(105)	—	—
	$C_8H_{10}Mo(CO)_3$	Orange crystals m.p. 115–118° d.	(103) (105)	(105)	4.15 ± 0.03*D* (cyclohexane) (105)	—
Cycloöcta-1,3,6-triene	$(C_8H_{10})_2Mo(CO)_2$	Yellow crystals d. 110–160°	(103) (105)	(105)	1.96 ± 0.05*D* (cyclohexane) (105)	—
	$(C_8H_{10})_2W(CO)_2$	Yellow crystals d. 117–170°	(103) (105)	(105)	—	—
Bicyclo[4,3.0]nonatriene	$C_9H_{10}Mo(CO)_3$	Red crystals m.p. 128° d.	(161) (162)	(162)	—	—
	$C_9H_{10}W(CO)_3$	Red crystals	(161) (162)	(162)	—	—
Butadiene	$(C_4H_6)_2Mo(CO)_2$	Yellow crystals d. >110°	(98)	(98)	—	—
Cyclohexa-1,3-diene	$(C_6H_8)_2Mo(CO)_2$	Yellow crystals d. >90°	(97)	(97)	—	—
Cyclopentadiene	$(C_5H_6)_2Cr(CO)_2$[a]	Yellow crystals m.p. 74–75°	(107)	(107)	—	—
Bicyclo[2.2.1]hepta-2,5-diene	$C_7H_8Cr(CO)_4$	Orange-yellow crystals m.p. 92–93°	(17)	(17)	—	(17)
	$C_7H_8Mo(CO)_4$	Pale yellow crystals m.p. 77°	(17) (201)	(17) (201)	—	(17)
	$C_7H_8W(CO)_4$[b]	Pale yellow solid	(17)	(17)	—	—
Cycloöcta-1,5-diene	$C_8H_{12}Cr(CO)_4$	Golden-yellow crystals d. 70°	(96)	(96)	—	—
	$C_8H_{12}Mo(CO)_4$	Pale yellow crystals d. 90–120°	(17) (18) (96)	(18) (96)	4.88 ± 0.06*D* (cyclohexane) (96)	(18)
	$C_8H_{12}W(CO)_4$	Yellow crystals d. >110° m.p. 147°	(96) (174)	(96) (174)	—	—
Dimethyldivinylsilane	$C_6H_{12}SiW(CO)_4$	Yellow crystals m.p. 45°	(175)	(175)	—	—
Bicyclo[2.2.2]octa-2,5-diene	$C_8H_{10}Mo(CO)_4$	Pale yellow crystals m.p. 80° d.	(17)	(17)	—	—
7,8-Dimethyltricyclo[4.2.2.0]^{2,5}-deca-3,9-diene (*endo-cis-anti*)	$C_{12}H_{16}Mo(CO)_4$	White crystals m.p. 152°	(14)	—	—	—
Tetraphenylcyclopentadienone	$(C_{29}H_{20}O)_2Mo(CO)_2$	Yellow crystals d. 205–210°	(238)	(238)	—	—
Dimer of cycloöctatetraene	$C_{16}H_{16}Mo(CO)_4$	Pale yellow solid m.p. 190° d.	(17)(18)	(17)	—	—
Acrylonitrile	$(C_3H_3N)_2Mo(CO)_2$		(180)	(180)	—	—

[a] May be π-$C_5H_5Cr(CO)_2C_5H_7$. [b] Identified by infrared spectrum only.

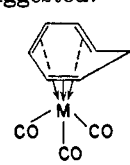
crystals, diamagnetic, easily soluble in the usual organic solvents, and usually sublimable *in vacuo*. Their infrared spectra show without exception three carbonyl stretching frequencies (2), whereas the arene metal tricarbonyls, which are normally yellow, usually show only two such frequencies (113). This suggests that the cycloheptatriene complexes have the lower symmetry. It is of interest that 1-phenylcycloheptatriene forms tricarbonyl complexes of chromium and molybdenum, the red color and infrared spectra of which suggest that the metal is attached to the seven-membered ring in preference to the six-membered ring (2). Dicycloheptatrienyl gives two complexes, depending on reaction conditions, in which metal tricarbonyl groups are attached to one and both rings respectively (2). The cycloheptatriene moiety is readily displaced from these complexes by a variety of ligands, and this provides a convenient method for preparing substituted tricarbonyl complexes of the Group VI metals (4)

$$C_7H_8Mo(CO)_3 + 3L \rightarrow Mo(CO)_3L_3 + C_7H_8$$

In Section IIIC, it was noted that cycloheptatriene appears to behave as a 4 π-electron donor in the complex (cycloheptatriene)Fe(CO)$_3$. Clearly in its Group VI metal tricarbonyl complexes, cycloheptatriene makes full use of its available 6 π-electrons, and structures XXII and XXIII may be suggested.



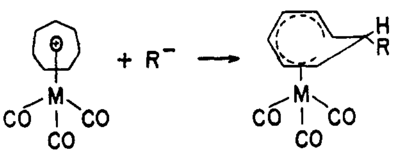
XXII



XXIII

In XXII, the metal atom is considered to be bonded to a planar quasi-aromatic system of 6 π-electrons which by-passes the methylene group, in a manner similar to that envisioned for "sandwich" compounds and for butadiene iron tricarbonyl. In XXIII, the metal atom is considered to be linked to three isolated double bonds, each supplying two π-electrons, the bonding being similar to that envisioned for olefin complexes of silver and platinum (Section II). The structure of the cycloheptatriene molybdenum carbonyl complex, recently determined by X-ray study (86), seems on the whole to favor the second picture. The three CO groups have approximately trigonal symmetry with respect to an axis through the metal atom, and one of them lies almost in a mirror plane of the ring. The methylene group of the ring points away from the metal atom, the remaining six carbon atoms are almost coplanar, and, significantly, the interatomic distances in the plane are approximately those expected for alternate single and double bonds in a conjugated triene. This last result contrasts notably with those obtained for (butadiene)$Fe(CO)_3$ (185) and (benzene)$Cr(CO)_3$ (64), but shows considerable resemblance to some recently published data on bis-benzenechromium(0); in this complex also, alternate single and double bond lengths have been observed in each ring (144b).

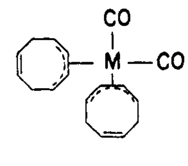
It is possible to abstract a hydride ion from the terminal methylene group of $C_7H_8Mo(CO)_3$ by means of trityl fluoroborate, giving the π-tropylium complex π-$C_7H_7Mo(CO)_3{}^+ BF_4{}^-$ (74). This has only one strong C–H stretching frequency in the infrared, and shows only one proton resonance in D_2SO_4, in contrast to the original cycloheptatriene complex, which shows at least four C–H stretching frequencies and a complex n.m.r. spectrum. The tropylium complex is therefore regarded as an arene complex. Treatment of the tropylium complex with numerous anions provides a convenient route to 1-substituted cycloheptatriene metal complexes (187)



($R = HCO_3^-, CN^-, OCH_3^-, C_6H_5^-, C_6H_4C(CH_3)_3^-$)

However, treatment with $C_6H_5^-$ yields, surprisingly, benzene chromium tricarbonyl, and the corresponding methyltropylium salt yields toluene chromium tricarbonyl, both presumably derived from collapse of the seven-membered ring (187).

The reaction of cycloöctatrienes with the Group VI metal hexacarbonyls is in some respects similar to that of cycloheptatriene (103, 105). The 1,3,5-isomer (XIX) gives red, diamagnetic, sublimable, crystalline complexes $C_8H_{10}M(CO)_3$ (M = Cr, Mo) which are very similar to their cycloheptatriene analogs, although they are somewhat less stable to air and light; this may be because the six carbon atoms containing the three double bonds are not so coplanar as in the cycloheptatriene complex. In addition, very stable, yellow, diamagnetic, sublimable complexes $(C_8H_{10})_2M(CO)_2$ (M = Mo, W) are obtained, which are believed to contain coördinated cycloöcta-1,3,6-triene (XXIV). They have dipole moments of about $2D$, which suggests that



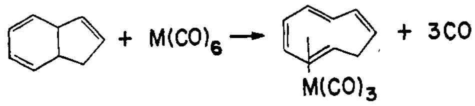
M = Mo, W

XXIV

the CO groups may be *cis*- to each other in an approximately octahedral configuration (105). As in the iron complexes, however, there is presumably the possibility here that bicyclo[4.2.0]octa-2,4-diene (XX), rather than cycloöcta-1,3,6-triene, is involved in complex formation.

In the arene, cycloheptatriene and cycloöctatriene series, there seems to be a general rule of reactivity and stability. It is usually found that $Cr(CO)_6$ reacts least readily and in rather low yield with these complexing systems, $Mo(CO)_6$ reacts most readily and in the highest yield, while $W(CO)_6$ is intermediate, often requiring higher reaction temperatures than the other two. Conversely, the molybdenum tricarbonyl complex is the least stable to air, the chromium complex is the most stable to air, and the tungsten complex is intermediate. It has been suggested that benzene is a stronger donor than cycloheptatriene, on the basis of dipole moment measurements on $C_6H_6Cr(CO)_3$ and $C_7H_8Cr(CO)_3$ (203).

Analogous complexes containing a nine-membered ring have been obtained by treating bicyclo[4.3.0]-nonatriene with $Mo(CO)_6$ and $W(CO)_6$ (161, 162)



The red complexes $C_9H_{10}M(CO)_3$ (M = Mo, W) are not very stable oxidatively, especially in solution. The molybdenum compound absorbs 1 mole of hydrogen on catalytic hydrogenation, suggesting that a cyclononatetraene unit is bound to the metal. The molybdenum compound is more stable than its tungsten analog. $Cr(CO)_6$ reacts with the nonatriene giving a very unstable product. This behavior is the exact reverse of that observed in, for example, the cycloheptatriene reactions, but there is no obvious explanation.

Table III shows clearly the difference in complexing behavior exhibited by conjugated and unconjugated diolefins respectively toward the Group VI metal hexacarbonyls. Chelate diolefins such as norbornadiene (V) and cycloöcta-1,5-diene (III), react under reflux with these carbonyls giving white or yellow, sublimable, diamagnetic complexes of the type (diolefin)$M(CO)_4$, which are both more numerous and more stable than the (diolefin)$Fe(CO)_3$ complexes containing unconjugated diolefins (14, 17, 18, 96, 174, 175, 201). There seems to be no general order of stability in comparing complexes of Cr, Mo and W with the same chelate diolefin. Thus 1,5-$C_8H_{12}Cr(CO)_4$ is reported to be less stable oxidatively than 1,5-$C_8H_{12}Mo(CO)_4$ (1,5-C_8H_{12} = cycloöcta-1,5-diene) (96), whereas the reverse is true for the norbornadiene complexes (17). An attempt (175) has been made to draw up a stability order for the complexing of various aromatic and olefinic systems for tungsten on the basis of displacement reactions such as

$$1,5\text{-}C_8H_{12}W(CO)_4 + \text{cycloheptatriene} \rightarrow C_7H_8W(CO)_3 + 1,5\text{-}C_8H_{12} + CO$$

The order is hexamethylbenzene > *p*-cymene > cycloocta-1,5-diene > hexa-1,5-diene. In general, these tetracarbonyl complexes show three or four carbonyl stretching frequencies, together with C=C stretching frequencies lowered by about 150 cm.$^{-1}$ owing to coordination, and they have dipole moments of about 4–5 *D*. They are best formulated as substitution products of the hexacarbonyls, with two double bonds occupying *cis*-positions in the octahedron, but there may be some distortion from the octahedral configuration. The proton resonance spectra of (norbornadiene)$M(CO)_4$ (M = Cr, Mo) (17) and (1,5-C_8H_{12})$Mo(CO)_4$ (18) differ only slightly from those of the parent olefins, which probably indicates that the double bonds are functioning independently in these complexes.

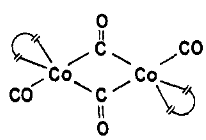
By contrast, conjugated diolefins, such as butadiene and cyclohexa-1,3-diene, react either thermally or, better, photochemically with the hexacarbonyls giving yellow, diamagnetic, sublimable complexes of general formula (diene)$_2M(CO)_2$, usually in poor yield (97, 98). No explanation for this difference in behavior has been advanced. The known representatives are shown in Table III; the cycloöctatriene complexes of this type already have been discussed, and these conjugated diene complexes probably have similar structures. The finite dipole moments indicate that the two CO groups may well be *cis* in an approximately octahedral configuration (97, 98). The complex $(C_5H_6)_2$-$Cr(CO)_2$, in which the diene cyclopentadiene behaves as a 4 π-electron donor, is formed as a by-product in the reaction of $(\pi\text{-}C_5H_5)_2Cr$ with CO and hydrogen, the main product being the hydride $\pi\text{-}C_5H_5Cr(CO)_3H$ (107). In the light of recent results (Section XI), it is possible that the formulation may have to be changed to $\pi\text{-}C_5H_5Cr(CO)_2C_5H_7$, but the reaction provides confirmation of other evidence that hydrogen, either free or bound to a transition metal, is able to attack a π-cyclopentadienyl ring.

Acrylonitrile reacts with $Mo(CO)_6$ giving a diamagnetic complex (acrylonitrile)$_2Mo(CO)_2$ which is almost insoluble in common organic solvents (180). The obvious formulation of this compound as an octahedral substitution product of $Mo(CO)_6$, with acrylonitrile behaving apparently as a 4 π-electron donor (see Section XIII for similar nickel complexes) fails to explain the insolubility, and some sort of polymeric constitution has been suggested (180).

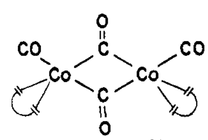
It has often been noted that the reaction of olefins with metal carbonyls yields dimers of those olefins, apart from any organometallic complexes. The reaction of $Mo(CO)_6$ with cycloöctatetraene is of interest in giving a complex $C_{16}H_{16}Mo(CO)_4$ which is believed to contain a dimer of cycloöctatetraene coördinated to molybdenum (18). The complex has one "free" double bond (17), so the dimer itself probably contains three double bonds, but the structure is unknown.

V. Olefin Complexes Derived from Dicobalt Octacarbonyl $Co_2(CO)_8$

A number of diolefins are capable of replacing terminal CO groups in $Co_2(CO)_8$ under mild thermal conditions (104, 245, 247), or under the influence of ultraviolet light (100), giving dimeric substitution products (Table IV). In general, these are of two types, $Co_2(CO)_6$(diene) and $Co_2(CO)_4$(diene)$_2$, although the former cannot always be isolated. Like the parent carbonyl, the complexes have bridging carbonyl bands in the infrared, so the basic structure of the carbonyl presumably is retained. The bridging carbonyl bands are usually at somewhat lower frequencies than those in $Co_2(CO)_8$. Although isomers of the disubstituted com-



XXV



XXVI

plexes are possible, none has been detected so far. In the case of the butadiene complex (200), infrared evidence has been adduced in favor of XXVI. Table IV shows clearly that conjugated dienes react particularly readily with $Co_2(CO)_8$, and, of the formally unconjugated diolefins, only norbornadiene gives complexes which can be isolated. Other monomeric olefin cobalt carbonyl complexes are discussed in Sections VIII and XI.

VI. π-Cyclopentadienyl Metal Olefin Complexes

This term refers to that class of metal–olefin complex in which a π-cyclopentadienyl (C_5H_5) group and an olefinic system both are coördinated to a metal atom. These complexes obey the Inert Gas Rule if five π-electrons are counted from each $\pi\text{-}C_5H_5$ group (or six

TABLE IV
OLEFIN CARBONYL COMPLEXES OF COBALT

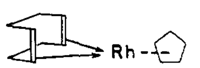
Organic ligand	Formula of complex	Physical properties	References Prepn.	References Infrared	Dipole moment (solvent)
Butadiene	$Co_2(CO)_4(C_4H_6)_2$	Copper-colored crystals d. 118°	(100)	(100)	—
Cyclohexa-1,3-diene	$Co_2(CO)_4(C_6H_8)_2$	Golden plates d. >100°	(245) (247)	(247)	—
Cycloöcta-1,3,6-triene	$Co_2(CO)_4(C_8H_{10})_2$	Yellow crystals d. 145°	(104)	(104)	3.02 ± 0.05*D* (benzene) (104)
2,3-Dimethylbuta-1,3-diene	$Co_2(CO)_6C_6H_{10}$	Red needles	(247)	(247)	—
	$Co_2(CO)_4(C_6H_{10})_2$	Red needles	(247)	(247)	—
Bicyclo[2.2.1]hepta-2,5-diene	$Co_2(CO)_6C_7H_8$	Red needles d. 97°	(245) (247)	(245) (247)	—
	$Co_2(CO)_4(C_7H_8)_2$	Red needles	(245) (247)	(245) (247)	—
Tetraphenylcyclopentadienone	$[Co(CO)_2(C_{29}H_{20}O)]_2Hg$	Dark red-black crystals d. 180–190°	(238)	(238)	—
	$(C_{29}H_{20}O)_4Co_3$	Black plates d. 400°	(238)	(238)	—
Tetraphenylcyclopentadienone	$(C_{29}H_{20}O)_2CoH$	Red crystals d. 295–300°	(238)	(238)	—
	$(C_{29}H_{20}O)_2CoCOCH_3$	Dark-brown crystals d. 300–311°	(238)	(238)	—
	$(C_{29}H_{20}O)_2CoCH_3$	Black crystals d. 343–345°	(238)	(238)	—
	$(C_{29}H_{20}O_2)CoNa$	Red-brown solid d. 314°	(238)	(238)	—
	$(C_{29}H_{20}O)_2CoK$	Brown solid	(238)	(238)	—

π-electrons from each π-C_5H_5 anion), and two π-electrons from each olefinic double bond.

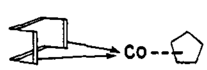
The first example was obtained by Chatt and Venanzi (46), who treated the dimeric rhodium complex of cycloöcta-1,5-diene with sodiocyclopentadiene, and obtained the monomeric yellow, diamagnetic compound π-$C_5H_5RhC_8H_{12}$

$$[C_8H_{12}RhCl]_2 + 2C_5H_5^- \rightarrow 2\pi\text{-}C_5H_5RhC_8H_{12} + 2Cl^-$$

It is probable that a family of related cobalt(I) and iridium(I) complexes exist. It is reported (189) that π-$C_5H_5Co(CO)_2$ reacts with cycloöctatetraene to give the orange complex π-$C_5H_5CoC_8H_8$ in 7% yield, and this reaction probably can be extended to include other conjugated and unconjugated diolefins. The light-induced reaction of π-$C_5H_5Co(CO)_2$ with a number of acetylenes, gives complexes of the type π-C_5H_5Co (cyclopentadienone), which are surveyed in Section VIII-A.



XXVII



XXVIII

The C_8H_8 ring in π-$C_5H_5CoC_8H_8$ probably has the "tub" form, and is not planar as in $C_8H_8Fe(CO)_3$. The evidence is (a) that the complex absorbs two moles of hydrogen, giving an unidentified orange compound which might be the cobalt analog of π-C_5H_5Rh (1,5-C_8H_{12}); (b) the infrared spectrum shows a band at 1635 cm.$^{-1}$ indicative of free double bonds; (c) it shows two proton resonances of equal intensity attributable to protons on the eight-membered ring, in addition to a single resonance due to the π-C_5H_5 protons (189).

The related complexes π-$C_5H_5MC_5H_6$ (M = Co, Rh, Ir) in which cyclopentadiene functions as a 4 π-electron donor, have been prepared by two methods: (a) reaction of $RhCl_3$ or $IrCl_3$ with KC_5H_5 and excess cyclopentadiene in a high-boiling ether (111, 112); yields are very poor (1–2%). The rhodium complex also has been obtained independently using NaC_5H_5 in tetrahydrofuran (123). The yield is still poor, and both methods require tedious purification procedures. (b) Reduction of the anhydrous cobalticenium and rhodicenium cations with sodium borohydride or lithium aluminum hydride (123)

$$M(C_5H_5)_2^+ + H^- \rightarrow \pi\text{-}C_5H_5MC_5H_6 \quad (M = Co, Rh)$$

This method gives high yields of the complexes, and has the further advantage that, by using $LiAlD_4$, the corresponding deutero compounds π-$C_5H_5MC_5H_5D$ can be prepared; these have proved invaluable in spectroscopic studies on this type of complex (123). Since complex hydrides, and no other reducing agent, effect reduction of the $M(C_5H_5)_2$ cations, it seems likely that direct hydride ion attack, either on the π-C_5H_5 ring, or initially on the metal atom, is involved.

