METAL π COMPLEXES WITH SUBSTITUTED OLEFINS

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CONTENTS

I. INTRODUCTION

The chemistry of metal–olefin π complexes originated in 1827 when Zeise isolated a colorless crystalline compound, which he described as $KCl \cdot PtCl_2 \cdot C_2H_4 \cdot H_2O$, from the reaction between platinum(IV) chloride and ethanol.[1,2] The composition of Zeise's salt, which was probably the first reported example of a compound containing an organic moiety together with a metal, was initially doubted.[3] However, when Birnbaum succeeded in preparing the analogous propylene– and amylene–platinum compounds,[4] Zeise's interpretation was accepted, and, although the nature of the bonding remained obscure for the better part of a century, characterization of many other metal–olefin π complexes followed.

Bonding between the olefinic ligand and the metal was not satisfactorily explained until 1951 when Dewar[5] showed that interaction between molecular antibonding orbitals on the olefin and hybrid atomic orbitals on the metal could account for the surprising stability of silver–olefin complexes. Chatt and Duncanson[6] applied Dewar's description to Zeise's salt, and their diagrammatic account of the bonding between platinum and the ethylene molecule, which is now generally accepted for metal–olefin π complexes, is given in Figure 1. Overlap between the filled ethylene π-molecular orbital and one of the vacant $5d6s6p^2$ platinum hybrid orbitals results in the formation of a single molecular μ bond.[5] This alone cannot account for the stability of metal–olefin π complexes, but overlap between the vacant olefinic antibonding π^*-molecular orbital and one of the filled 5d6p platinum hybrid atomic orbitals provides additional bonding. This is usually referred to as back-bonding, an expression which will be used throughout this review. The spatial arrangement of atoms required by the proposed[6] orbital overlap in Zeise's salt was confirmed by an X-ray structure determination.[7]

There is mounting evidence that the degree of back-bonding, which is π in character, plays an important role in the resultant stability of the complex (*vide infra* and particularly section V). Different nomenclature for the bond between olefin and metal is used; for instance, Guy and Shaw[8] suggested the term $\sigma\pi$ bond to emphasize its dual nature. In the present account the expression π bond is used to imply σ forward and π back-bonding since this is the term most generally employed. In the structural formulas an arrow is used for bonding between metal and olefin when this is thought to be π in nature. Cases in which only weak interaction between the double bond and the metal is postulated are emphasized by using a broken line arrow. This classification is by no means clear-cut and should be regarded merely as a guide to the bonding situation. For all other bonds (including donor bonds from atoms with lone pairs), a straight line is used.

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(1) W. C. Zeise, *Pogg. Ann.*, **9**, 632 (1827).
(2) W. C. Zeise, *ibid.*, **21**, 497 (1931).
(3) J. Liebig, *