In addition to the parent complexes, a series of substituted cobalt complexes have been prepared by reactions starting from cobaltocene which are summarized below (123)

$$(\pi\text{-}C_5H_5)_2Co \xrightarrow{CH_3I} (\pi\text{-}C_5H_5)_2Co^+I^- + \pi\text{-}C_5H_5Co(1\text{-}CH_3 \cdot C_5H_5)$$

$$(\pi\text{-}C_5H_5)_2Co \xrightarrow{CCl_4} \pi\text{-}C_5H_5Co(1\text{-}CCl_3C_5H_5) \xrightarrow{LiAlH_4} \pi\text{-}C_5HCo(1\text{-}CHCl_2C_5H_5)$$

The properties of these compounds are summarized in Table V. The colors of the parent complexes go from red through orange to yellow down the series Co, Rh and Ir. Chemical studies reveal the presence of a reactive hydrogen atom in the π-$C_5H_5MC_5H_6$ compounds. For example, the cobalt and rhodium compounds react with dilute acid giving the corresponding π-cyclopentadienyl metal cations, hydrogen and C_5 olefinic hydrocarbons, and they react with carbon tetrachloride giving the same cations and chloroform (123)

$$\pi\text{-}C_5H_5MC_5H_6 + H^+ \rightarrow (\pi\text{-}C_5H_5)_2M^+ + \tfrac{1}{2}H_2$$

$$\pi\text{-}C_5H_5MC_5H_6 + CCl_4 \rightarrow (\pi\text{-}C_5H_5)_2M^+ + CHCl_3$$

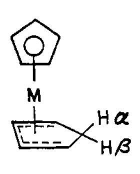
TABLE V

π-CYCLOPENTADIENYL AND π-ARENE METAL AND METAL CARBONYL OLEFIN COMPLEXES

Organic ligand	Formula of complex	Physical properties	Prepn.	Infra-red	Dipole moment (solvent)	N.m.r.
Ethylene	π-$C_5H_5Mn(CO)_2C_2H_4$	Orange-red solid m.p. 116–118° d.	(165)	(165)	—	—
Ethylene	$[\pi C_5H_5Fe(CO)_2C_2H_4]^+$ salts	PF_6^- salt: fine yellow crystalline powder d. ~ 165°	(93)	(93)	—	—
Ethylene	$[\pi$-$C_5H_5Mo(CO)_3C_2H_4]^+$ salts	PF_6^- salt: bright yellow crystalline powder d. ~ 104°	(93)	(93)	—	—
Ethylene	$[\pi$-$C_5H_5W(CO)_3C_2H_4]^+$ salts	PF_6^- salt: pale yellow fine crystalline powder d. ~ 120°	(93)	(93)	—	—
Ethylene (arene = mesitylene)	π-$C_9H_{12}Cr(CO)_2C_2H_4$	Orange solid	(98)	—	—	—
Cyclopentene	π-$C_5H_5Re(CO)_2C_5H_8$	White crystals m.p. 95–96°	(126)	(126)	—	(126)
Cyclopentadiene	π-$C_5H_5Re(CO)_2C_5H_6$	Yellow crystals m.p. 111–112°	(110) (126)	(126)	3.85 *D* (benzene) (110)	(126)
Cyclopentadiene	π-$C_5H_5CoC_5H_6$	Wine-red crystals m.p. 98–99°	(123)	(123)	—	(123)
Cyclopentadiene	π-$C_5H_5RhC_5H_6$	Orange-yellow crystals m.p. 118–120° (111) m.p. 121–122° (123)	(111) (112)	(111) (123)	—	(123)
Cyclopentadiene	π-$C_5H_5IrC_5H_6$	Bright yellow crystals m.p. 130–132°	(111)	(111)	—	—
Cyclopentadiene	π-$C_6H_6FeC_5H_6$[a]	Orange-red crystals m.p. 135–136°	(124)	(124)	—	(124)
Cyclopentadiene	π-$C_9H_{12}FeC_5H_6$[a]	Deep red oil m.p. ~ −10°	(124)	(124)	—	(124)
1-Deuteriocyclopentadiene	π-$C_5H_5CoC_5H_5D$	Wine-red crystals m.p. 78–79°	(123)	(123)	—	(123)
	π-$C_6H_6FeC_5H_5D$[a]	Not stated	(124)	(124)	—	(124)
1-Methylcyclopentadiene	π-$C_5H_5Co(C_5H_5CH_3)$	Red oil m.p. ~ −10°	(123)	(123)	—	(123)
	π-$C_5H_4CH_3Co(C_5H_5{\cdot}CH_3)$	Dark red oil m.p. ~ −5°	(123)	(123)	—	(123)
1-Dichloromethylcyclopentadiene	π-$C_5H_5Co(C_5H_5CHCl_2)$	Orange-red crystals m.p. 50–51°	(123)	(123)	—	(123)
1-Trichloromethylcyclopentadiene	π-$C_5H_5Co(C_5H_5CCl_3)$	Orange-red crystals m.p. 79–80°	(123)	(123)	—	(123)
1-Trifluoromethylcyclopentadiene	π-$C_5H_5Co(C_5H_5CF_3)$	Red oil	(123)	—	—	(123)
Cycloöctatetraene	π-$C_5H_5CoC_8H_8$	Brown crystals m.p. 81–82°	(189)	(189)	—	(189)
Cycloöcta-1,5-diene	π-$C_5H_5RhC_8H_{12}$	Yellow solid m.p. 108–108.5°	(46)	—	—	—
Butadiene	π-$C_5H_5Mn(CO)C_4H_6$	Red needles m.p. 134–136° d.	(98)	(98)	—	—
Butadiene	π-$C_5H_5V(CO)_2C_4H_6$	Red crystals m.p. 135–140° d.	(98)	(98)	—	—
2,3-Dimethylbuta-1,3-diene	π-$C_5H_5V(CO)_2C_6H_{10}$	Red crystals m.p. 135–136° d.	(98)	(98)	—	—
Cyclohexa-1,3-diene	π-$C_5H_5V(CO)_2C_6H_8$	Dark red crystals m.p. 98–100° d. ~ 140°	(98)	(98)	—	—
Tetramethylcyclopentadienone	π-$C_5H_5Co(C_9H_{12}O)$	Orange crystals m.p. 178–180°	(178)	(178)	—	—
Tetraphenylcyclopentadienone	π-$C_5H_5Co(C_{29}H_{20}O)$	Red crystals m.p. 327–329°	(178)	(178)	—	—

[a] May be π-$C_5H_5FeC_6H_7$, π-$C_5H_5FeC_9H_{13}$ and π-$C_5H_5FeC_6H_6D$, respectively.

The π-$C_5H_5MC_5H_6$ complexes show bands in their infrared spectra at about 1450 cm.$^{-1}$ assignable to a complexed C═C stretching frequency (111), characteristic bands due to π-C_5H_5, and bands in the aliphatic C–H stretching region (111) (123). In addition, however, they show intense bands at about 2750 cm.$^{-1}$ which shift by about $1/\sqrt{2}$ in the corresponding deuterio-compounds, and which must be assigned as a C–H fundamental. This remarkably low value for a C–H stretching frequency is believed by Wilkinson and co-workers (123) to be due to the close approach of one of the hydrogen atoms (Hα) of the CH_2 group of C_5H_6 to the metal atom, causing steric or electrostatic interactions (XXIX).



XXIX

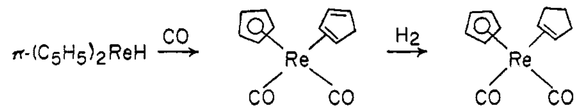
In agreement with this, there is a marked difference in the proton resonances of the methylene hydrogen atoms Hα and Hβ. It is surprising that, in the 1-substituted complexes containing —CH_3, —CCl_3 and —$CHCl_2$ as substituent, it seems to be the Hα atom near the metal rather than the Hβ atom which is replaced, since the band at 2750 cm.$^{-1}$ disappears in these complexes (123). Presumably the cyclopentadiene ring can be oriented suitably to accommodate the substituents.

Analogous complexes of the type (arene)FeC_5H_6 have been described as resulting from lithium aluminum hydride reduction of the cations [π-C_5H_5Fe-(π-arene)]$^+$, the aromatic systems being benzene and mesitylene (124). Both complexes show the low, intense C–Hα stretching frequency. It may be noted that the structure assigned to these iron complexes presupposes that the π-C_5H_5 ring is reduced rather than the aromatic ring. Since it is now known (Section XI) that the coördinated π-arene ring also can be reduced by hydride ion, it may prove necessary to reformulate these iron complexes as, for example, π-$C_5H_5FeC_6H_7$. Likewise, the complex assumed to be a zerovalent, tetrahedral, olefin complex of nickel, $Ni(C_5H_6)_2$, has been reformulated as π-$C_5H_5NiC_5H_7$ (Section XI).

VII. OLEFIN-SUBSTITUTED π-CYCLOPENTADIENYL METAL CARBONYLS

The first of this class of complex to be prepared was a white, air-stable compound $C_{10}H_{11}Re(CO)_2$ obtained from the reaction of $(\pi$-$C_5H_5)_2ReH$ with carbon monoxide at 100° (250 atm) (110). This was formulated initially as a complex hydride π-$C_5H_5ReH(CO)_2\sigma$-C_5H_5 (110), but subsequent infrared and n.m.r. studies (126) show the correct formulation to be π-$C_5H_5Re(CO)_2$·

C_5H_6, in which cyclopentadiene is coördinated to the metal atom through only one of its double bonds. The free double bond can be hydrogenated to give a similar cyclopentene complex π-$C_5H_5Re(CO)_2C_5H_8$ (126).



Attempts to synthesize independently these and similar complexes by direct thermal replacement reactions on π-$C_5H_5Re(CO)_3$ with the appropriate olefins were not successful and, in general, the CO groups in the cyclopentadienyl metal carbonyls are not removed readily by other ligands. Recently, Fischer and coworkers (98) have shown that replacement of CO groups in π-$C_5H_5V(CO)_4$ and π-$C_5H_5Mn(CO)_3$ by butadiene and cyclohexa-1,3-diene proceeds readily at moderate temperatures under the influence of ultraviolet irradiation, and in the presence of mercury. Stable, red, diamagnetic complexes of formula π-$C_5H_5V(CO)_2$ (diene) and π-$C_5H_5Mn(CO)$ (diene) are obtained, whose general properties are summarized in Table V. An orange-yellow complex of formula C_5H_6-$CrC_4H_6(CO)_2$ is obtained from $[\pi$-$C_5H_5Cr(CO)_3]_2$ and butadiene under the same conditions, but this complex may instead be π-$C_5H_5Cr(CO)_2C_4H_7$ (Section XI). This preparative method will undoubtedly prove capable of further extension, and of particular interest are recent reports (98, 165) that complexes containing the simplest mono-olefin, ethylene, have been prepared by the reactions

$$\gamma\text{-}C_5H_5Mn(CO)_3 + C_2H_4 \xrightarrow[Hg]{h\nu} \pi\text{-}C_5H_5Mn(CO)_2C_2H_4 + CO \quad 1\%\ \text{yield}$$

$$(\text{mesitylene})Cr(CO)_3 + C_2H_4 \xrightarrow[Hg]{h\nu} (\text{mesitylene})Cr(CO)_2C_2H_4 + CO$$

Analogous cationic ethylene-containing complexes have been obtained very recently by reaction of π-cyclopentadienyl carbonyl halides of molybdenum, tungsten and iron with ethylene under pressure, in the presence of aluminum chloride (93)

$$\pi\text{-}C_5H_5M(CO)_3Cl + C_2H_4 + AlCl_3 \rightarrow [\pi\text{-}C_5H_5M(CO)_3C_2H_4]^+AlCl_4^- \quad M = Mo, W$$

$$\pi\text{-}C_5H_5Fe(CO)_2Cl + C_2H_4 + AlCl_3 \rightarrow [\pi\text{-}C_5H_5Fe(CO)_2C_2H_4]^+AlCl_4^-$$

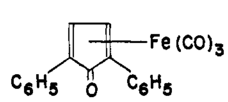
The cations are isolated in the form of their salts with heavy anions, such as PF_6^-, $[Cr(NH_3)_2(NCS)_4]^-$, $[B(C_6H_5)_4]^-$. The infrared spectrum of π-C_5H_5Mn-$(CO)_2C_2H_4$ shows at least four strong CO stretching frequencies, instead of the two expected for two linear, non-*trans* CO groups, and it is possible that the presence of the ethylene causes non-linearity in one or both of the CO groups (165). A similar effect may be at work in $(1,3\text{-}C_6H_8)_2Mo(CO)_2$ ($1,3\text{-}C_6H_8$ = cyclohexa-1,3-diene), which shows three CO stretching frequencies instead of the expected two (97). A slight non-linearity of one of the CO groups was observed in the X-ray study of (cycloheptatriene)$Mo(CO)_3$ (86). The thermal reaction of π-$C_5H_5V(CO)_4$ with cycloheptatriene gives a π-tropylium complex π-C_5H_5V-π-C_7H_7, which is paramagnetic with one unpaired spin (161a). This reaction probably proceeds *via* the intermediate π-$C_5H_5V(CO)C_7H_8$, which subsequently loses CO and hydrogen. Possibly this intermediate could be isolated under the milder photochemical conditions described above.

VIII. Metal Complexes of Cyclic Unsaturated Ketones

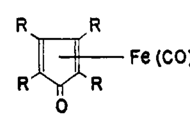
A. Cyclopentadienone Complexes

The cyclic unsaturated ketone cyclopentadienone and its substituted congeners, such as tetraphenylcyclopentadienone (tetracyclone) form an extensive series of metal–olefin complexes which merit separate consideration because of their striking similarity to the metal cyclopentadienyls. Many of the simpler cyclopentadienones cannot be isolated in the free state owing to their tendency to dimerize, and the fact that they nevertheless form stable metal complexes represents an example of stabilization of an unstable olefinic species by metal complex formation.

In 1955, Jones, Wailes and Whiting (147) obtained a stable, yellow, crystalline complex from the reaction of $Fe(CO)_5$ with phenylacetylene in the presence of nickel carbonyl, which they formulated as iron tetracarbonyl bis-(phenylacetylide), $Fe(CO)_4(C_6H_5C{\equiv}C)_2$. Subsequently the reaction was re-investigated by several groups independently (68, 139, 140, 167, 212, 215, 238), who showed, on the basis of degradative and spectral evidence, that the complex is in fact (2,5-diphenylcyclopentadienone)$Fe(CO)_3$ (XXX)



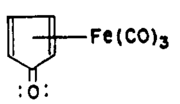
XXX



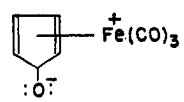
XXXI

In this reaction, therefore, the complexing olefinic ligand is built up from simpler starting materials and further consideration is given to this type of reaction in Section XII. For the present, it is sufficient to note that reaction of diverse substituted acetylenes with $Fe_3(CO)_{12}$ provides a convenient route to substituted cyclopentadienone iron tricarbonyls, although the position of the substituents in the ring is not always certain (139). The first member of the series, (cyclopentadienone)$Fe(CO)_3$, is obtained from reaction of $Fe(CO)_5$ with acetylene under pressure in polar and non-polar solvents (124, 207, 239). Also, the photochemical reaction of $Fe(CO)_5$ with various alkyl-substituted acetylenes takes a somewhat different course, giving substituted quinone iron carbonyls (Section VIII-B). Many aryl-substituted cyclopentadienone iron tricarbonyls can be prepared by direct interaction of $Fe_3(CO)_{12}$ with the appropriate cyclopentadienone, or with the dimer thereof, if this is capable of reversible dissociation (238).

The properties of known cyclopentadienone iron tricarbonyls are summarized in Table II. In general, they are yellow, air-stable, diamagnetic compounds, which decompose on strong heating, regenerating the ketone, or its dimerization products. They show three strong terminal carbonyl stretching frequencies. Of particular interest is the effect on the keto-group of coördination to the metal of the dienone. The ketonic C=O stretching frequency, which occurs at about 1700–1720 cm.$^{-1}$ in the uncomplexed cyclopentadienones, is found in the 1600–1660 cm.$^{-1}$ region in these iron tricarbonyl complexes, and the complexes no longer give the characteristic reactions of a keto-group (139, 140, 238). These observations, implying that the bond-order of the keto-group has been reduced by complex formation, can be explained by invoking an increased contribution from the canonical form (XXXIII), caused by the tendency of the five-membered ring

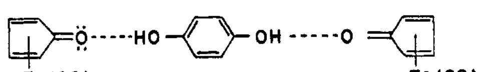


XXXII



XXXIII

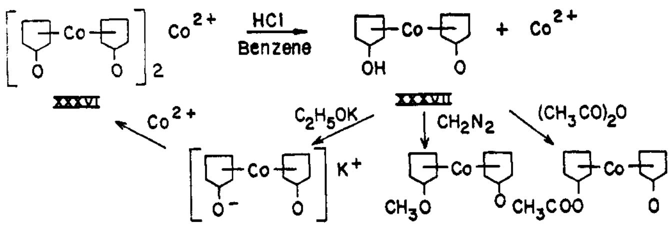
to attain its aromatic sextet; at the same time, this serves to drain negative charge from the metal atom. The enhancement of polarity of the keto-group is shown by the fact that cyclopentadienone iron tricarbonyls form 1:1 and 2:1 adducts with hydrogen iodide and with hydroquinone, whose structure is probably as shown in XXXV (239)



XXXV

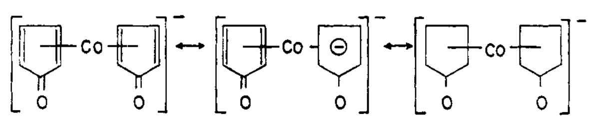
Ligands such as triphenylphosphine and triphenylphosphite replace one CO in the cyclopentadienone iron tricarbonyls without displacing the organic moiety, and complexes such as (tetracyclone)$Fe(CO)_2P(C_6H_5)_3$ and (tetracyclone)$Fe(CO)_2P(OC_6H_5)_3$ have been described (238). This behavior contrasts with that of $C_8H_8Fe(CO)_3$ with these ligands (176).

The reactions of tetracyclone with various other metal carbonyls have been reported in some detail (238). Thus, $Mo(CO)_6$ and tetracyclone at 160° give the yellow, diamagnetic, air-stable complex (tetracyclone)$_2Mo(CO)_2$, as would be expected for a conjugated diene system (Section IV). The mercury derivative of cobalt carbonyl $Hg[Co(CO)_4]_2$ reacts to give dark-red [(tetracyclone)$Co(CO)_2]_2Hg$. Cobalt carbonyl and tetracyclone at 60° give a deep-brown air-sensitive solution which may contain [(tetracyclone)-$Co(CO)_2]_2$, and at 130–160° a violet air-stable compound (tetracyclone)$_4Co_3$ is obtained which does not decompose thermally below 400°. This remarkable complex is believed to be a salt, Co^{2+}[Co·(tetracyclone)$_2]_2$, on the basis of a series of reactions which are outlined.



XXXVI XXXVII XXXVIII XXXIX XL

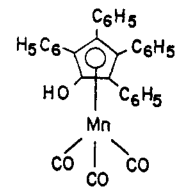
Phenyl substituents are omitted for the sake of clarity. In these complexes, the ketonic C—O stretching frequencies are shifted even further to lower frequency (1480–1600 cm.$^{-1}$) than in the iron tricarbonyl complexes, and their intensity is considerably reduced. This is particularly true of salts XXXVI and XXXVIII in which polarization of the keto-group obviously is assisted by the presence of the cation. It is suggested (238) that the complex cobalt anion is better regarded as a derivative of $(\pi\text{-}C_5H_5)_2Co$, with resonance between the forms



Phenyl substituents are omitted for the sake of clarity. The hydroxy-complex (XXXVII) shows no OH bands in the infrared, so there is presumably intermolecular or intramolecular hydrogen bonding. In the methyl (XXXIX) and acetyl (XL) derivatives, the methyl and acetyl groups are attached to the oxygen of one ring, which behaves as an aromatic system, while the remaining ring is similar to that in the iron tricarbonyl complexes in showing a keto-band at about 1600 cm.$^{-1}$. The isoelectronic species [(tetracyclone)$_2Fe]^{2-}$ and (tetracyclone)$_2Ni$ also have been mentioned briefly (238).

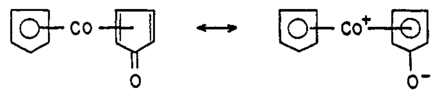
The tendency of tetracyclone to form cyclopentadienyl type complexes is shown clearly by its reaction with $Mn_2(CO)_{10}$ at 150° giving an unstable solution which yields tetracyclone and the yellow substituted π-cyclopentadienyl complex (XLI) on treatment with water (238).

The photochemical reaction of $\pi\text{-}C_5H_5Co(CO)_2$ with acetylenes such as but-2-yne and diphenylacetylene (Section XII) gives high yields of related cyclopentadienone complexes of general formula $\pi\text{-}C_5H_5Co$(cyclo-



XLI

pentadienone) (178). These are orange or red crystalline solids which are air-stable and of considerable thermal stability. The ketonic C–O stretching frequency occurs at 1569 cm.$^{-1}$, and 1:1 adducts are formed with hydrogen chloride, indicating that here again there is considerable polarization of the keto-group due to resonance between the structures



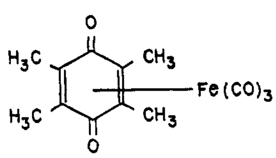
Further evidence of this polarization is shown in the case of the tetramethylcyclopentadienone complex, which is hygroscopic and very soluble in water. A recent X-ray study of this compound has shown that the C–C lengths in the cyclopentadienone ring are essentially equal in length (1.43 Å.), and that the keto-group is tilted somewhat out of the plane of the other carbon atoms, away from the cobalt atom (72).

In all the complexes described here, the cyclopentadienone system may be regarded as donating four π-electrons to the metal atom, which thereby attains the inert gas configuration. However, there are experimental and theoretical grounds for believing that cyclopentadienone may function also as a six π-electron donor under certain circumstances. This point is discussed in greater detail in Sections XI and XV.

B. COMPLEXES OF OTHER CYCLIC UNSATURATED KETONES

Data published at present suggest that six- and seven-membered cyclic unsaturated ketones are by no means so prone to complex formation as the cyclopentadienones, and this is indeed in agreement with theoretical expectation (25).

From the photo-induced reaction of $Fe(CO)_5$ with but-2-yne, orange crystals of empirical formula $Fe(CO)_5 \cdot (CH_3C_2CH_3)_2$ have been isolated (223). The infrared spectrum of the complex shows two terminal carbonyl stretching frequencies, and two bands in the 1600 cm.$^{-1}$ region assignable to ketonic carbonyl stretching frequencies. Acid treatment affords durohydroquinone and decomposition by air gives duroquinone, so that a reasonable formulation of the structure is (XLII)



XLII

Analogous complexes are obtained starting from pent-1-yne and hex-3-yne; they all appear to be considerably less stable thermally and oxidatively than the cyclopentadienone complexes.

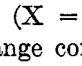
Very recently, a red, crystalline monomeric complex $(duroquinone)_2Ni$ has been obtained from the reaction of nickel carbonyl and duroquinone in benzene (217). It is diamagnetic, and shows a ketonic carbonyl stretching frequency in the 1600 cm.$^{-1}$ region. Presumably it is a tetrahedral complex of nickel(0), although its stability to air and dilute acids, and its limited solubility in organic solvents, are remarkable for such a compound. The nature of the complexes obtained in these reactions seems to be very sensitive to the nature of the substituents present in the ring (the same point is noted in the formation of complexes from acetylenes, Section XII). Thus, nickel carbonyl and *p*-benzoquinone give a black amorphous compound of formula $Ni(quinone)_2$, which is paramagnetic with a moment of 3.31 B.M. Treatment with dilute acids gives nickel(II) and quinhydrone, so the compound is probably a quinhydrone salt of nickel(II) (223).

The iron tricarbonyl complex of cycloheptatrienone (tropone) is one of the products isolated from the reaction of acetylene with $Fe(CO)_5$ in non-polar solvents (Section XII), and it also may be obtained by heating $Fe_3(CO)_{12}$ with tropone at 80° (142). It forms red crystals which exist in two modifications having identical infrared spectra. It is not known whether one of the double bonds of the seven-membered ring is uncomplexed, as seems to be the case with (cycloheptatriene)$Fe(CO)_3$ (34).

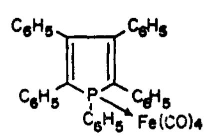
Theoretical considerations suggest that the three-membered cyclic ketone cyclopropenone should form metal complexes (29, 196), and such complexes have been suggested as the intermediates in the Reppe synthesis of acrylic acid derivatives from acetylene and nickel carbonyl (63, 204). However, experiments on the reaction of diphenylcyclopropenone with nickel carbonyl are not in favor of this idea (21).

C. COMPLEXES OF OTHER HETEROCYCLIC UNSATURATED SYSTEMS

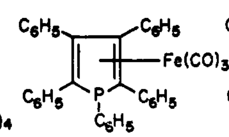
A limited number of complexes have been described containing olefinic systems of the type



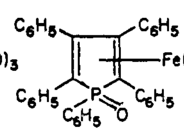
where X is some group which does not contain carbon. Pentaphenylphosphole ($X = PC_6H_5$) reacts with $Fe_3(CO)_{12}$ forming an orange complex (XLIII), in which



XLIII



XLIV



XLV

coördination is from the phosphorus atom, a yellow complex (XLIV), in which coördination takes place from the two double bonds, and a binuclear complex of uncertain formula in which both types of coördination may occur (23). When the donor function of the phosphorus atom is blocked, as in pentaphenylphosphole oxide, coördination takes place exclusively from the double bonds, and a yellow complex (XLV) is isolated.

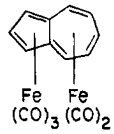
Analogous complexes also have been prepared from the thiophene dioxides (X = SO_2) and iron carbonyls (238). Thiophene itself (X = S), which forms arene complexes such as $C_4H_4SCr(CO)_3$ with the Group VI metals (100a), does not appear to form either an arene or an olefin-type complex with iron. Reaction of thiophene with $Fe_3(CO)_{12}$ gives the binuclear complex $C_4H_4Fe_2(CO)_6$ (Section XII), sulfur being eliminated as iron sulfide (151). A report that an arene complex $C_4H_4SFe(CO)_2$ is formed (32) must be discounted, although the possibility of forming a complex $C_4H_4SFe(CO_3)$ remains to be investigated.

IX. AZULENE METAL CARBONYLS AND RELATED COMPOUNDS

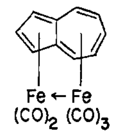
The hydrocarbon azulene has ten π-electrons, and it is therefore difficult to predict the stoichiometry of its metal complexes from naïve counting of electrons on the basis of the Effective Atomic Number Rule.

Table VI lists the complexes of azulene and substituted azulenes which have been described, together with their salient properties. Prolonged reaction of azulene with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ in inert solvents gives two complexes: (a) $C_{10}H_8Fe_2(CO_5)$, a diamagnetic, dark red crystalline solid which is stable to air, moderately soluble in polar organic solvents and sparingly soluble in non-polar solvents (32) (33); (b) $(C_{10}H_8)_2Fe_5(CO)_{13}$, a light brown solid, which is sparingly soluble in nearly all organic solvents (33). Its infrared spectrum indicates the presence of bridging carbonyl groups, and it is stated to be paramagnetic (33). Nothing else is known about it.

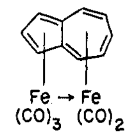
Possible structures for $C_{10}H_8Fe_2(CO)_5$ which satisfy the requirement of diamagnetism are



XLVI



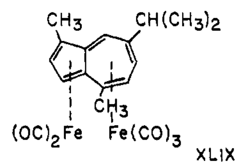
XLVII



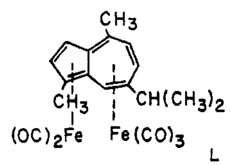
XLVIII

It is not known with certainty whether the two iron atoms are on the same side of the ring system (*cis*-configuration), or on opposite sides (*trans*-configuration). Nor is the distribution of $Fe(CO)_3$ and $Fe(CO)_2$ groups between each half of the azulene nucleus known. However, the observed dipole moment (3.97 *D*) of $C_{10}H_8Fe_2(CO)_5$ is believed to favor the *cis*-configuration (33).

Investigation of the high-resolution proton resonance spectra of the $Fe_2(CO)_5$ complexes of azulene, 1,3-dideuterioazulene and 4,6,8-trimethylazulene shows that, in contrast to the free hydrocarbons, protons or groups at positions 1,8 and 7 are not equivalent to those at 3,4 and 5, respectively, *i.e.*, there is asymmetry about the C_2–C_6 axial plane. This means that a complex derived from a symmetrically substituted azulene has enantiomorphic forms, and that a complex derived from an unsymmetrically substituted azulene has two geometrical isomers, each of which has two enantiomorphs (33). In the case of (guaiazulene)$Fe_2(CO)_5$, the two geometrical isomers can be separated chromatographically. Both isomers give the parent azulene on decomposition, and have almost identical infrared and ultraviolet spectra, but their n.m.r. spectra and melting points differ markedly. Geometrically isomeric structures can be written on the basis of any of the structures proposed; some possibilities for the guaiazulene complex are shown in XLIX and L



XLIX



L

TABLE VI

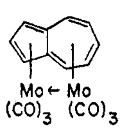
AZULENE METAL COMPLEXES

Organic group	Formula of complex	Physical properties	Preparation	Infrared	Dipole moment (solvent)	N.m.r.
Azulene	$C_{10}H_8Fe_2(CO)_5$	Dark red solid d. >100°	(32)	(33)	3.97 (benzene)	(33)
Azulene	$(C_{10}H_8)_2Fe_5(CO)_{13}$	Pale brown solid d. >170°	(33)	(33)	—	—
Azulene	$C_{10}H_8Mo_2(CO)_6$	Black solid d. >150°	(33)	(33)	—	—
Azulene	$(C_{10}H_8)_2Mn_2(CO)_6$	Pale yellow solid 153–154 d.	(35)	—	—	—
1,3-Dideuterioazulene	$(C_{10}H_6D_2)Fe_2(CO)_5$	Dark red solid d. >100°	(33)	(33)	—	(33)
4-Methylazulene	$C_{11}H_{11}Fe_2(CO)_5$	Dark red oil	(33)	(33)	—	(33)
	$-C_{13}H_{14}Fe_2(CO)_5$	Dark red solid d. 122–125°	(33)	(33)	—	(33)
	$-C_{13}H_{14}Mo_2(CO)_6$	Black solid d. >170°	(33)	(33)	—	—
4,6,8-Trimethylazulene	$-(C_{13}H_{14})_2Mn_2(CO)_6$	Pale yellow solid	(33)	(33)	—	—
	$-C_{13}H_{14}RhCl_3$	—	(33)	—	—	—
	$-C_{13}H_{14}PdCl_2$	—	(33)	—	—	—
Guiaiazulene	$C_{15}H_{18}Fe_2(CO)_5$ (isomer A)	Dark red solid 97–99°	(33)	(33)	—	(33)
Guaiazulene	$C_{15}H_{18}Fe_2(CO)_5$ (isomer B)	Dark red solid 110–111°	(33)	(33)	—	(33)
Guaiazulene	$C_{15}H_{18}Mo_2(CO)_6$	Black solid d. >170°	(33)	(33)	—	—

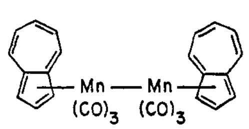
Attempts to separate each geometrical isomer into its enantiomorphs on *d*-lactose were not successful (33).

On the basis of a molecular-orbital treatment, Brown (28) has suggested that the $Fe(CO)_2$ groups should be attached to the five-membered ring of azulene, but since a *trans*-configuration for the azulene complex was assumed, it is not known whether the conclusion is valid. X-ray studies on some of these complexes would be most valuable.

The remaining metal–azulene complexes have been less thoroughly studied by physical methods, mainly because of their limited solubility in organic solvents. A number of complexes of general formula (azulene)-$Mo_2(CO)_6$ (Table VI) have been obtained from prolonged reaction of $Mo(CO)_6$ with the azulenes (33, 35). They are black, diamagnetic solids which are slightly soluble, even in polar solvents, giving dark red solutions. (A preliminary report indicating paramagnetism for the simple azulene complex is incorrect (35).) It is not known whether the metal atoms are *cis*- or *trans*-, but structure LI which satisfies the requirements of diamagnetism has been suggested. Azulene also reacts with $Mn_2(CO)_{10}$ giving a yellow, air-stable, diamagnetic dimeric complex of empirical formula (azulene)-$Mn(CO)_3$, which is presumably a substitution product of $Mn_2(CO)_{10}$ (33)

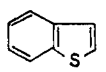


LI

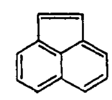


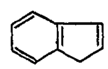
LII

Some complexes related to these azulene compounds have been obtained from the reaction of some polycyclic hydrocarbons with $Fe_3(CO)_{12}$. Thus, thianaphthene (LIII) which, like azulene, has ten π-electrons, gives an orange-red diamagnetic complex $C_8H_6SFe_2(CO)_5$, which seems to be analogous to the azulene compound, but differs from it in showing only one proton resonance in solution (162).



LIII


LIV


LV

Acenaphthylene (LIV), which has twelve available π-electrons, reacts with $Fe_3(CO)_{12}$ giving red-violet, diamagnetic $C_{12}H_8Fe_2(CO)_6$, which is formally analogous to $C_8H_8Fe_2(CO)_6$ (162). A formulation similar to $C_8H_8Fe_2(CO)_6$ would require two free double bonds, but the complex cannot be hydrogenated. It seems likely that, in the field of metal complexes of polycyclic hydrocarbons, the distinction between "sandwich" complexes and "olefin" complexes becomes more blurred than it is already. It may be noted that both thianaphthene and acenaphthylene give complexes of the type (arene)$M(CO)_3$ (M = Cr). Indene (LV) is remarkable in forming a $Cr(CO)_3$ complex (metal attached to six-membered ring) (99) and [indene $Mo(CO)_3]_2$ (metal attached to five-membered ring) (162).

X. METAL COMPLEXES OF CYCLOBUTADIENE

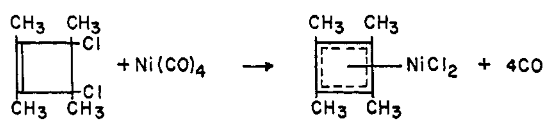
It was pointed out in 1956 that the entity cyclobutadiene, which had eluded all attempts to synthesize it by classical organic procedures (15), should be stabilized by formation of transition metal complexes (169). The experimental justification of this prediction is important not only for this isolated case, but because stabilization of otherwise unstable entities by metal complex formation may well become an important theme in future publications in the field of metal–olefin chemistry.

By basic molecular-orbital theory, cyclobutadiene has a doubly degenerate non-bonding orbital containing two unpaired electrons of e_{1g} symmetry, and this is suitable for overlap with the d_{xz} and d_{yz} orbitals of a transition metal (possibly hybridized with the p_x and p_y orbitals, respectively), which also have e_{1g} symmetry. The MO treatment was applied to a hypothetical complex $C_4H_4MA_2$ (A = ligand), and it was concluded that 16-electron complexes such as $C_4H_4PdCl_2$ should be stable for metals in 2- or 3-valent states, while 18-electron complexes should be stable for metals in low-valent states, *e.g.*, $C_4H_4Fe(CO)_3$ (169). A number of reactions of salts of palladium and gold with acetylene were reformulated tentatively as involving cyclobutadiene complexes. In particular, it was suggested that the polymerization of acetylene in the presence of a non-aqueous solution of nickel cyanide to cycloöctatetraene, rather than to the thermodynamically favored benzene, could be explained on the basis of a $C_4H_4Ni(CN)_2$ intermediate, which then underwent subsequent bimolecular reaction forming C_8H_8.

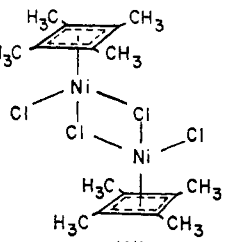
The original prediction has been substantiated, as is shown in the following sub-sections. We shall not deal in this review with cyclobutadiene complexes of palladium (81).

A. TETRAMETHYLCYCLOBUTADIENE DICHLORONICKEL(II)

In a search for the predicted complexes of the type $C_4H_4NiA_2$, Criegee and Schroder (70, 71) treated 3,4-dichloro-1,2,3,4-tetramethylcyclobut-1-ene with nickel carbonyl in refluxing, inert organic solvents. All four CO groups of the carbonyl were replaced, and a red-violet, diamagnetic complex of empirical formula $C_8H_{12}NiCl_2$ was obtained. This complex is insoluble



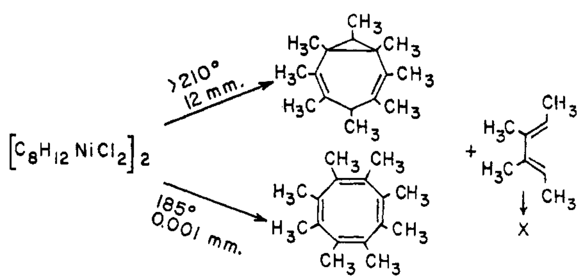
in non-polar organic solvents, moderately soluble in polar organic solvents such as acetone, and very soluble in chloroform and dichloromethane. The relative simplicity of the infrared spectrum of the complex, the occurrence of only one proton resonance signal, and the decomposition of the complex by aqueous sodium nitrate to give 3,4-dihydroxy-1,2,3,4-tetramethylcyclobut-1-ene, provide strong indications of the presence of a methyl-substituted cyclobutadiene ring (71), and full confirmation is obtained from the X-ray study not yet published in full (85). The complex does, however, show unexpected features; it forms an addition compound with chloroform, and its molecular weight in bromoform is ten times that expected for a monomeric species (71). The X-ray study shows that, in the solid state, the molecule $C_8H_{12}NiCl_2$ is dimeric, with the structure (LVI).



LVI

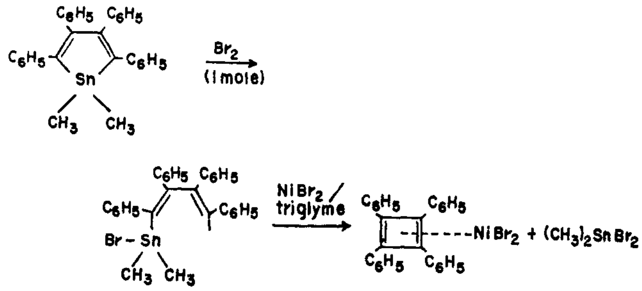
Presumably the behavior with chloroform reflects the tendency of 5-coördinate nickel(II) to make use of its vacant p-orbital for bonding to various ligands; somewhat similar behavior has been observed with the $Rh(CNC_6H_5)_4^+$ species (171a). It is remarkable also that the nickel complex is readily soluble in water with retention of the cyclobutadiene nucleus giving a bright red, conducting solution which probably contains the corresponding diaquo species $[C_8H_{12}Ni(H_2O)_2]^{2+}$ (71).

Some thermal decomposition reactions of the complex are summarized



These decomposition products can be envisioned readily as arising from an unstable tetramethylcyclobutadiene intermediate. The tetramethylbutadiene presumably arises from a hydrogen abstraction reaction by this intermediate, and it may be noted that butadiene frequently is obtained in high temperature organic elimination reactions believed to involve cyclobutadiene as an intermediate (15).

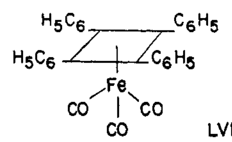
Very recently, tetraphenylcyclobutadiene nickel dibromide has been prepared by the reaction sequence (115)



This complex appears to be very similar to the tetramethyl compound. The intermediate in the formation of the complex reacts readily with radical reagents, such as oxygen, dienophiles, thiophenol and nitric oxide, and, in the absence of such reagents, it readily dimerizes. It seems probable that the intermediate is tetraphenylcyclobutadiene in its triplet ground state (116).

B. TETRAPHENYLCYCLOBUTADIENE IRON TRICARBONYL

The possibility of obtaining cyclobutadiene by dimerization of acetylene led Longuet-Higgins and Orgel (169) to suggest that a complex $C_7H_4O_3Fe$ obtained from an iron carbonyl-acetylene reaction (207) was $C_4H_4Fe(CO)_3$. This is not so (see Section XIIE), but the corresponding tetraphenyl derivative has been obtained in very low yield as a bright yellow solid, m.p. 234°, from the reaction of $Fe_3(CO)_{12}$ with diphenylacetylene in inert solvents (139). Higher yields are obtained from reaction of $Fe(CO)_5$ and the acetylene at higher temperatures. The complex has considerable thermal stability, subliming unchanged *in vacuo* at 180°. Lithium aluminum hydride reduction affords 1,2,3,4-tetraphenylbutadiene, and sodium in liquid ammonia gives 1,2,3,4-tetraphenylbutane; chemical studies show that no free double bonds are present. This evidence can all be explained on the basis of complexed tetraphenylcyclobutadiene, but it is not conclusive. However, X-ray study (79) shows clearly the presence of the cyclobutadiene moiety (structure LVII)

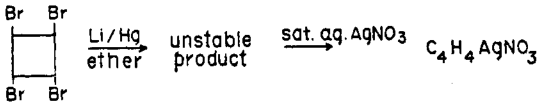


LVII

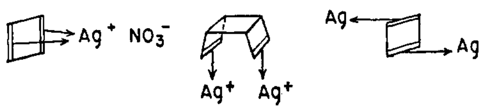
The CO groups have trigonal symmetry; the phenyl groups are twisted out of the plane of the ring and bent away from the $Fe(CO)_3$ group.

C. CYCLOBUTADIENE SILVER NITRATE

This silver complex is the only compound so far isolated which is thought to contain unsubstituted cyclobutadiene, and is prepared by the reaction sequence (11):



The intermediate product contains mercury but no halogen, and it may be a mercury–cyclobutadiene complex. The silver complex is white and crystalline, and it can be recrystallized from ethanol. Apart from a structure containing coördinated cyclobutadiene, it is necessary to consider the possibility of a structure (LIX) derived from a dimer of cyclobutadiene formed by cyclo-addition

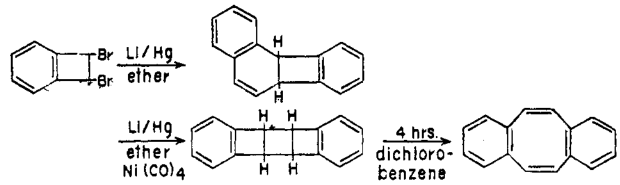


LVIII LIX LX

The relevant evidence may be summarized: (a) on treatment with water, the complex gives metallic silver, polymer, and less than 1% of a gas whose empirical formula is CH (11); (b) on treatment with aqueous sodium chloride, and subsequent ether-extraction, a solution of this gas is obtained, which is believed to be the dimer involved in structure LIX (13); (c) the gas, or its solution in ether, reacts with aqueous silver nitrate regenerating the original complex (13); (d) the infrared spectrum of the complex is relatively simple, and is believed to favor the chain structure LX, although LVII cannot be entirely excluded, and the ring is thought unlikely to be completely symmetrical (118). The spectrum differs completely from those of the cycloöctatetraene silver complexes.

It is argued (13) that LIX would liberate the stable liquid dimer cycloöctatetraene on treatment with water, so that the observed polymerization behavior favors LVIII or LX. The reformation of the original complex from the dimeric gas can then be explained only by assuming that the dimer breaks down again to cyclobutadiene, with the fission of single bonds (13). This is not unprecedented (see, for example, reference (161a)), though formation of a cycloöctatetraene complex might perhaps have been expected. It is obvious that a definitive X-ray study of the silver complex is required in order to establish with certainty the presence of a cyclobutadiene ring in it.

Two other experiments are of interest in connection with this problem. The intermediate unstable mercury compound fails to react with either nickel carbonyl or nickel chloride, but with nickel acetate in dioxane, as 12% yield of cycloöctatetraene is obtained, although no complex can be isolated (12). This provides some evidence of the correctness of the cyclobutadiene-intermediate hypothesis to explain the Reppe synthesis of cycloöctatetraene. The second experiment is outlined



In the presence of nickel carbonyl, a new dimer of benzocyclobutadiene is obtained which is the analog of the dimer of cyclobutadiene already mentioned (10). Presumably, the reaction proceeds *via* an intermediate nickel complex similar to that described by Criegee and Schroder (71), although no direct evidence could be found for its existence. It seems possible that the extreme mobility of hydrogen atoms renders cyclobutadiene unstable even when attached to a metal, and it may be that stable complexes will be obtained principally when all four positions on the ring are substituted by alkyl or aryl groups. In connection with this, the marked reluctance of $C_8H_{12}NiCl_2$ to give octamethylcycloöctatetraene may be noted (71).

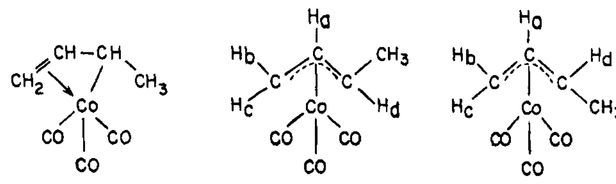
XI. "EN-YL" METAL COMPLEXES

The work summarized in previous sections shows that conjugated diolefins and triolefins donate four or six π-electrons to transition metals essentially by overlap of delocalized π-orbitals with suitable metal orbitals. Many of the complexes so formed, especially the mononuclear complexes, can be simply regarded as substitution products of the appropriate metal carbonyl, each double bond replacing one CO group. It is clear that the metal complexes of conjugated olefins are closely related to π-cyclopentadienyl and π-arene metal complexes on the one hand, and to the complexes of monoölefins and unconjugated diolefins on the other. Indeed, the term "π-complex" frequently is used to include the entire gamut of cyclopentadienyl, arene and olefin complexes of the transition metals.

On this basis, there is evidently no reason why the number of π-electrons donated by an olefinic system should be limited to 2, 4 or 6, and in fact a number of complexes are now known in which 3 and 5 π-electrons are supplied to the metal atom by the olefinic system. In these cases, it is usually possible to write structures in which one or two double bonds are coördinated to the metal atom in the usual manner together with a σ-bond formed from one of the carbon atoms. However, the evidence available in most cases suggests that, just as in the conjugated diene systems already considered, the electrons involved in bonding to the metal are in delocalized orbitals encompassing all the carbon atoms involved. Complexes of this type, in which 3 and 5 π-electrons are supplied to the metal, have been termed "en-yl" complexes. An alternative and equivalent way of considering "en-yl" complexes is to imagine olefinic systems carrying a formal negative or positive charge coördinated to the metal atom, and donating 4 or 6 π-electrons to it. The situation is best illustrated by examples.

A. ALLYL COBALT TRICARBONYL AND RELATED COMPOUNDS

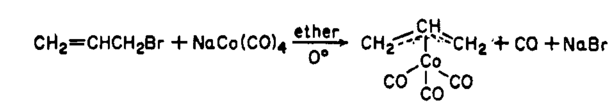
The first example of an "en-yl" compound to be discovered was a red-brown liquid of formula $C_4H_7Co(CO)_3$ obtained from the reaction of cobalt carbonyl hydride $Co(CO)_4H$ with butadiene (145). This is found to be monomeric and diamagnetic, and it no longer contains the metal–hydrogen bond characteristic of the original hydride. Originally the complex was formulated as shown in LXI (8, 145); three CO groups supply



LXI LXII LXIII

six electrons, and the double bond donates two π-electrons to the metal atom, which then reaches its closed shell configuration by forming a σ-bond to one of the carbon atoms. More detailed investigation (8, 133, 183, 186) has shown that two isomeric complexes are formed in the reaction, the less stable isomer being converted to the more stable isomer on heating. The respective proton resonance spectra show that the isomers may be represented as LXII and LXIII, the former being the more stable (186). The two allenic carbon–carbon bonds are equivalent, and the four protons and methyl group are thought to be approximately coplanar. Thus, the complex may be named systematically as 1-butenyl cobalt tricarbonyl, or 1-methylallyl cobalt tricarbonyl; the allyl group may be regarded as supplying 3 π-electrons to the cobalt atom.

The parent compound, allyl cobalt tricarbonyl $C_3H_5Co(CO)_3$ has been obtained as a low-melting yellow crystalline solid by the reaction (132, 133, 183)



LXIV

This complex is also diamagnetic, and its proton resonance spectrum shows three peaks whose intensities are in the ratio 2:2:1. The two methylene groups are equivalent, but the two hydrogen atoms on each methylene group are different, two being near the cobalt atom, and two away from it. Structure LXIV is indicated. The complex reacts with triphenylphosphine giving a stable substitution product which still contains the coördinated allyl group, *viz.*, $C_3H_5Co(CO)_2P(C_6H_5)_3$. The mechanisms of formation of allyl cobalt tricarbonyl and its congeners by both preparative methods is of considerable interest, particularly in connection with the proposed mechanisms for the Oxo (Hydroformylation) Reaction.

$$RCH{=}CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} RCH_2CH_2CHO$$

Heck and Breslow (133) have carried out the reactions represented in outline in Fig. 2, which can be interpreted readily if the following points are borne in mind: (a) alkyl and acyl metal carbonyls, which contain a transition metal to carbon σ-bond, can be made by reaction of the sodium salt of the carbonyl hydride with an alkyl or acyl halide, usually in an ether solvent

$$RX + NaCo(CO)_4 \rightarrow RCo(CO)_4 + NaX \quad (1)$$

$$RCOX + NaCO(CO)_4 \rightarrow RCOCo(CO)_4 + NaX \quad (2)$$

(b) There is an equilibrium whose position depends on the reaction conditions between acyl metal carbonyls on the one hand, alkyl metal carbonyls and carbon monoxide on the other

$$RCOM(CO)_x \rightleftarrows RM(CO)_x + CO$$

(c) It is established from experiments using labeled carbon monoxide in the system

$$CH_3COMn(CO)_5 \rightleftarrows CH_3Mn(CO)_5 + CO$$

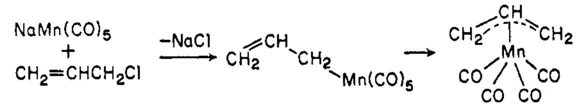
that the acyl carbonyl group is derived from carbon monoxide attached to the metal atom, and is not obtained directly from the gas phase (52).

(d) It follows from (c) that the carbon monoxide displaced from an alkyl metal carbonyl by triphenylphosphine will insert itself between the metal atom and the alkyl group giving a triphenylphosphine substitution product of an acyl metal carbonyl.

$$RCo(CO)_4 + P(C_6H_5)_3 \rightarrow R\cdot CO\cdot Co(CO)_3P(C_6H_5)_3$$

A similar effect has been noted with other ligands in the manganese carbonyl series (153). If a coördinated double bond was present initially in the σ-bonded complex, this may be set free in the above process. The significance of these results to the mechanisms proposed for the Oxo Reaction are discussed in recent papers (24, 163, 164, 225).

So far, π-allylmanganese complexes have been less thoroughly investigated than their cobalt analogs, although the indications are that both σ- and π-bonded manganese complexes should be the more stable. The product formed in high yield from the reaction of sodium pentacarbonylmanganate (−1) with allyl chloride is the yellow liquid (σ-allyl)$Mn(CO)_5$, which on heating under reduced pressure gives yellow, crystalline (π-allyl)$Mn(CO)_4$ (152, 183)



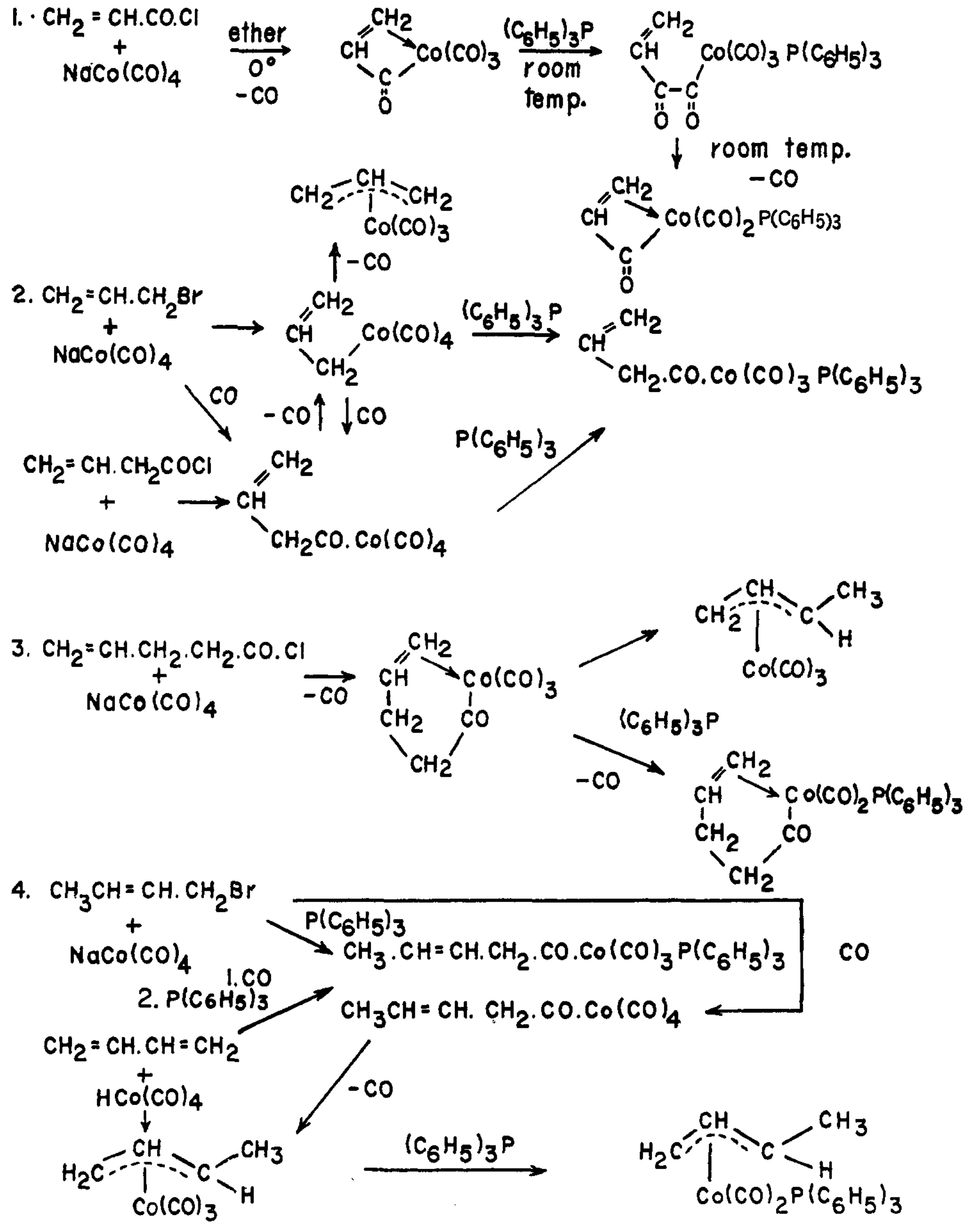


Fig. 2

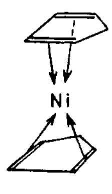
The σ-compound shows an uncomplexed C=C stretching frequency at 1617 cm.$^{-1}$ in its infrared spectrum, and its n.m.r. spectrum resembles that of allyl bromide. On the other hand, the π-allyl compound shows a weak band at 1560 cm.$^{-1}$, which may be a complexed C=C stretching frequency, and its n.m.r. spectrum is very similar to that of allyl cobalt tricarbonyl. Some substituted π-allyl manganese carbonyl complexes have been prepared recently (183) (Table VII). The evidence summarized here suggests that the allyl radical C_3H_5 is capable of forming metal complexes which involve a form of delocalized bonding similar to that envisioned for π-cyclopentadienyl metal compounds. The allyl radical may be supposed to supply three π-electrons to the metal atom. Alternatively, bonding may be regarded as occurring from the allyl anion $[C_3H_5]^-$, which supplies four π-electrons to the metal atom. These outlooks are of course equivalent, since, in the second case, the electron on the allyl anion is formally regarded as derived from the metal atom, whose valence is thereby reduced by one. Exactly the same problem of formalism arises in cyclopentadienyl compounds; thus, in ferrocene, one may start either with a neutral iron atom and two C_5H_5 radicals, or with bivalent iron and two C_5H_5 anions.

The recognition of the possibility of delocalized bonding to a transition metal from a three-carbon chain has led to the re-examination of some other metal–olefin complexes. From the reaction of nickel carbonyl with monomeric cyclopentadiene it is possible to isolate deep red crystals with the composition $C_{10}H_{12}Ni$ (108). The complex is monomeric and diamagnetic and was formulated by Fischer and Werner (108) as a diolefin complex of zerovalent tetrahedral nickel, $(C_5H_6)_2Ni$,

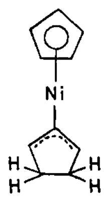
TABLE VII
EN-YL METAL COMPLEXES

Organic radical	Formula of complex	Physical properties	Preparation	Infrared	Dipole moment (solvent)	N.mr.
π-Allyl	π-$C_3H_5Co(CO)_3$	Orange-red liquid m.p. −33° b. 39° (15 mm.)	(132) (133) (183)	(132) (133) (183)	—	(132). (133) (183)
π-Allyl	π-$C_3H_5Co(CO)_2[P(C_6H_5)_3]$	Yellow prisms m.p. 132° d.	(132) (133)	(133)	—	(133)
π-Allyl	π-$C_3H_5Mn(CO)_4$	Pale yellow solid b. 66° (14 mm.) m.p. 52.5–53° (152) 55–56° (183)	(152) (183)	(152) (183)	—	(152) (183)
π-Allyl	π-$[C_3H_5NiBr]_2$	Dark red crystals d. 93–95°	(92)	(92)	1.31 ± 0.06*D* (benzene) (92)	—
π-Allyl	π-C_5H_5Niπ-C_3H_5	Red oil b. ~ 40° (0.05–0.02 mm.)	(92) (183)	(183)	—	(183)
1-Methylallyl[2-butenoyl]	π-$C_4H_7Co(CO)_3$	Orange liquid (2 isomers) b.p. 36° (4–5 mm.)	(8) (132) (133) (145) (183) (186)	(8) (133) (183) (186)	—	(183) (186)
1-Methylallyl[2-butenoyl]	π-$C_4H_7Mn(CO)_4$	Yellow liquid b.p. 68° (7 mm.)	(183)	(183)	—	(183)
1-Methylallyl[2-butenoyl]	π-$C_4H_7Co(CO)_2[P(C_6H_5)_3]$	Orange-red crystals m.p. 91.5–94°	(133)	(133)	—	—
Acrylyl	$C_3H_3OCo(CO)_3$	Not isolated	(133)	(133)	—	—
Acrylyl	$C_3H_3OCo(CO)_2[P(C_6H_5)_3]$	Yellow crystals m.p. 106–107° (darkens 100°)	(133)	(133)	—	—
4-Pentenoyl	$C_5H_7OCo(CO)_3$	Not isolated	(133)	(133)	—	—
4-Pentenoyl	$C_5H_7OCo(CO)_2[P(C_6H_5)_3]$	Yellow crystals m.p. 106.5–107°	(133)	(133)	—	—
2-Chloroallyl	π-$C_3H_4ClCo(CO)_3$	Amber liquid b.p. 30° (2 mm.)	(183)	(183)	—	(183)
1-Chloroallyl	π-$C_3H_4ClCo(CO)_3$	Amber liquid b.p. 38° (2 mm.)	(183)	(183)	—	(183)
1-Chloroallyl	π-$C_3H_4ClMn(CO)_4$	Yellow liquid b.p. 85° (6 mm.)	(183)	(183)	—	(183)
2-Methylallyl	π-$C_4H_7Mn(CO)_4$	Yellow liquid b.p. 50° (2.5 mm.)	(183)	(183)	—	(183)
1,1-Dimethylallyl	π-$C_5H_9Mn(CO)_4$	Yellow liquid b.p. 48–52° (1 mm.)	(183)	(183)	—	(183)
π-Cyclopentenyl	π-C_5H_5Niπ-C_5H_7	Red solid m.p. 42–43°	(84) (108)	(108) (117)	1.16 ± 0.07*D* (cyclohexane) (108)	(84) (109) (146)
π-Cyclohexadienyl	π-$C_6H_7Mn(CO)_3$	Pale yellow plates m.p. 78°	(246)	(246)	—	(246)
π-Cyclohexadienyl	[π-$C_6H_7Fe(CO)_3]^+$ salts	BF_4^- salt: pale yellow solid	(94)	(94)	—	—
π-Cycloheptadienyl	[π-$C_7H_9Fe(CO)_3]^+$ various salts	BF_4^- salt: yellow crystals (73) d. >150° $FeCl_4^-$ salt: yellow crystals (34)	(34) (73)	(34) (73)	—	(34)
π-(Triphenylmethyl)cycloheptadienyl	[π-C_7H_8·$(C_6H_5)_3C$·$Fe(CO)_3]^+$	BF_4^- salt: pale yellow crystals d. >150°	(34)	(34)	—	—

analogous to nickel carbonyl. The structure of the



LXV



LXVI

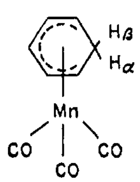
complex has been reformulated recently by various groups independently (84, 109, 117, 146, 218) as π-cyclopentadienyl π-cyclopentenyl nickel π-$C_5H_5NiC_5H_7$ (LXVI), in which the cyclopentenyl radical is behaving as a three π-electron donor like the allyl radical. The evidence for the revised structure comes principally from the proton resonance spectrum, which shows a sharp peak clearly assignable to the five equivalent protons of the π-cyclopentadienyl ring, together with peaks assignable to the three olefinic and four aliphatic protons of the cyclopentenyl ring (84, 109, 146). In addition, an independent synthesis of the complex has been achieved by treating anhydrous nickel bromide with a mixture of NaC_5H_5 and cyclopentenyl magnesium bromide (84). The original method of preparation is of interest in showing that in reactions involving metal carbonyls and olefinic systems, the possibility of hydrogen gain, loss or transfer must always be taken into account (see also Sections IIIC and IIIE).

It may be noted here that analogous complexes of palladium containing the allyl (C_3H_5) and cyclohexenyl (C_6H_9) groups have also been characterized; they are surveyed in the review by Doyle (81). Also, very recently, a dimeric π-allyl nickel bromide complex $[C_3H_5NiBr]_2$ has been obtained by reaction of nickel carbonyl with allyl bromide (92). This probably has a structure containing π-allyl groups and bridging bromine atoms, and its reaction with NaC_5H_5 is reported to give monomeric π-C_5H_5Ni-π-C_3H_5, analogous to π-C_5H_5-NiC_5H_7 (92, 183). The chromium complexes $(C_5H_6)_2Cr$-$(CO)_2$ and $C_5H_6Cr(CO)_2C_4H_6$ (Section VII) may well be π-$C_5H_5Cr(CO)_2C_5H_7$ and π-$C_5H_5Cr(CO)_2C_4H_7$.

B. CYCLOHEXADIENYL MANGANESE TRICARBONYL AND RELATED COMPOUNDS

Delocalized bonding to a metal from a five-carbon chain is best exemplified by the metal cyclopentadienyl complexes, but a number of metal–olefin complexes are now known which also share this feature. Undoubtedly more will be discovered.

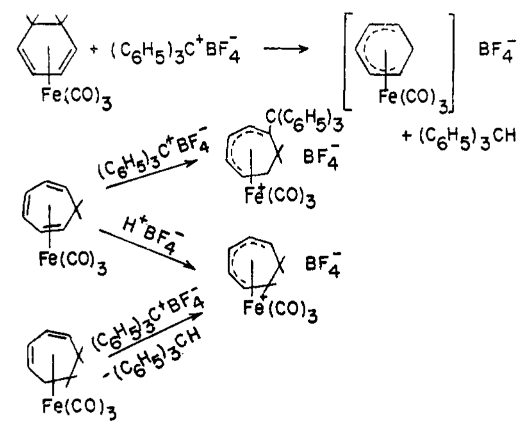
Cyclohexa-1,3-diene reacts with manganese carbonyl giving an extremely stable, yellow, sublimable, diamagnetic complex, which, unexpectedly, is cyclohexadienyl manganese tricarbonyl $C_6H_7Mn(CO)_3$ (246). This reaction contrasts with the behavior of the diene with the carbonyls of iron, cobalt and molybdenum, in which the C_6H_8 unit is retained intact in the complexes isolated. Probably the hydrogen lost in the manganese carbonyl reaction reduces some of the cyclohexa-1,3-diene present to cyclohexene. The same complex is obtained by sodium borohydride reduction of the arene complex cation $[C_6H_6Mn(CO)_3]^+$ in aqueous solution, and this method of preparation provides a convenient route to substituted derivatives (246). It seems likely that bonding involves overlap between a suitable metal orbital and a π-orbital encompassing the five carbon chain; the physical properties of $C_6H_7Mn(CO)_3$ show a remarkable resemblance to those of π-$C_5H_5Mn(CO)_3$. The infrared spectrum shows a C–H stretching frequency at the low value of 2800 cm.$^{-1}$, so presumably there is an Hα-Hβ pair of methylene hydrogen atoms, just as in the π-$C_5H_5MC_5H_6$ compounds (Section VI). The proton resonance spectrum of the compound is in agreement with this. Structure (LXVII) is suggested (246).



LXVII

It seems possible that the complex formulated as π-$C_6H_6FeC_5H_6$ (124), obtained by borohydride reduction of the cation $[\pi$-$C_6H_6Fe\ \pi$-$C_5H_5]^+$ should be reformulated as π-$C_5H_5FeC_6H_7$ in the light of these results.

Obviously another possible route to cyclohexadienyl and related complexes lies in hydride ion abstraction reactions carried out on the corresponding cyclohexadiene and related complexes, just as the π-tropylium complex π-$C_7H_7Mo(CO)_3^+$ is obtained from (cycloheptatriene)$Mo(CO)_3$ (74). Treatment of (cyclohexa-1,3-diene)$Fe(CO)_3$ and (cyclohepta-1,3-diene)$Fe(CO)_3$ with triphenylmethyl fluoroborate gives triphenylmethane and the corresponding cyclohexadienyl and cycloheptadienyl iron tricarbonyl cations, respectively, $[C_6H_7Fe(CO)_3]^+BF_4^-$ and $[C_7H_9Fe(CO)_3]^+BF_4^-$ (73, 94). The former is clearly isoelectronic with $C_6H_7Mn(CO)_3$, and it can be regarded formally in three equivalent ways (a) $C_6H_7^-Fe^{2+}(CO)_3$, 6 π-electrons from the $C_6H_7^-$ anion, which is iso-π-electronic with $C_5H_5^-$; (b) $C_6H_7Fe^+(CO)_3$, 5 π-electrons from the C_6H_7 radical, which is iso-π-electronic with C_5H_5; (c) $C_6H_7^+Fe(CO)_3$, 4 π-electrons from the $C_6H_7^+$ cation, which is iso-π-electronic with cyclohexa-1,3-diene. The cycloheptadienyl iron tricarbonyl cation can also be obtained by hydrogen ion *addition* to cycloheptatriene iron tricarbonyl, using anhydrous hydrogen chloride, hydrogen bromide, or fluoroboric acid; it is isolated either as a tetrachloroferrate or fluoroborate salt (34, 73). This reaction is a clear indication that (cycloheptatriene)-$Fe(CO)_3$ has a free double bond which can be protonated (Section IIIC). Likewise, the reaction of triphenylmethyl cation with (cycloheptatriene)$Fe(CO)_3$ does not lead to hydride ion abstraction, but to triphenylmethyl cation addition; no triphenylmethane is formed. The product is the cation $[C_7H_8\{(C_6H_5)_3C\}Fe(CO)_3]^+$, isolated as its fluoroborate salt, which may be regarded as a derivative of $[C_7H_9Fe(CO)_3]^+$ (73). These reactions are shown in outline in Fig. 3.



The cycloheptadienyl iron species $C_7H_9Fe(CO)_3^+$ is reported to react with iodide ion giving a complex formulated as π-$C_7H_7Fe(CO)_2I$, (73) but it is not clear whether this contains the long-sought π-$C_7H_7Fe(CO)_2^+$ cation, or whether the iodine is covalently bound to the iron atom.

The reaction of cycloheptatriene iron tricarbonyl with anhydrous acids is of interest, since there have been reports of the solubility of other diolefin iron tricarbonyl complexes (*e.g.*, those of butadiene and cycloöctatetraene) in concentrated sulfuric acid without decomposition, and their recovery unchanged on dilution (129, 176). The proton resonance spectrum of cycloheptatriene iron tricarbonyl in concentrated sulfuric acid shows clearly the presence of $[C_7H_9Fe(CO)_3]^+$, and evidence has been presented for the corresponding species $[C_8H_9Fe(CO)_3]^+$ in sulfuric acid solutions of cycloöctatetraene iron carbonyl (75). Protonation of olefin metal complexes may well be a general phenomenon; the proton may be attached either to "uncomplexed" double bonds, or to the transition metal itself (76). Rapid developments in this field are to be expected.

XII. METAL CARBONYL–ACETYLENE REACTIONS

This section deals with reactions in which the olefin required for metal–complex formation is synthesized from simpler starting materials. The most well-known reactions of this type are the reactions of metal carbonyls with acetylenes, which were first investigated by Reppe and co-workers, and which have proved to be of immense importance in organic synthesis (63). In this review, attention is focused on the acetylene and olefin complexes which frequently are formed in these reactions, and whose structure often assists in elucidating possible mechanisms for the formation of the organic products.

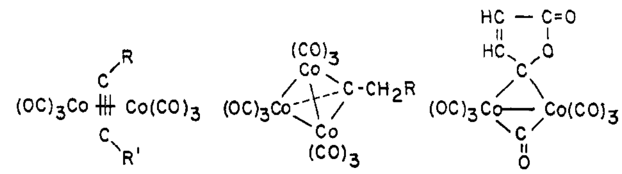
Although the types of metal complex which are formed in metal carbonyl–acetylene reactions are of almost limitless variety, two possibilities can in general be distinguished: either the acetylene may be incorporated into the complex so that it remains essentially unchanged, *i.e.*, the acetylene unit is still present in the complex, though it may be somewhat modified by coördination to the metal atoms; alternatively, two or more acetylene molecules combine, frequently with one or more carbon monoxide groups as well, to give a cyclic olefin unit, such as cyclobutadiene, cyclopentadienone or quinone, which is bound to one or more transition metal atoms.

A. METAL-ACETYLENE CARBONYL AND RELATED COMPLEXES

Cobalt carbonyl reacts with a wide variety of acetylenes at room temperature and pressure giving red or purple diamagnetic complexes of general formula $(RC_2R')Co_2(CO)_6$ (22, 127, 222). Since they show no bridged carbonyl frequencies, it is clear that the acetylenes have replaced the two bridging carbonyl groups of $Co_2(CO)_8$ (*cf.* reaction of $Co_2(CO)_8$ with diolefins, Section V, in which bridging carbonyls are retained). The infrared spectra also show no C≡C absorption, and the fairly high dipole moment (2.1*D*) of the diphenylacetylene complex eliminates a symmetrical structure for the complex (127). The X-ray study of the latter shows that the acetylene unit lies above the Co–Co axis and is almost at right-angles to it (220). This arrangement probably reflects the ability of acetylene to use its doubly degenerate p_x and p_y orbitals, which are mutually at right angles, for bonding to a pair of metal atoms (LXVIII). The importance of metal–metal bonding in these complexes has been emphasized on theoretical grounds (30). Analogous complexes of formula $Co_4(CO)_{10}RC_2R'$ derived from $Co_4(CO)_{12}$ have been mentioned briefly (140). The reaction of $Co_2(CO)_8$ with acetylenes is one of the few replacement reactions of this type whose kinetics have been studied (230). The results are interpreted in terms of a reactive cobalt carbonyl intermediate $Co_2(CO)_8$ having an unpaired electron on each metal atom, and an intermediate complex $Co_2(CO)_7(RC_2R')$.

On acid treatment of those complexes of the type $(RC_2H)Co_2(CO)_6$, *i.e.*, those in which the acetylene has an α-hydrogen atom, new trinuclear complexes of general formula $Co_3(CO)_9(RC_2H)H$ are formed (179). Recent work suggests that these are neither acetylene nor olefin complexes, but contain metal to carbon σ-bonds (LXIX) (166).

On treatment with carbon monoxide under pressure, the complexes $Co_2(CO)_6(RC_2R')$ give a further type of complex of general formula $Co_2(CO)_9(RC_2R')$ (224); chemical (224) and X-ray studies (184) show that these too are neither acetylene nor olefin complexes, but contain a lactone ring attached to one of the bridging carbonyl groups of $Co_2(CO)_8$ (LXX). The formation of

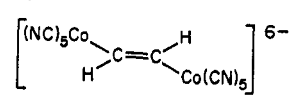


LXVIII LXIX LXX

these complexes may be of considerable significance from the viewpoint of mechanisms of succinic acid synthesis, and for mechanisms of chemisorption of acetylene. For further details, references and papers given in the Report of the Coördination Chemistry Conference, London, April, 1959 (225) should be consulted.

A series of complexes of general formula $[\pi\text{-}C_5H_5Ni]_2\text{-}RC_2R'$, which are entirely analogous to $[Co(CO)_3]_2\text{-}RC_2R'$, may be obtained either by replacing the bridging carbonyl groups of $[\pi\text{-}C_5H_5Ni(CO)]_2$ with the acetylene (228, 229), or by direct reaction of nickelocene with acetylene (82). Fluoroacetylenes behave similarly (22). They are generally green or greenish, black diamagnetic solids, and their structure almost certainly contains an acetylene unit bridging two $\pi\text{-}C_5H_5Ni$ units. It may be noted that although $Co_2(CO)_8$, $[\pi\text{-}C_5H_5Ni(CO)]_2$ and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ each contain two bridging carbonyl groups, the latter does not seem to give acetylene complexes of this type. This is believed to be because, in $Co_2(CO)_8$ and $[\pi\text{-}C_5H_5Ni(CO)]_2$, the bridging CO groups are not coplanar with the metal atoms, so that there is a vacant coördination position to which an acetylene molecule could attach itself initially. In $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, on the other hand, the bridging CO groups are coplanar with the two metal atoms, and there is no vacant coördination position (184, 229). The reaction of $[\pi\text{-}C_5H_5Ni(CO)]_2$ with diphenylbutadiyne yields two products: $[\pi\text{-}C_5H_5Ni]_2\text{-}C_6H_5C_2\cdot C_2C_6H_5$ and $[\pi\text{-}C_5H_5Ni]_4C_6H_5C_2\cdot C_2H_6H_5$, corresponding to coördination of one and both triple bonds of the diyne, respectively (228). Using the same diyne, it is also possible to obtain mixed metal complexes of iron and nickel, and nickel and cobalt, respectively (228).

Iron complexes which are probably analogous to $(RC_2R')Co_2(CO)_6$ and $[\pi\text{-}C_5H_5Ni]_2RC_2R'$ are dealt with in Section XIIC. Acetylene is also thought to act as a bridging group in the complex $2K_3Co(CN)_5 \cdot C_2H_2 \cdot 4H_2O$ formed by passing acetylene into a solution of the complex cobalt(II) cyanide (128). Structure LXXa was suggested for the anion



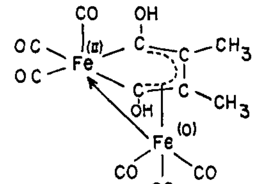
LXXA

B. REPPE AND VETTER'S COMPLEX $Fe_2C_{10}H_4O_8$

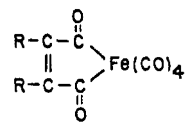
In 1953, Reppe and Vetter (207) isolated a yellow crystalline complex of formula $Fe_2C_{10}H_4O_8$ from the reaction of acetylene with an alkaline solution of iron carbonyl hydride at elevated temperature and pressure. Later work (221, 240) showed that the active species is $[HFe(CO)_4]^-$, hence that excess alkali should be avoided, and also that higher yields of the complex are obtained at room temperature and pressure. Reppe and Vetter suggested no structure for the compound, although they noted its acidic properties. $Fe_2C_{10}H_4O_8$, and similar complexes derived from substituted acetylenes, have been investigated in more detail by two groups independently (47, 221, 240), with the following results.

$Fe_2C_{10}H_4O_8$ shows three terminal carbonyl stretching frequencies and two OH stretching frequencies in the infrared. It has two acidic hydrogen atoms whose pK_a values are comparable with those of *p*-nitrophenol and phenol, respectively. The presence of two acidic hydroxyl groups is further shown by the formation of a dibenzoate on treatment with benzoyl chloride, and a dimethyl ether on treatment with dimethyl sulfate in alkaline solution (221). It also has been observed (47) that, whereas mild acetylation of $Fe_2C_{10}H_4O_8$ readily affords a diacetate, the propyne complex gives only a monoacetate under identical conditions, and the but-2-yne complex is not acetylated. Under more vigorous conditions, all three complexes give diacetates, but the propyne complex diacetate affords, on treatment with hot methanol, a monoacetate which is isomeric with, but distinct from, the first monoacetate. The cause of these differences in behavior is clearly steric, and it was suggested that the OH groups in the complex must be sufficiently near the acetylene residue to undergo marked steric hindrance from substituents on the latter, and, further, that the OH groups could not be symmetrically placed with respect to the acetylene moiety.

Although various guesses were made by both groups concerned as to the structure of $Fe_2C_{10}H_4O_8$, the question was not fully resolved, as so often in this field, until a definitive X-ray study had been carried out. The structure of the but-2-yne complex, as determined by Hock and Mills (136, 137), is shown diagrammatically in LXXI. It may be noted that this structure determination not only solved this particular problem, but also paved the way for the interpretation of other iron carbonyl–acetylene reactions dealt with in subsequent sections. The acetylene unit in these complexes



LXXI



LXXII

forms a five-membered ring with two CO groups and a $Fe(CO)_3$ group, and this diene system is coördinated to another $Fe(CO)_3$ group. By donation of an unshared pair of electrons from the latter iron atom to the former, each achieves an inert gas configuration. The carbon–carbon bond lengths in the coördinated diene system are almost equal (1.42 Å.) just as in (butadiene) $Fe(CO)_3$ and $\pi\text{-}C_5H_5Co$(tetramethylcyclopentadienone); the iron–iron distance (2.49 Å.) is similar to those found in $Fe_2(CO)_9$ and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$. It is clear that the two iron atoms differ markedly both in their formal valence (0 and 2) and in their stereochemistry. The situation with regard to the zerovalent iron atom is similar to that noted for (butadiene)$Fe(CO)_3$, while the coordination about the bivalent iron atom is a distorted square pyramid (137).

It is remarkable that, on treatment with aqueous ferric chloride under acid conditions, the complexes of the $Fe_2C_{10}H_4O_8$ type are split, the iron-carbon σ-bonds being preserved and a CO group being transferred (38). The products are formulated as alkyl derivatives of iron carbonyl hydride (LXXII). A qualitative MO treatment of $Fe_2C_{10}H_4O_8$ has been given (27) (see also Section XV).

C. REACTION OF IRON DODECACARBONYL WITH DIPHENYLACETYLENE

The reaction of $Fe_3(CO)_{12}$ with diphenylacetylene in inert non-polar solvents, which has been studied thoroughly by two groups independently (139, 140, 211, 213), gives a mixture of six organometallic complexes, which may be separated by chromatographic and fractional crystallization procedures. These complexes contain maximally only two diphenylacetylene units per molecule. Smaller amounts of organic products such as hexaphenylbenzene and tetracyclone are also formed, probably arising from trimerization of the acetylene and decomposition of the complexes (141). The evidence relating to the structures of the complexes may be summarized:

1. $Fe(CO)_3[(C_6H_5)_2C_2]_2$.—This is known by X-ray study (79) to be the iron tricarbonyl derivative of tetraphenylcyclobutadiene, and is considered in Section XB

2. $Fe(CO)_4[(C_6H_5)_2C_2]_2$.—This is (tetracyclone)$Fe(CO)_3$ (XXXI, R = C_6H_5), as shown by its thermal decomposition to tetracyclone, and by its independent synthesis from $Fe_3(CO)_{12}$ and tetracyclone.

3. $Fe_2(CO)_6[(C_6H_5)_2C_2]$.—This complex, which is formed only in very low yield, is believed to be a true acetylene complex, analogous to the $Co_2(CO)_6(RC_2R')$ complexes.

4. $Fe_2(CO)_6[(C_6H_5)_2C_2]_2$.—This orange complex, which is the major product of the reaction, is almost certainly analogous to the Reppe and Vetter complex (Section XIIB), with a structure shown diagrammatically in LXXIII. The chemical degradative evidence for this is outlined in Fig. 3. Any symmetrical structure, involving, for example, tetraphenylcyclobutadiene bridging two iron atoms, is excluded by the high dipole moment (3.3*D*) in benzene. The degradation reactions summarized in Fig. 3 also show clearly that the two iron atoms in the complex are complexed in different ways, and suggest that the iron–carbon σ-bonds are weaker than the iron–diene bonds.

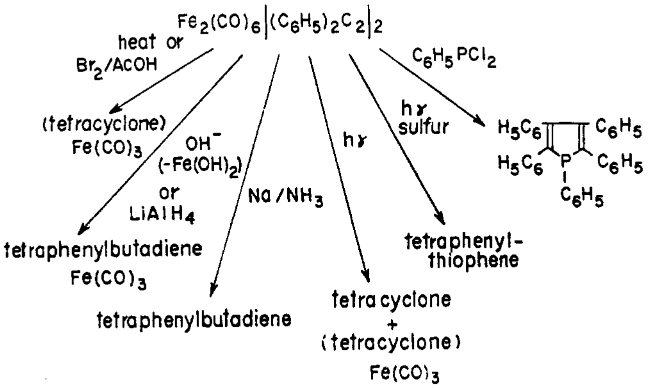
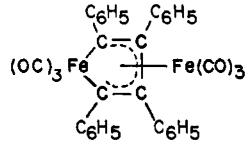
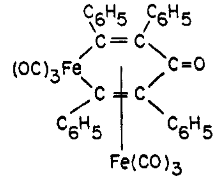


Fig. 3. Degradation reactions of $Fe_2(CO)_6[(C_6H_5)_2C_2]_2$.

5. $Fe_2(CO)_7[(C_6H_5)_2C_2]_2$.—This is believed to be analogous to (4), with a five-membered dienone unit bridging the two iron atoms [LXXIV]. The evidence for this lies in the isolation of tetraphenyl *p*-quinone in



LXXIII



LXXIV

low yields when the complex is treated with lithium aluminum hydride, sodium in liquid ammonia (139) or dilute nitric acid (213). In nearly all the thermal and photochemical degradative reactions which the complex undergoes, however, the main product is tetracyclone or its iron tricarbonyl complex, presumably formed by collapse of the six-membered ring containing $Fe(CO)_3$ as a hetero-group. This would accord with the general observation that complexes of six-membered ring unsaturated ketones are less stable than their five-membered ring counterparts (Section VIIIB).

6. $Fe_3(CO)_8[(C_6H_5)_2C_2]_2$.—The obvious formulation of this complex as a simple acetylene complex derived from $Fe_3(CO)_{12}$ seems to be eliminated by its reaction with triphenylphosphine, which gives the known complex $Fe_2(CO)_6[(C_6H_5)_2C_2]_2$ in addition to $[(C_6H_5)_3P]_2Fe(CO)_3$, and also by various reductive reactions, which give 1,2,3,4-tetraphenylbutane and (1,2,3,4-tetraphenylbutadiene)$Fe(CO)_3$. These reactions suggest that a four carbon chain is pre-formed in this complex as in $Fe_2(CO)_6[(C_6H_5)_2C_2]_2$. The infrared spectrum shows a bridging CO frequency, but the exact structure is unknown.

D. REACTION OF IRON CARBONYLS WITH PHENYLACETYLENE

The reaction of $Fe_3(CO)_{12}$ with phenylacetylene in inert solvents is reported to give at least seven different organometallic complexes, apart from organic products such as 1,2,4-triphenylbenzene (141), but little information has been published concerning the structures of these complexes. Table II shows that, compared with the corresponding diphenylacetylene reaction, no trinuclear complex is formed, and that complexes containing relatively more acetylene units per molecule are formed.

The yellow monomeric complex $Fe(CO)_4(C_6H_5C_2H)_2$ is identical with the complex first obtained by reaction of $Fe(CO)_5$ with phenylacetylene in the presence of $Ni(CO)_4$ (Section VIIIA), and shown subsequently by several groups (68, 139, 167, 214, 215) to be (2,5-diphenylcyclopentadienone)$Fe(CO)_3$. Although three isomers of diphenylcyclopentadienone are possible, only the 2,5- complex is formed, so that ring formation is evidently stereospecific. The CO group seems to go to the carbon atom of the acetylene which carries the of largest − I effect.

The complex $Fe_2(CO)_6(C_6H_5C_2H)_2$ undoubtedly has a structure similar to its diphenylacetylene analog (LXXIII).

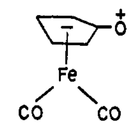
It already has been noted (Section VIIIB) that dimethylacetylene reacts with $Fe(CO)_5$ under the influence of light to give exclusively the six-membered ring complex (duroquinone)$Fe(CO)_3$ (223), whereas diphenylacetylene gives predominantly five-membered ring complexes. It is not known whether this difference is due to a difference in the inductive and mesomeric effects of methyl and phenyl, or due to a steric effect, or both. It seems possible, however, that some of the phenylacetylene complexes listed in Table II contain six-membered ring systems bonded to one or more iron atoms.

E. REACTION OF IRON CARBONYLS WITH ACETYLENE

The somewhat scanty information which has been published on this subject serves to show the importance of reaction conditions, such as temperature, pressure, nature of solvent, and nature of carbonyl, in determining what complexes are formed in iron carbonyl–acetylene reactions.

Reppe and Vetter (207) first investigated the reaction of $Fe(CO)_5$ and acetylene in aqueous alcohol under pressure, the products being ethyl acrylate, hydroquinone, and a yellow complex of formula $FeC_{11}H_7O_5$. The latter is readily decomposed by hot water or dilute acids, giving hydroquinone and a second complex $FeC_8H_4O_4$. Base treatment and subsequent mild oxidation of $FeC_8H_4O_4$ gives a third complex $FeC_7H_4O_3$, which had been tentatively formulated as a cyclobutadiene complex $C_4H_4Fe(CO)_3$ in 1956 (169).

There is agreement among subsequent investigators of this reaction (124, 239) that the complex $FeC_8H_4O_4$ is (cyclopentadienone)$Fe(CO)_3$, on the basis of comparison of its infrared spectrum with those of known substituted cyclopentadienone complexes. It is soluble not only in polar organic solvents, but also in water, probably owing to the enhanced polarity of the keto-group (Section VIIIA). The complex $C_7H_4O_3Fe$ is believed by both groups of investigators (124, 239) to be (cyclopentadienone)$Fe(CO)_2$, in which cyclopentadienone apparently functions as a formal six π-electron donor. Chemical evidence cited by Weiss, Mérenyi and Hübel (239) in support of this formulation is that the complex reacts with carbon monoxide under pressure re-forming (cyclopentadienone)$Fe(CO)_3$, and with triphenylphosphine giving (cyclopentadienone) $Fe(CO)_2[P(C_6H_5)_3]$, identical with the product obtained by direct substitution in (cyclopentadienone)$Fe(CO)_3$. In fact, this evidence is not unambiguous, in view of the known mobility of carbon monoxide when attached to transition metals, and the known tendency to form five-membered ring complexes. However, the infrared spectrum shows a band at 1567 cm.$^{-1}$, which probably is due to the stretching frequency of a strongly polarized keto-group (124). Weiss, Mérenyi and Hübel (239) state that molecular weight determinations in tetramethylene sulfone and X-ray studies (of which no details are given) support a dimeric structure for (cyclopentadienone)$Fe(CO)_2$, whereas Green, Pratt and Wilkinson (124) state that the complex is monomeric in boiling benzene. There can be little doubt that the complex is associated in the solid state, since, in contrast to (cyclopentadienone)$Fe(CO)_3$, it is insoluble in water, less soluble in organic solvents, involatile *in vacuo,* and has a high decomposition point. Further, the terminal carbonyl stretching frequencies show a marked solid state splitting effect, indicative of association (124) and it has been suggested (124) that the polarization in the dicarbonyl complex is in a direction opposite to that suggested for other cyclic dienone complexes (LXXV). In accord with this, the terminal carbonyl stretching frequencies are considerably lower than in (cyclopentadienone)$Fe(CO)_3$. It may be that there is an equilibrium between monomeric and dimeric (cyclopentadienone)$Fe(CO)_2$ in solution, but, as yet, no explanation for the dimerization and solid-state association is forthcoming.



, LXXV

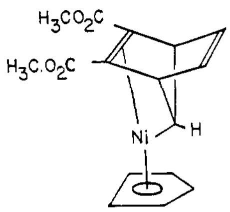
The oxidation of $FeC_8H_4O_4$ to $FeC_7H_4O_3$ may proceed *via* carbonyl hydride intermediate (cyclopentadienone)$Fe(CO)_2H_2$ (195).

The complex $C_{11}H_7O_5Fe$ is almost certainly dimeric, and it has been found to be identical with the 2:1 adduct of (cyclopentadienone)$Fe(CO)_3$ with hydroquinone, the bonding being as discussed in Section VIIIA (239). Suggestions (124) that the compound is monomeric with formula $C_{11}H_6O_5Fe$ made on the basis of examination of its n.m.r. spectrum, and that it contains a cyclopentadienone system substituted with a cyclopropene-containing unit bonded to iron, can be safely rejected; it is likely that the hydroxyl proton resonance of the hydroquinone unit was missed (202a), and the low value of the molecular weight observed in boiling benzene undoubtedly is caused by dissociation.

It is considered unlikely that the complex $FeC_{11}H_7O_5$ is the true intermediate for the formation of hydroquinone in the original Reppe and Vetter reaction. A more likely intermediate is (hydroquinone)$Fe(CO)_3$ (239), analogous to the known complex (duroquinone) $Fe(CO)_3$ (223).

Reaction of $Fe_3(CO)_{12}$ with acetylene in inert solvents has been reported briefly (142) to give: (a) orange $C_4H_4Fe_2(CO)_6$, which also is obtained as a by-product in the Reppe reaction discussed above (124), and which probably has a structure analogous to LXXIII. The same compound is obtained in the reaction of thiophene with iron carbonyls (151); (b) two isomeric complexes of formula $(C_2H_2)_3Fe_2(CO)_6$, one of which is a fulvene complex (XXIB, R = H) (143); (c) tropone iron tricarbonyl, identical with the product obtained from $Fe_3(CO)_{12}$ and tropone, (d) a complex $C_2H_2Fe(CO)_6$, which has a structure as shown in LXII (R = H). It is evident that much remains to be discovered and published about the reactions of acetylenes and metal carbonyls. Other metal carbonyls apart from iron are stated to form organometallic complexes on reaction with acetylenes (140), but full details are lacking. Manganese carbonyl is reported to react with acetylene giving a substituted π-cyclopentadienyl complex, π-dihydropentalenyl manganese tricarbonyl (50, 51).

The marked effect which a substituent can have on these acetylene reactions is well shown by comparing the reaction of nickelocene with acetylene on the one hand, and with dimethylacetylene dicarboxylate on the other. In the first case, as already noted (Section XIIA), a bridged acetylene complex is obtained. In the second case, the acetylene undergoes a Diels–Alder addition with one of the cyclopentadienyl rings, giving a complex (LXXVI) (83), whose structure is somewhat analogous to that of π-$C_5H_5NiC_5H_7$ (Section XIA).



LXXVI

XIII. MECHANISM OF OLEFIN–COMPLEX FORMATION; SOME NEW TYPES OF OLEFIN COMPLEX

Very few studies have been carried out on the mechanisms of any of the reactions outlined in this Review. Nor would such studies be easy in view of the complexity of most of the reactions, *i.e.*, the use of elevated reaction products, polymerization of the olefins, *etc.*

Orgel (195) has presented some general considerations of the reaction steps which may be involved in the synthesis of olefin and acetylene metal complexes. Emphasis is placed on the importance of "coördinately unsaturated" and "coördinately over-saturated" species as possible intermediates. The former have fewer electrons than are required for a closed shell configuration, and therefore tend to take up any available ligand, while the latter have electrons in excess of the closed shell configuration, and tend to expel ligands in order to reach it.

The three main steps are summarized by Orgel (195): (1) reactions of coördinately saturated molecules (often, metal carbonyls) with ligands; (2) equilibration of carbonyl or other groups within the intermediate complex; (3) rapid reactions of the coördinately unsaturated species with ligands, which may be CO in the environment.

Step (1) may involve SN1 monomolecular decomposition of the carbonyl

$$M(CO)_n \rightarrow M(CO)_{n-1} + CO$$

followed by a rapid reaction of type (3). Alternatively, it may involve an SN2 reaction, in which a coördinately over-saturated molecule is formed, either as a transition state or as a true intermediate, which can then lose a ligand or undergo carbonyl equilibration, or both.

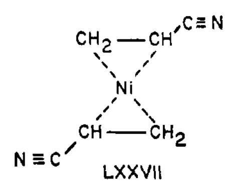
In view of the stability of metal carbonyls, it is not surprising that step (1) requires considerable activation energy, both for SN1 and SN2 mechanisms, and hence that the reactions require high temperatures. In the case of iron carbonyl reactions, it is frequently observed that complex formation occurs much more readily under ultraviolet irradiation, and that trimeric iron tetracarbonyl $Fe_3(CO)_{12}$ reacts thermally much more readily than $Fe(CO)_5$. These observations suggest that the 16-electron molecule $Fe(CO)_4$ is an intermediate in the reaction of iron carbonyls with olefins and acetylenes, and also in the photochemical decomposition of $Fe(CO)_5$ itself.

$$Fe(CO)_5 \text{ (excess)} \xrightarrow{h\nu} Fe(CO)_4 + CO$$
$$Fe(CO)_4 + Fe(CO)_5 \rightarrow Fe_2(CO)_9$$
$$Fe_2(CO)_9 \xrightarrow{\text{heat}} Fe(CO)_5 + Fe(CO)_4$$
$$3Fe(CO)_4 \rightarrow Fe_3(CO)_{12}$$

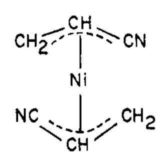
However, an early study of the photochemical decomposition of $Fe(CO)_5$ (90), and a more recent exchange study of labelled carbon monoxide with $Fe(CO)_5$ (156a), are not in favor of the SN1 mechanism, with $Fe(CO)_4$ as intermediate. On the other hand, exchange and photochemical studies (197, 226) on the Group VI metal hexacarbonyls show evidence in favor of the existence of a transient metal pentacarbonyl intermediate.

Examples of step (2) are now well-known, *e.g.*, the reactions discussed briefly in Section XIA. The importance of unsaturated and over-saturated intermediates is shown by the ability of a number of olefinic ligands to vary the number of π-electrons which they supply to transition metal atoms, *e.g.*, cycloheptatriene supplies four π-electrons in its iron tricarbonyl complex, and six π-electrons in its chromium tricarbonyl complex (see, however, Section XV), and a similar situation apparently exists in the tricarbonyl- and dicarbonyl iron complexes, respectively, of cyclopentadienone. Furthermore, a limited number of olefin complexes now are known, as stable isolable entities, in which the closed shell inert gas configuration is not attained.

Nickel carbonyl reacts with acrylonitrile to give a red, crystalline complex of formula $(acrylonitrile)_2Ni$ (214, 216) which is sparingly soluble in organic solvents and is pyrophoric. The involvement of the π-electrons of acrylonitrile in bonding to nickel is shown by the shift of vinyl absorption in the infrared, and by the fact that the C≡N stretching frequency is lowered slightly (119, 214); if bonding occurred through the nitrogen, as in $(acrylonitrile)_2 \cdot PdCl_2$, an increase in the C≡N stretching frequency would be expected. Possible formulations for the complex are shown in LXXVII and LXXVIII.



LXXVII



LXXVIII

Formally, there are insufficient π-electrons available from acrylonitrile for the closed shell configuration, and in fact (acrylonitrile)$_2$Ni behaves in some respects like an electron-deficient molecule. It shows a small, but definite, magnetic moment (the magnitude of which, 1.2 B.M., remains unexplained) and it is capable of adding one and two molecules of triphenylphosphine successively, giving yellow complexes of formula Ni(acrylonitrile)$_2$[$(C_6H_5)_3P$] and Ni(acrylonitrile)$_2$·[$(C_6H_5)_3P$]$_2$, both of which are diamagnetic and very unstable in air (214, 215, 216).

An important observation is that Ni(acrylonitrile)$_2$·[$(C_6H_5)_3P$] appears to be the catalytically active intermediate in the reaction of acrylonitrile with acetylene in the presence of the Reppe [$(C_6H_5)_3P$]Ni(CO)$_3$ catalyst giving 2,4,6-heptatrienenitrile (36). It is formed by the reaction

$$Ni(CO)_3[P(C_6H_5)_3] + 2CH_2{=}CHCN \rightarrow Ni(CH_2{=}CHCN)_2[P(C_6H_5)_3] + 3CO$$

and presumably there are further intermediates such as $Ni(CH_2{=}CHCN)_2(C_2H_2)_2$ and $Ni(CH_2{=}CHCN)_2(C_2H_2)_2[P(C_6H_5)_3]$ which then rearrange in some manner to give heptatrienenitrile (214). Further, bis-acrylonitrile nickel catalyzes the polymerization of acetylene to cycloöctatetraene, so that the rearrangements may involve cyclobutadiene intermediates (214).

The replacement of all four CO ligands of nickel carbonyl by acrylonitrile is remarkable in view of the reluctance with which it undergoes substitution reactions with most olefin systems. Analogs of (acrylonitrile)$_2$Ni are obtained by this method only when the double bond is activated by one or more electron-withdrawing substituents in the α-position (*e.g.*, CN, CHO) (214, 216). Table VIII shows the complexes of this type which have been prepared. Obviously, an electron-withdrawing substituent will assist in the back-donation of electrons from the nickel atom to antibonding orbitals of the olefin, and it will simultaneously hinder donation of electrons in the reverse direction from the π-orbitals of the olefin. It has been noted that the difference between the lowest π*-levels of olefins and the ionization potential of nickel is smallest for acrylonitrile and acrolein (216). The final effect may be to cause rehybridization at the carbon atoms, and lead to metal to carbon bonds with partial σ-character.

The corresponding acrolein complexes are notably less stable than their acrylonitrile analogs, and differ somewhat from them in their infrared spectra (119, 216). The C=C stretching frequency in (acrolein)$_2$Ni is only slightly lower than in free acrolein, whereas that in (acrylonitrile)$_2$Ni is 164 cm.$^{-1}$ lower than in free acrylonitrile. Further, the C–O stretching frequency in (acrolein)$_2$Ni is 157 cm.$^{-1}$ lower than in free acrolein. These facts suggest that in (acrolein)$_2$Ni, bonding to nickel occurs through the carbonyl oxygen atom, or at least that there is a considerable contribution from the limiting form $^+CH_2{-}CH{=}CH{-}O^-$ in the final structure. In (acrylonitrile)$_2$Ni, on the other hand, there is probably an increased contribution from the form $^+CH_2{-}CH{=}C{=}N^-$. These spectral differences are much less marked in the triphenylphosphine nickel complexes of both acrolein and acrylonitrile, presumably owing to the shift of π-electron density on the phosphorus atoms.

The effect on complex formation of a strongly electron withdrawing substituent attached to carbon atoms of the double bond is shown by the reaction of fluoroölefins with metal carbonyls. Tetrafluoroethylene was reported initially to react with $Fe_3(CO)_{12}$ or $Fe(CO)_5$ giving an olefin complex $(C_2F_4)_2Fe(CO)_3$ (236), but subsequent work (138, 172, 237) has shown that

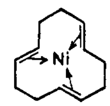
TABLE VIII
ZEROVALENT NICKEL–OLEFIN COMPLEXES

Organic ligand	Formula of complex	Physical properties	Preparation	Infrared	Dipole moment, D (solvent)
Acrylonitrile	$(CH_2{=}CHCN)_2Ni$	Red crystals	(214) (216)	(119) (214) (216)	—
	$(CH_2{=}CHCN)_2Ni[P(C_6H_5)_3]$	Yellow powder m.p. 185°	(214) (216)	(119) (214) (216)	—
	$(CH_2{=}CHCN)_2Ni[P(C_6H_5)_3]_2$	Yellow, fluorescent crystals d. >140°	(215) (216)	(119) (215) (216)	6.00 ± 0.07 (benzene) (215)
Acrolein	$(CH_2{=}CHCHO)_2Ni$	Not stated	(215) (216)	(119) (215) (216)	—
	$(CH_2{=}CHCHO)_2Ni[P(C_6H_5)_3]_2$	Yellow-red crystals d. ~140°	(215) (216)	(119) (215) (216)	—
Fumaronitrile	$(NC\cdot CH{=}CHCN)_2Ni$	Not stated	(216)	—	—
Cinnamonitrile	$(C_6H_5CH{=}CHCN)_2Ni$	Not stated	(216)	—	—
Duroquinone	$(C_{10}H_{12}O_2)_2Ni$	Red crystals	(217)	(217)	—
Cycloöcta-1,5-diene	$(C_8H_{12})_2Ni$	Yellow crystals	(241)	—	—
Cycloöcta-1,5-diene	$C_8H_{12}Ni[P(C_6H_5)_3]_2$	Not stated	(243)	—	—
trans, trans, trans-Cyclododeca-1,5,9-triene	$C_{12}H_{18}Ni$	Red crystals d. 140–150°	(241)	—	—
Cycloöctatetraene	C_8H_8Ni	Black crystals	(241)	—	—

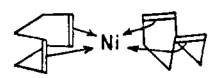
this complex is $(CF_2)_4Fe(CO)_4$, with σ-bonds to the metal. The compound $C_6F_8Fe(CO)_3$ obtained from $Fe_3(CO)_{12}$ and perfluorocyclohexa-1,3-diene does appear to be a genuine olefin complex, however (236, 237).

A consideration of possible mechanisms for metal carbonyl–acetylene reactions leads logically to a consideration of new methods of forming metal–olefin complexes. In most of the experiments surveyed here, olefin complexes of metals in low or zero-valent states have been prepared by carrying out substitution reactions on the most stable, low-valent metal complexes known, namely, the metal carbonyls. As pointed out by Pauson (199), this approach is limited by the resistance to complete substitution of the metal carbonyls, so that, for example, starting from $Cr(CO)_6$, one can obtain (benzene)$Cr(CO)_3$, but not (benzene)$_2$Cr. A very general approach to the preparation of low-valent metal complexes is to treat a salt of the metal with the ligand in the presence of a strong reducing agent, which may on occasion be the ligand itself (40). Hitherto, this method has found little application to the preparation of metal–olefin complexes, mainly because most of the usual reducing agents destroy either the olefin or the final complex. However, it is known from the work of Zeiss and co-workers (250) that compounds such as triphenylchromium tris-tetrahydrofuranate $(C_6H_5)_3Cr \cdot 3C_4H_8O$, and related complexes of other transition metals, are capable of polymerizing acetylenes to benzene and naphthalene derivatives. Under appropriate conditions, metal complexes, such as bis-benzene chromium, may be isolated, and hydrogen abstraction reactions forming cyclohexa-1,3-dienes also have been observed (250). Wilke and Kröner (242) have shown that a Ziegler-type catalyst made from a mixture of chromyl chloride and triethylaluminum is capable of trimerizing and complexing but-2-yne to bis(hexamethylbenzene)chromium(0), and of trimerizing butadiene to a mixture of *cis, trans, trans* and *trans, trans, trans*-cyclododeca-1,5,9-triene. It seems likely that the true catalysts are trialkyl or triaryl chromium(III) complexes (250), which react with the acetylene or butadiene giving intermediate π-complexes containing three acetylene or butadiene units bound to chromium (241). Subsequently, the acetylene or butadiene molecules cyclize, and, depending on the reaction conditions, the synthesized cyclic unit may or may not remain complexed to the metal atom.

Although efforts to isolate the intermediate in the trimerization of butadiene by chromium catalysts are reported to be unsuccessful so far (241), experiments using similar reduced nickel catalysts have been more rewarding (241, 243). First, it seems to be possible to control stereospecifically the nature of the dimers and trimers produced in the reaction by varying the nature of the catalyst. Second, one of the likely intermediates in the reaction actually has been isolated by treating nickel acetylacetonate in ether with all-*trans*-cyclododeca-1,5,9-triene in the presence of aluminum trialkyls (241). This complex is cyclododeca-1,5,9-triene-nickel(0) (LXXIX), which forms red, air-sensitive, diamagnetic crystals.



LXXX



LXXIX

In this complex, nickel(0) has a 16-electron shell, counting six π-electrons from the three double bonds, and it has not reached the inert gas configuration usually found for zerovalent nickel. It probably is analogous to (acrylonitrile)$_2$Ni$[(C_6H_5)_3P]$ in forming sp^2 hybrid bonds.

The triene in the above complex can be replaced by cycloöcta-1,5-diene, although the reaction is reversible. The product is the yellow, sublimable, diamagnetic, 18-electron complex bis(cycloöcta-1,5-diene)nickel(0) (LXXX) (241). This probably contains tetrahedral, zerovalent nickel similar to nickel carbonyl, and it is of interest that all attempts to replace the CO groups of nickel carbonyl with cycloöcta-1,5-diene have been unsuccessful (46). In contrast, the reductive method of forming cyclododecatriene nickel, followed by ligand exchange reactions, has yielded complexes such as $[(C_6H_5)_3P]_2Ni(0)(1,5\text{-}C_8H_{12})$, (acac)$Ni(1,5\text{-}C_8H_{12})$ with cycloöcta-1,5-diene, and $(C_8H_8)_2Ni$ and C_8H_8Ni with cycloöctatetraene (241, 243), which have so far proved completely inaccessible by other methods. More detailed accounts of this work, and its extension to other systems, are awaited with interest.

XIV. PROTON RESONANCE SPECTRA OF METAL–OLEFIN COMPLEXES

The possibility of obtaining information about the nature of olefin to metal bonding has led to the measurement of the high resolution proton resonance spectra of a wide variety of complexes. These measurements are facilitated by the good solubility of many of the complexes, especially the carbonyl complexes, in organic solvents. However, although n.m.r. has been of great value in solving problems relating to the structures of various complexes, as mentioned elsewhere in this review, it has not on the whole provided much information about the actual bond-type, *i.e.*, on whether the double bonds remain essentially as such in the complex, or whether structures involving σ-bonds to the metal are involved.

In the olefin complexes of silver and platinum, the olefinic proton resonance does not differ greatly from that in the free olefin, which is good evidence for the retention of the double bond in these complexes (202). In the complexes of type [(diene)RhCl]$_2$ and (diene)M-$(CO)_4$ (M = Cr, Mo) formed by cycloöcta-1,5-diene and norbornadiene, the olefinic proton resonances are shifted somewhat to higher field compared with the free diene (18, 123, 124, 126), and in (norbornadiene)-$Fe(CO)_3$ the shift is sufficient to bring the olefinic proton resonance well into the aliphatic region. In the case of metal complexes of conjugated diolefins and tri-olefins, such as butadiene, cyclopentadiene, cyclohexa-1,3-diene and cycloheptatriene, there is a characteristic separation of the coördinated olefin proton resonances into a low-field and a high-field band; the former is due to the central protons of the diene system, the latter to the terminal protons (17, 33, 34, 123, 124). The high-field bands occur in the "aliphatic" region of the spectrum, and, if the simple correlation rules found experimentally between the chemical environment of a hydrogen atom and the relative position of its resonance line in the case of organic molecules were assumed to be valid for these complexes, then structures involving σ-bonds to the metal (*e.g.*, structure X for $C_4H_6Fe(CO)_3$, modified by coördination of the double bond to iron) would be favored. However, infrared and X-ray data do not favor σ-bonded structures. The initial problem is therefore reversed, and it is required now to be able to explain the observed n.m.r. spectrum, knowing the structure and bonding in the complex.

The resonance position of a proton in any olefin depends on diamagnetic shielding by the electrons of the C–H σ-bond. The shielding alters with changes in the electronegativity of the carbon atoms, as, for example, when the π-electrons of a double bond are involved in bonding to a metal. Nevertheless, such an effect probably would not be large enough to explain the observed upfield shifts, and it should furthermore affect all the olefinic protons approximately equally. It is known that proton resonances can be altered by a "long-range" shielding effect which arises from the electrons in other bonds, especially π-electrons (144a). The magnetic moment induced in the π-electrons by the applied magnetic field produces small, additional magnetic fields at the protons which alters their line positions; this effect can only arise from bonds which are magnetically anisotropic. The effect produced by this anisotropy can be represented approximately by supposing a point magnetic dipole to be placed at the middle of each bond, with its axis pointing along the direction of maximum polarizability, and then calculating the magnetic field due to this dipole at the various proton positions.

In a metal–olefin bond, the electrical center will be displaced from the center of the C=C bond toward the metal atom, so that the long-range shielding will be altered when the π-electrons are involved in bonding to a metal. Also, the direction of maximum susceptibility of the bond depends on the direction of the metal to C=C axis, and changes in this affect the distance and orientation of the point dipole relative to the olefinic protons. In the complexes of cyclic poly-olefins and chelating diolefins, the conformation of the olefin does not allow the metal atom to occupy a position normal to the C=C bond axis, as it does in the ethylene complexes. Using known structural data on (cycloheptatriene)·$Mo(CO)_3$ (86), it is possible to reproduce the main features of the observed proton resonances of this complex by assuming the point dipole to be located about one-third of the distance toward the metal atom, and pointing along the metal to C=C axis (17). It is also possible to explain qualitatively the observed resonances in (norbornadiene)$M(CO)_4$ (M = Cr, Mo) (17), (norbornadiene)$Fe(CO)_3$ and the iron tricarbonyl complexes of conjugated dienes on this model (202a). As more X-ray data become available on a wider range of these compounds, it is probable that more refined calculations will be made.

XV. Theoretical Treatments

The information surveyed here suggests that olefin complexes may be classified with the more familiar cyclopentadienyl and arene complexes under the loose term of "π-complexes." The complexes of monoölefins and unconjugated diolefins may be considered as the simplest example of π-complexes, since, in these compounds, the π-orbital of the olefin involved in bonding to the metal is spread over just two carbon atoms, whereas in the complexes of conjugated olefins, the π-orbital may be spread over 3, 4, 5, 6, 7 or 8 carbon atoms. It is not surprising, therefore, that molecular-orbital treatments of the bonding in these complexes follow the same lines as those used for the metal cyclopentadienyls and, specifically, the "half-sandwich" metal carbonyls and nitrosyls (196, 244).

The simplest case to consider is that of a cyclic planar polyolefin system C_nH_n, whose molecular π-orbitals are determined by symmetry only, attached to a transition metal atom in, for example, $C_nH_nMY_3$ (25, 196). An example of the treatment is provided by the paper predicting the stability of cyclobutadiene complexes $C_4H_4NiA_2$ (169). For the sake of simplicity, it is necessary to classify the π-orbitals and the ligand (Y) orbitals in terms of their respective local symmetries, while the metal orbitals are classified with respect to the ring system. Since the final results are purely qualitative, this assumption leads to no great error. It is found that the stable, filled, totally symmetrical orbital of the ring is stabilized by mixing with one component of the (4s $\pm$ 4Pz) orbitals of the metal, one orbital is directed toward the ring system, the other toward the ligands. The bonds so formed are the μ-bonds, and they involve charge transfer to the metal atom. The doubly degenerate e_1 π-orbitals of the ring system can overlap with the metal hybrids $3d_{xz}/4p_x$ and $3d_{yz}/4p_y$, forming π-bonds. Lastly, there is the possibility of overlap of empty

e_2 π-orbitals on the ring with filled metal $3d_{xy}$ orbitals; these are δ-bonds, and they tend to remove negative charge from the metal atom. Approximate group overlap calculations, made on the assumption that the main source of stability arises from e_1 π-binding, suggest that overlap is a maximum for five- and six-membered ring systems, and that it decreases rapidly for larger ring systems (25); also that phenyl-substituted ring systems should form more stable complexes than unsubstituted or alkyl substituted ring systems (31). However, the notable stability of $C_8H_8Fe(CO)_3$ does not seem to bear out the former prediction. This case is of interest, since the cyclooctatetraene ring, if planar, would be a diradical with two unpaired e_2 electrons, and these are available for bonding with e_2 electrons of the metal (d_{xy} and $d_{x^2-y^2}$) (65).

The treatment has been extended to the complexes formed from ring systems containing hetero-groups, such as $>C{=}O$ in the cyclic unsaturated ketone complexes (26, 29). The lower symmetry of the cyclic system in this case allows a more complicated interaction of the ring π-orbitals with the metal orbitals, and it is found that it is necessary for the metal $3d_{xz}$ orbitals to be empty, since they have to overlap with filled orbitals of the ring system and the ligands (26). Consequently, in the case of the higher members of the first transition series, such as iron, which possess filled $3d_{xz}$ and $3d_{yz}$ orbitals, the presence on the ring system of a suitable low-lying vacant orbital is required, since this can accommodate electrons promoted from the metal atom. Such an orbital is available in systems of the type C_4H_4Z, Z being the hetero-group.

The qualitative treatment also has been extended to include binuclear complexes in which the π-system is located symmetrically between two metal atoms, *e.g.*, $Y_mMC_nH_nMY_m$ (25). The symmetry interactions of metal, ligand and ring π-orbitals are almost identical with those in the mononuclear case, except that a given π-orbital overlaps on both sides of its nodal plane with identical hybrid metal orbitals. Thus the metal–olefin overlap can be regarded as consisting of three-center π-orbitals covering the metal atom and the π-system (25, 27).

No evidence has been published at the time of writing concerning the existence of such symmetrical binuclear complexes, but the essentials of the treatment have been carried over to include complexes such as Reppe and Vetter's complex $Fe_2C_{10}H_4O_8$ (Section XIIB) (27) and the azulene complexes (Section IX) (28). In the former case, it is believed that overlap occurs in perpendicular planes of different π-orbitals of the butadiene residue with orbitals of the two metal atoms, and the delocalized electrons can be regarded as occupying bent three-center orbitals.

The applicability of the Inert Gas Rule to π-complexes has been criticized strongly on theoretical grounds (29). It is pointed out that donation from π-orbitals of the ligands to empty metal orbitals involves impossibly large charge transfer to the metal atom, and that, in π-complexes, a particular metal hybrid orbital may overlap with a number of π-orbitals of the organic system which have the same symmetry. This happens, for example, in the case of (cycloheptatrienone)$Fe(CO)_3$ (29). In (cyclopentadienone)$Fe(CO)_3$ and (cycloheptatrienone)$Fe(CO)_3$, there are two and four π-electrons, respectively, in excess of the closed shell configuration, and their presence is balanced by the presence on the ring systems of vacant low-lying orbitals (26, 29). If the ring system supplies more than four π-electrons in, for example, an iron tricarbonyl complex, it is necessary to make use of the vacant ring orbitals in order to remove excess charge from the metal atom. On this basis, the tendency to basic behavior observed in (cycloheptatriene)$Fe(CO)_3$ and cyclopentadienone complexes can be attributed to donation of electrons in these ring orbitals to suitable electron acceptors.

Nevertheless, the Inert Gas Rule is essentially a formalism which does seem to work for a wide variety of complexes, especially carbonyl containing complexes. It makes no claim to provide an accurate picture of the bonding and charge distribution in these complexes. Furthermore, in the case of complexes such as (cyclopentadienone)$Fe(CO)_3$, the Inert Gas Rule still holds true if one counts only the π-electrons of the olefinic double bonds, and excludes those of the keto-group. As pointed out in Section VIII, the observed properties of cyclopentadienone complexes, including their tendency to combine with electron acceptors, can be explained reasonably by invoking resonance between two valence-bond structures, one of which involves donation of a shared pair of electrons on the metal atom to the ring system. Similarly, the basic properties of (cycloheptatriene)$Fe(CO)_3$ can be explained by assuming that one of the double bonds takes essentially no part in bonding to the metal.

It is true, however, that on the basis of the Inert Gas Rule, complexes of formula (cycloheptatrienone)Fe$(CO)_2$ and (cycloheptatriene)$Fe(CO)_2$ would be expected to exist, rather than the tricarbonyl complexes (29). In fact, very few mononuclear dicarbonyl complexes of aromatic systems are known; thus, (mesitylene)$Fe(CO)_2$ and similar arene compounds have not been discovered as yet, although π-$C_5H_5Co(CO)_2$ is well established. (Cyclopentadienone)$Fe(CO)_2$ may be another example, although more investigation of this complex is required, and one of the rings in (azulene)-$Fe_2(CO)_5$ must carry an $Fe(CO)_2$ group. Perhaps it is not only the presence of vacant low-lying orbitals on the organic ligand which is of importance, but also the presence of a sufficient number of additional ligands with low-lying vacant orbitals, such as CO, in order to remove negative charge from the metal atom. It seems probable that the extent of charge transfer to the metal would be far greater in, say, (mesitylene)$Fe(CO)_2$ than in π-$C_5H_5Co(CO)_2$, and this would account for the stability of the latter compared with the former.

To summarize, the Inert Gas Rule merely expresses in simple form the fact that complexes containing more than 18 electrons must have electrons in antibonding orbitals or in higher energy orbitals on the metal, and, as Brown (29) points out, the rule may no longer apply when the organic ligand contains low-lying vacant orbitals. Further, the existence of stable metal-olefin complexes which do not have an 18-electron outer shell shows that the rule can be violated.

At present, there is no explanation for the almost complete equalization of interatomic carbon–carbon distances observed in (butadiene)$Fe(CO)_3$ and π-C_5H_5Co(tetramethylcyclopentadienone), in contrast to the alternating single- and double-bond lengths observed in bis-benzene chromium and (cycloheptatriene)-$Mo(CO)_3$. It seems at first sight that, in the latter complexes, three conjugated double bonds are functioning essentially independently, but, as Craig (69) has emphasized, there is no consistent way of using bond lengths as a measure of aromaticity even in carbon compounds, without introducing the additional variable of complexing to different transition metals.

XVI. CONCLUSION

It is not difficult to predict that many new compounds belonging to the ever-growing family of π-complexes will be discovered, and, in particular, developments can be anticipated in the isolation of stable complexes which contain electrons in excess of the 18-electron shell, and those which contain fewer than 18 electrons. There are likely to be many developments in the field of organic synthetic reactions based on labile π-complex intermediates.

A number of π-complexes are now known in which the organic moiety acts essentially as a bridging group between two transition metal atoms and, in at least one case (30), the importance of metal–metal bonding has been emphasized on theoretical grounds. Developments in this field may be related to current interest in metal–metal interaction in other binuclear and polynuclear transition metal complexes.

The importance of accurate X-ray studies on a number of reference compounds cannot be over-emphasized. With accurate structural data, it should be possible to refine and extend the crude, qualitative theoretical treatments which have been given so far. This is especially true of the binuclear π-complexes already mentioned, for whose structures it is frequently difficult to write formal valence-bond representations. In these cases, the Inert Gas Formalism is considerably less useful than in the mononuclear complexes. It may be noted finally that only in the case of the silver–olefin complexes has any attempt been made to evaluate the metal–olefin bond energy, and it is possible that measurements on the heats of combustion of many of the complexes surveyed here would provide information on this point.

The author wishes to thank the U. S. Atomic Energy Commission for support (Contract AT(11–1)–113) during the period in which this review was prepared. Thanks are due to Professor Arthur Adamson for his criticisms and comments on the manuscript, to Professor Geoffrey Wilkinson, who first suggested that the review be written, to Dr. L. Pratt for helpful discussions, and, last but not least, to Mrs. D. Hartzler for her careful typing of the manuscript. Acknowledgment also is due to the Chemical Society, London, for permission to quote from reference (46), and to reproduce Fig. 12 from reference (185).

XVII. REFERENCES

(1) Abel, E. W., Apar Singh, and Wilkinson, G., *J. Chem. Soc.* 1321 (1960).
(2) Abel, E. W., Bennett, M. A., Burton, R., and Wilkinson, G., *J. Chem. Soc.*, 4559 (1958).
(3) Abel, E. W., Bennett, M. A., and Wilkinson, G., *Proc. Chem. Soc.*, 152 (1958).
(4) Abel, E. W., Bennett, M. A., and Wilkinson, G., *J. Chem. Soc.*, 2323 (1959).
(5) Abel, E. W., Bennett, M. A., and Wilkinson, G., *J. Chem. Soc.*, 3178 (1959).
(6) Abel, E. W., Hargreaves, G. B., and Wilkinson, G., *J. Chem. Soc.*, 3149 (1958).
(7) Adams, D., and Chatt, J., *Chemistry and Industry*, 149 (1960).
(8) Aldridge, C. L., Jonassen, H. B., and Pulkkinen, E., *Chemistry and Industry*, 374 (1960).
(9) Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.*, **70**, 3261 (1948).
(9a) Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.*, **71**, 2379 (1949).
(10) Avram, M., Dinu, D., and Nenitzescu, C. D., *Chemistry and Industry*, 257 (1959).
(11) Avram, M., Marica, E., and Nenitzescu, C. D., *Chem. Ber.*, **92**, 1088 (1959).
(12) Avram, M., Marica, E., Pogany, J., and Nenitzescu, C. D., *Angew. Chem.*, **71**, 626 (1959).
(13) Avram, M., Mateescu, G., Dinulescu, I. G., Marica, E., and Nenitzescu, C. D., *Tetrahedron Letters* No. 1, 21 (1961).
(14) Avram, M., Sliam, E., and Nenitzescu, C. D., *Ann.*, **636**, 184 (1960).
(15) Baker, W., and McOmie, J. F. W., "Non-benzenoid Aromatic Compounds," Interscience Publishers, New York, N.Y., 1959, Chap. 2, p. 43.
(16) Basolo, F., and Pearson, R. G., "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N.Y., Chap. 8, p. 352.
(17) Bennett, M. A., Pratt, L., and Wilkinson, G., *J. Chem. Soc.*, 2037 (1961).
(18) Bennett, M. A., and Wilkinson, G., *Chemistry and Industry*, 1516 (1959).

(19) Bennett, M. A., and Wilkinson, G., *J. Chem. Soc.*, 1418 (1961).
(20) Bird, C. W., Cookson, R. C., and Hudeč, J., *Chemistry and Industry*, 20 (1960).
(21) Bird, C. W., and Hudeč, J., *Chemistry and Industry*, 570 (1959).
(21a) Blake, D., Calvin, G., and Coates, G. E., *Proc. Chem. Soc.*, 396 (1959).
(22) Boston, J. L., Sharp, D. W. A., and Wilkinson, G., *Chemistry and Industry*, 1137 (1960).
(23) Braye, E. H., and Hübel, W., *Chemistry and Industry*, 1250 (1959).
(24) Breslow, D. S., and Heck, R. F., *Chemistry and Industry*, 467 (1960).
(25) Brown, D. A., *J. Inorg. Nucl. Chem.*, **10**, 39 (1959).
(26) Brown, D. A., *J. Inorg. Nucl. Chem.*, **10**, 49 (1959).
(27) Brown, D. A., *J. Inorg. Nucl. Chem.*, **11**, 9 (1959).
(28) Brown, D. A., *Chemistry and Industry*, 126 (1959).
(29) Brown, D. A., *J. Inorg. Nucl. Chem.*, **13**, 212 (1960).
(30) Brown, D. A., *J. Chem. Phys.*, **33**, 1037 (1960).
(31) Brown, D. A., abstracts of papers presented at the International Conference on Coordination Chemistry, London, April, 1959, Chemical Society Special Publication No. 13, p. 124.
(32) Burton, R., Green, M. L. H., Abel, E. W., and Wilkinson, G., *Chemistry and Industry*, 1592 (1958).
(33) Burton, R., Pratt, L., and Wilkinson, G., *J. Chem. Soc.*, 4290 (1960).
(34) Burton, R., Pratt, L., and Wilkinson, G., *J. Chem. Soc.*, 594 (1961).
(35) Burton, R., and Wilkinson, G., *Chemistry and Industry*, 1205 (1958).
(36) Cairns, T. L., Engelhardt, V. A., Jackson, H. L., Kalb, G. H., and Sauer, J. C., *J. Am. Chem. Soc.*, **74**, 5636 (1952).
(37) Carter, F. L., and Hughes, E. W., *Acta Cryst.*, **10**, 801 (1957).
(38) Case, J. R., Clarkson, R., Jones, E. R. H., and Whiting, M. C., *Proc. Chem. Soc.*, 150 (1959).
(39) Chatt, J., *Chem. Rev.*, **48**, 7 (1951).
(40) Chatt, J., lecture delivered at the International Symposium on the Chemistry of Coordination Compounds, Rome, September, 1957; *J. Inorg. Nucl. Chem.*, **8**, 515 (1958).
(41) Chatt, J., and Duncanson, L. A., *J. Chem. Soc.*, 2939 (1953).
(42) Chatt, J., and Hayter, R. G., *J. Chem. Soc.*, 896 (1961).
(43) Chatt, J., Pauson, P. L., and Venanzi, L. M., "ACS Monograph on Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., Chap. 10, p. 468.
(44) Chatt, J., and Shaw, B. L., *Chemistry and Industry*, 931 (1960).
(45) Chatt, J., and Venanzi, L. M., *Nature*, **177**, 852 (1956).
(46) Chatt, J., and Venanzi, L. M., *J. Chem. Soc.*, 4735 (1957).
(47) Clarkson, R., Jones, E. R. H., Wailes, P. C., and Whiting, M. C., *J. Am. Chem. Soc.*, **78**, 6206 (1956).
(48) Coates, G. E., "Organometallic Compounds," 2nd Ed., Methuen, London, 1960, Chap. 6, p. 233.
(49) Coates, G. E., and Glockling, F., "ACS Monograph on Organometallic Chemistry," Reinhold Publishing Corp., New York, N.Y., Chap. 9, p. 426.
(50) Coffield, T. H., Ihrman, K. G., and Burns, W., *J. Am. Chem. Soc.*, **82**, 1204 (1960).
(51) Coffield, T. H., Ihrman, K. G., and Burns, W., *J. Am. Chem. Soc.*, **82**, 4209 (1960).
(52) Coffield, T. H., Kozikowski, J., and Closson, R. D., abstracts of papers presented at the International Conference on Coordination Chemistry, London, April, 1959; Chemical Society Special Publication No. 13, p. 126.
(53) Colton, R., Levitus, R., and Wilkinson, G., *Nature*, **233**, 186 (1960).
(54) Comyns, A. E., and Lucas, H. J., *J. Am. Chem. Soc.*, **79**, 4339 (1957).
(55) Comyns, A. E., and Lucas, H. J., *J. Am. Chem. Soc.*, **79**, 4341 (1957).
(56) Cope, A. C., and Bumgardner, C. L., *J. Am. Chem. Soc.*, **78**, 2812 (1956).
(57) Cope, A. C., and Campbell, H. C., *J. Am. Chem. Soc.*, **74**, 179 (1952).
(58) Cope, A. C., and Hochstein, F. A., *J. Am. Chem. Soc.*, **72**, 2515 (1950).
(59) Cope, A. C., and Kintner, M. R., *J. Am. Chem. Soc.*, **72**, 630 (1950).
(60) Cope, A. C., and Marshall, D. J., *J. Am. Chem. Soc.*, **75**, 3208 (1953).
(61) Cope, A. C., McLean, D. C., and Nelson, N. A., *J. Am. Chem. Soc.*, **77**, 1628 (1955).
(62) Cope, A. C., Stevens, C. L., and Hochstein, F. A., *J. Am. Chem. Soc.*, **72**, 2510 (1950).
(63) Copenhaver, J. W., and Bigelow, M. H., "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N.Y., 1949.
(64) Corradini, P., and Allegra, G., *J. Am. Chem. Soc.*, **81**, 2271 (1959).
(65) Cotton, F. A., *J. Chem. Soc.*, 400 (1960).
(66) Cotton, F. A., and Leto, J. R., *J. Am. Chem. Soc.*, **80**, 4823 (1958).
(67) Cotton, F. A., and Leto, J. R., *Chemistry and Industry* 1368 (1958).
(68) Cotton, F. A., and Leto, J. R., *Chemistry and Industry*, 1592 (1958).
(69) Craig, D. P., "Non-benzenoid Aromatic Compounds," Interscience Publishers, New York, N.Y., 1959, Chap. 1, p. 6.
(70) Criegee, R., and Schröder, G., *Angew Chem.*, **71**, 70 (1959).
(71) Criegee, R., and Schröder, G., *Ann.*, **623**, 1 (1959).
(72) Dahl, L. F., and Smith, D. L., *J. Am. Chem. Soc.*, **83**, 752 (1961).
(73) Dauben, H. J., Jr., and Bertelli, D. J., *J. Am. Chem. Soc.*, **83**, 497 (1961).
(74) Dauben, H. J., Jr., and Honnen, H. R., *J. Am. Chem. Soc.*, **80**, 5570 (1958).
(75) Davison, A., McFarlane, W., Pratt, L., and Wilkinson, G., *Chemistry and Industry*, 553 (1961).
(76) Davison, A., and Wilkinson, G., *Proc. Chem. Soc.*, 356 (1960).
(77) Dewar, M. J. S., *Bull. soc. chim. France*, **18**, C79 (1951).
(78) Dickens, B., and Lipscomb, W. N., *J. Am. Chem. Soc.*, **83**, 481 (1961).
(79) Dodge, R. P., and Schomaker, V., *Nature*, **186**, 798 (1960).
(80) Dorsey, W. S., and Lucas, H. J., *J. Am. Chem. Soc.*, **78**, 1665 (1956).
(81) Doyle, J. R., *Chem. Rev.*, to be published.
(82) Dubeck, M., *J. Am. Chem. Soc.*, **82**, 502 (1960).
(83) Dubeck, M., *J. Am. Chem. Soc.*, **82**, 6193 (1960).
(84) Dubeck, M., and Filbey, A. H., *J. Am. Chem. Soc.*, **83**, 1257 (1961).
(85) Dunitz, J. D., Mez, H. C., and Shearer, H. M. M., paper presented at the 17th International Congress for Pure and Applied Chemistry, Munich, 1959.
(86) Dunitz, J. D., and Pauling, P., *Helv. Chim. Acta*, **43**, 2188 (1960).
(87) Eberz, W. F., Welge, H. J., Yost, D. M., and Lucas, H. J., *J. Am. Chem. Soc.*, **59**, 45 (1937).
(88) Eley, D. D., "Cationic Polymerization," Heffer and Sons, Cambridge, 1953, p. 6.

(89) Ercoli, R., Calderazzo, F., and Mantica, E., *Chimica e Industria*, **41**, 1404 (1959).
(90) Eyber, G., *Z. physik, Chem.*, **144A**, 1 (1929).
(91) Fischer, E. O., lecture delivered at the International Conference on Coordination Chemistry, London, April 1959, Chemical Society Special Publication No. 13, p. 73.
(92) Fischer, E. O., and Bürger, G., *Z. Naturforsch.*, **16b**, 77 (1961).
(93) Fischer, E. O., and Fichtel, K., *Chem. Ber.*, **94**, 1200 (1961).
(94) Fischer, E. O., and Fischer, R. D., *Angew Chem.*, **72**, 919 (1960).
(95) Fischer, E. O., and Fritz, H. P., "Advances in Inorganic Chemistry and Radiochemistry," Academic Press, New York, N.Y., 1959, Vol. I, p. 55.
(96) Fischer, E. O., and Fröhlich, W., *Chem. Ber.*, **92**, 2995 (1959).
(97) Fischer, E. O., and Fröhlich, W., *Z. Naturforsch.*, **15b**, 266 (1960).
(98) Fischer, E. O., Kögler, H. P., and Kuzel, P., *Chem. Ber.*, **93**, 3006 (1960).
(99) Fischer, E. O., and Kriebitzsch, N., *Z. Naturforsch.*, **15b**, 465 (1960).
(100) Fischer, E. O., Kuzel, P., and Fritz, H. P., *Z. Naturforsch.*, **16b**, 138 (1961).
(100a) Fischer, E. O., and Öfele, K., *Chem. Ber.*, **91**, 2395 (1958).
(101) Fischer, E. O., Öfele, K., Essler, H., Fröhlich, W., Mortensen, J. P., and Semmlinger, W., *Z. Naturforsch.*, **13b**, 458 (1958).
(102) Fischer, E. O., Öfele, K., Essler, H., Fröhlich, W., Mortensen, J. P., and Semmlinger, W., *Chem. Ber.*, **91**, 2763 (1958).
(103) Fischer, E. O., and Palm, C., *Z. Naturforsch.*, **14b**, 347 (1959).
(104) Fischer, E. O., and Palm, C., *Z. Naturforsch.*, **14b**, 598 (1959).
(105) Fischer, E. O., Palm, C., and Fritz, H. P., *Chem. Ber.*, **92**, 2645 (1959).
(106) Fischer, E. O., and Plesszke, K., *Chem. Ber.*, **91**, 2719 (1958).
(107) Fischer, E. O., and Ulm, K., *Z. Naturforsch.*, **15b**, 59 (1960).
(108) Fischer, E. O., and Werner, H., *Chem. Ber.*, **92**, 1423 (1959).
(109) Fischer, E. O., and Werner, H., *Tetrahedron Letters*, No. 1, 17 (1961).
(110) Fischer, E. O., and Wirzmüller, A., *Z. Naturforsch.*, **12b**, 737 (1957).
(111) Fischer, E. O., and Zahn, U., *Chem. Ber.*, **92**, 1624 (1959).
(112) Fischer, E. O., Zahn, U., and Baumgärtner, F., *Z. Naturforsch.*, **14b**, 133 (1959).
(113) Fischer, R. D., *Chem. Ber.*, **93**, 165 (1960).
(114) Francis, A. W., *J. Am. Chem. Soc.*, **73**, 3709 (1951).
(115) Freedman, H. H., *J. Am. Chem. Soc.*, **83**, 2194 (1961).
(116) Freedman, H. H., *J. Am. Chem. Soc.*, **83**, 2195 (1961).
(117) Fritz, H. P., *Chem. Ber.*, **94**, 1217 (1961).
(118) Fritz, H. P., McOmie, J. F. W., and Sheppard, N., *Tetrahedron Letters*, No. 26, 35 (1960).
(119) Fritz, H. P., and Schrauzer, G. N., *Chem. Ber.*, **94**, 650 (1961).
(120) Gardner, P. D., Brandon, R. L., and Nix, N. J., *Chemistry and Industry*, 1363 (1958).
(121) Gilliland, E. R., Bliss, H. L., and Kip, C. E., *J. Am. Chem. Soc.*, **63**, 2088 (1941).
(122) Gilliland, E. R., Seebold, J. E., Fitzhugh, J. R., and Morgan, P. S., *J. Am. Chem. Soc.*, **61**, 1960 (1939).
(123) Green, M. L. H., Pratt, L., and Wilkinson, G., *J. Chem. Soc.*, 3753 (1959).
(124) Green, M. L. H., Pratt, L., and Wilkinson, G., *J. Chem. Soc.*, 989 (1960).
(125) Green, M. L. H., Street, C. N., and Wilkinson, G. Z., *Naturforsch.*, **14b**, 738 (1959).
(126) Green, M. L. H., and Wilkinson, G., *J. Chem. Soc.*, 4314 (1958).
(127) Greenfield, H., Sternberg, H. W., Friedel, R. A., Wotiz, J. H., Markby, R., and Wender, I., *J. Am. Chem. Soc.*, **8**, 1629 (1959).
(129) Hallam, B. F., and Pauson, P. L., *J. Chem. Soc.*, 642 (1958).
(130) Hallam, B. F., and Pauson, P. L., *J. Chem. Soc.*, 646 (1958).
(131) Halpern, J., Harrod, J. F., and James, B. R., *J. Am. Chem. Soc.*, **83**, 754 (1961).
(132) Heck, R. F., and Breslow, D. S., *J. Am. Chem. Soc.*, **82**, 750 (1960).
(133) Heck, R. F., and Breslow, D. S., *J. Am. Chem. Soc.*, **83**, 1097 (1961).
(134) Helmkamp, G. K., Carter, F. L., and Lucas, H. J., *J. Am. Chem. Soc.*, **79**, 1306 (1957).
(135) Hepner, F. R., Trueblood, K. N., and Lucas, H. J., *J. Am. Chem. Soc.*, **74**, 1333 (1952).
(136) Hock, A. A., and Mills, O. S., *Proc. Chem. Soc.*, 233 (1958).
(137) Hock, A. A., and Mills, O. S., *Acta Cryst.*, **14**, 139 (1961).
(138) Hoehn, H. H., Pratt, L., Watterson, K. F., and Wilkinson, G., *J. Chem. Soc.*, 1961.
(139) Hübel, W., and Braye, E. H., *J. Inorg. Nucl. Chem.*, **10**, 250 (1959).
(140) Hübel, W., Braye, E. H., Clauss, A., Weiss, E., Krüerke, U., Brown, D. A., King, G. S. D., and Hoogzand, C., *J. Inorg. Nucl. Chem.*, **9**, 204 (1959).
(141) Hübel, W., and Hoogzand, C., *Chem. Ber.*, **93**, 103 (1960).
(142) Hübel, W., and Weiss, E., *Chemistry and Industry*, 703 (1959).
(143) Hübel, W., and Weiss, E., *Angew Chem.*, **73**, 298 (1961).
(144) Irving, R. J., *J. Chem. Soc.*, 2879 (1956).
(144a) Jackman, L. M., "Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry," Pergamon Press, London, 1959.
(144b) Jellinek, F., *Nature*, **187**, 871 (1960).
(144c) Jensen, K. A., *Acta Chem. Scand.*, **7**, 868 (1953).
(145) Jonassen, H. B., Stearns, R. I., Kenttämaa, J., Moore, D. W., and Whittaker, A. G., *J. Am. Chem. Soc.*, **80**, 2586 (1958).
(146) Jones, D., Parshall, G. W., Pratt, L., and Wilkinson, G., *Tetrahedron Letters*, No. 2, 48 (1961).
(147) Jones, E. R. H., Wailes, P. C., and Whiting, M. C., *J. Chem. Soc.*, 4021 (1955).
(148) Jones, W. O., *J. Chem. Soc.*, 2036 (1953).
(149) Jones, W. O., *J. Chem. Soc.*, 312 (1954).
(150) Jones, W. O., *J. Chem. Soc.*, 1808 (1954).
(151) Kaesz, H. D., King, R. B., Manuel, T. A., Nichols, L. D., and Stone, F. G. A., *J. Am. Chem. Soc.*, **82**, 4749 (1960).
(152) Kaesz, H. D., King, R. B., and Stone, F. G. A., *Z. Naturforsch.*, **15b**, 682 (1960).
(153) Keblys, K. A., and Filbey, A. H., *J. Am. Chem. Soc.*, **82**, 4204 (1960).
(154) Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.*, **71**, 1723 (1949).
(155) Keefer, R. M., Andrews, L. J., and Kepner, R. E., *J. Am. Chem. Soc.*, **71**, 2381 (1949).
(156) Keefer, R. M., Andrews, L. J., and Kepner, R. E., *J. Am. Chem. Soc.*, **71**, 3906 (1949).
(156a) Keeley, D. F., and Johnson, R. E., *J. Inorg. Nucl. Chem.*, **11**, 33 (1959).
(157) Keller, R. N., *Chem. Revs.*, **28**, 229 (1941).

(158) Kepner, R. E., and Andrews, L. J., *J. Org. Chem.*, **13**, 208 (1948).
(159) Kettle, S. F. A., and Orgel, L. E., *Chemistry and Industry*, 49 (1960).
(160) King, R. B., Manuel, T. A., and Stone, F. G. A., *J. Inorg. Nucl. Chem.*, **16**, 233 (1961).
(161) King, R. B., and Stone, F. G. A., *Chemistry and Industry*, 232 (1960).
(161a) King, R. B., and Stone, F. G. A., *J. Am. Chem. Soc.*, **81**, 5263 (1959).
(162) King, R. B., and Stone, F. G. A., *J. Am. Chem. Soc.*, **82**, 4557 (1960).
(163) Kirch, M., and Orchin, M., *J. Am. Chem. Soc.*, **80**, 4428 (1958).
(164) Kirch, M., and Orchin, M., *J. Am. Chem. Soc.*, **81**, 3597 (1959).
(165) Kögler, H. P., and Fischer, E. O., *Z. Naturforsch.*, **15b**, 676 (1960).
(166) Krüerke, U., and Hübel, W., *Chem. and Ind.*, 1264 (1960).
(167) Leto, J. R., and Cotton, F. A., *J. Am. Chem. Soc.*, **81**, 2970 (1959).
(168) Lipscomb, W. N., quoted in reference 173.
(169) Longuet-Higgins, H. C., and Orgel, L. E., *J. Chem. Soc.*, 1969 (1956).
(170) Lucas, H. J., Billmeyer, F. W., and Pressman, D., *J. Am. Chem. Soc.*, **65**, 220 (1943).
(171) Lucas, H. J., Moore, R. S., and Pressman, D., *J. Am. Chem. Soc.*, **65**, 227 (1943).
(171a) Malatesta, L., and Vallarino, L., *J. Chem. Soc.*, 1867 (1956).
(172) Manuel, T. A., Stafford, S. L., and Stone, F. G. A., *J. Am. Chem. Soc.*, **83**, 249 (1961).
(173) Manuel, T. A., and Stone, F. G. A., *Proc. Chem. Soc.*, 90 (1959).
(174) Manuel, T. A., and Stone, F. G. A., *Chemistry and Industry*, 1349 (1959).
(175) Manuel, T. A., and Stone, F. G. A., *Chemistry and Industry*, 231 (1960).
(176) Manuel, T. A., and Stone, F. G. A., *J. Am. Chem. Soc.*, **82**, 366 (1960).
(177) Manuel, T. A., and Stone, F. G. A., *J. Am. Chem. Soc.*, **82**, 6240 (1960).
(178) Markby, R., Sternberg, H. W., and Wender, I., *Chemistry and Industry*, 1381 (1959).
(179) Markby, R., Wender, I., Friedel, R. A., Cotton, F. A., and Sternberg, H. W., *J. Am. Chem. Soc.*, **80**, 6529 (1958).
(180) Massey, A. G., and Orgel, L. E., *Chem. and Ind.*, 436 (1961).
(181) Mathews, F. S., and Lipscomb, W. N., *J. Am. Chem. Soc.*, **80**, 4745 (1958).
(182) Mathews, F. S., and Lipscomb, W. N., *J. Phys. Chem.*, **63**, 845 (1959).
(183) McClellan, W. R., Hoehn, H. H., Cripps, H. N., Muetterties, E. L., and Howk, B. W., *J. Am. Chem. Soc.*, **83**, 1601 (1961).
(184) Mills, O. S., and Robinson, G., *Proc. Chem. Soc.*, 156 (1959).
(185) Mills, O. S., and Robinson, G., *Proc. Chem. Soc.*, 421 (1960).
(186) Moore, D. W., Jonassen, H. B., Joyner, T. B., and Bertrand, A. J., *Chemistry and Industry*, 1304 (1960).
(187) Munro, J. D., and Pauson, P. L., *Proc. Chem. Scc.*, 267 (1959).
(188) Nakamura, A., and Hagihara, N., *Bull. Chem. Soc. Japan*, **32**, 880 (1959).
(189) Nakamura, A., and Hagihara, N., *Bull. Chem. Soc. Japan*, **33**, 425 (1960).
(190) Nast, R., *Angew. Chem.*, **72**, 26 (1960).
(191) Natta, G., Ercoli, R., and Calderazzo, F., *Chimica e Industria*, **40**, 287 (1958).
(192) Nicholls, B., and Whiting, M. C., *Proc. Chem. Soc.*, 152 (1958).
(193) Nicholls, B., and Whiting, M. C., *J. Chem. Soc.*, 551 (1959).
(194) Nyburg, S. C., and Hilton, J., *Acta Cryst.*, **12**, 116 (1959).
(195) Orgel, L. E., lecture delivered at the International Conference on Coordination Chemistry, London, April 6–11, 1959, Chemical Society Special Publication No. 13, p. 93.
(196) Orgel, L. E., "An Introduction to Transition Metal Chemistry," Methuen, London, 1960, Chap. 10, p. 150.
(197) Pajaro, G., Calderazzo, F., and Ercoli, R., *Gazz. chim. ital*, **90**, 1486 (1960).
(198) Pauson, P. L., "Non-benzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N.Y., 1959, Chap. 3, p. 107.
(199) Pauson, P. L., Tilden Lecture, 1960; *Proc. Chem. Soc.*, 297 (1960).
(200) Pauson, P. L., "A.C.S. Monograph on Organometallic Compounds," Chap. 7, p. 346.
(201) Pettit, R., *J. Am. Chem. Soc.*, **81**, 1266 (1959).
(202) Powell, D. B., and Sheppard, N., *J. Chem. Soc.*, 2519 (1960).
(202a) Pratt, L., private communication.
(203) Randall, E. W., and Sutton, L. E., *Proc. Chem. Soc.*, 93 (1959).
(204) Raphael, R. A., "Acetylenic Compounds in Organic Synthesis," Academic Press, Inc., New York, N. Y., 1955.
(205) Rausch, M. D., and Schrauzer, G. N., *Chemistry and Industry*, 957 (1959).
(206) Reihlen, H., Gruhl, A., Hessling, G., and Pfrengle, O., *Ann.*, **482**, 161 (1930).
(207) Reppe, W., and Vetter, H., *Ann.*, **582**, 133 (1953).
(208) Riemschneider, R., Becker, O., and Franz, H., *Monatsh.*, **90**, 571 (1959).
(209) Rundle, R. E., and Goring, J. H., *J. Am. Chem. Soc.*, **72**, 5337 (1950).
(210) Rundle, R. E., and Smith, H., *J. Am. Chem. Soc.*, **80**, 5075 (1958).
(211) Schrauzer, G. N., *Chemistry and Industry*, 1403 (1958).
(212) Schrauzer, G. N., *Chemistry and Industry*, 1404 (1958).
(213) Schrauzer, G. N., *J. Am. Chem.Soc.*, **81**, 5307 (1959).
(214) Schrauzer, G. N., *J. Am. Chem. Soc.*, **81**, 5210 (1959).
(215) Schrauzer, G. N., *J. Am. Chem. Soc.*, **82**, 1008 (1960).
(216) Schrauzer, G. N., *Chem. Ber.*, **94**, 642 (1961).
(217) Schrauzer, G. N., and Thyret, H., *J. Am. Chem. Soc.*, **82**, 6420 (1960).
(218) Shaw, B. L., and Sheppard, N., *Chemistry and Industry*, 517 (1961).
(219) Slade, P. E., Jr., and Jonassen, H. B., *J. Am. Chem. Soc.*, **79**, 1277 (1957).
(220) Sly, W. G., *J. Am. Chem. Soc.*, **81**, 18 (1959).
(221) Sternberg, H. W., Friedel, R. A., Markby, R., and Wender, I., *J. Am. Chem. Soc.*, **78**, 3621 (1956).
(222) Sternberg, H. W., Greenfield, H., Friedel, R. A., Wotiz, J. H., Markby, R., and Wender, I., *J. Am. Chem. Soc.*, **76**, 1457 (1954).
(223) Sternberg, H. W., Markby, R., and Wender, I., *J. Am. Chem. Soc.*, **80**, 1009 (1958).
(224) Sternberg, H. W., Shukys, J. G., Donne, C. D., Markby, R., Friedel, R. A., and Wender, I., *J. Am. Chem. Soc.*, **81**, 2339 (1959).
(225) Sternberg, H. W., and Wender, I., lecture delivered at the International Conference on Coordination Chemistry, London, April, 1959, Chemical Society Special Publication No. 13, p. 35.

(226) Strohmeier, W., and Gerlach, K., *Chem. Ber.*, **94**, 398 (1961).
(227) Taufen, H. J., Murray, M. J., and Cleveland, F. F., *J. Am. Chem. Soc.*, **63**, 3500 (1941).
(228) Tilney-Bassett, J. F., *J. Chem. Soc.*, 577 (1961).
(229) Tilney-Bassett, J. F., and Mills, O. S., *J. Am. Chem. Soc.*, **81**, 4757 (1959).
(230) Tirpak, M. R., Wotiz, J. H., and Hollingsworth, C. R., *J. Am. Chem. Soc.*, **80**, 4265 (1958).
(231) Traynham, J. G., and Sehnert, M. F., *J. Am. Chem. Soc.*, **78**, 4024 (1956).
(232) Traynham, J. G., and Olechowski, J. R., *J. Am. Chem. Soc.*, **81**, 571 (1959).
(233) Tropsch, H., and Mattox, W. J., *J. Am. Chem. Soc.*, **57**, 1102 (1935).
(233a) Trueblood, K. N., and Lucas, H. J., *J. Am. Chem. Soc.*, **74**, 1338 (1952).
(234) Ullman, E. F., *Chem. and Ind.*, 1173 (1958).
(235) Ward, A. L., and Makin, E. C., *J. Am. Chem. Soc.*, **69**, 657 (1947).
(236) Watterson, K. F., and Wilkinson, G., *Chemistry and Industry*, 991 (1959).
(237) Watterson, K. F., and Wilkinson, G., *Chemistry and Industry*, 1358 (1960).
(238) Weiss, E., and Hübel, W., *J. Inorg. Nucl. Chem.*, **11**, 42 (1959).
(239) Weiss, E., Merényi, R., and Hübel, W., *Chemistry and Industry*, 407 (1960).
(240) Wender, I., Friedel, R. A., Markby, R., and Sternberg, H. W., *J. Am. Chem. Soc.*, **77**, 4946 (1955).
(241) Wilke, G., paper presented at meeting of German Chemical Society, April, 1960, Stuttgart; *Angew Chem.*, **72**, 581 (1960).
(242) Wilke, G., and Kröner, M., *Angew. Chem.*, **71**, 574 (1959).
(243) Wilke, G., Müller, E. W., and Kröner, M., paper presented at Nordwestdeutsche Chemiedozenten Tagung, Hannover, September, 1960; *Angew. Chem.*, **73**, 33 (1961).
(244) Wilkinson, G., and Cotton, F. A., "Progress in Inorganic Chemistry," Interscience Publishers, Inc., New York, N.Y., 1959, Vol. I, p. 1.
(245) Winkhaus, G., and Wilkinson, G., *Chemistry and Industry*, 1083 (1960).
(246) Winkhaus, G., and Wilkinson, G., *Proc. Chem. Soc.*, 311 (1960).
(247) Winkhaus, G., and Wilkinson, G., *J. Chem. Soc.*, 602 (1961).
(248) Winstein, S., and Lucas, H. J., *J. Am. Chem. Soc.*, **60**, 836 (1938).
(249) Xavier, J., Thiel, M., and Lippincott, E. R., *J. Am. Chem. Soc.*, **83**, 2403 (1961).
(250) Zeiss, H. H., "A.C.S. Monograph on Organometallic Chemistry," Chap. 8, p. 380.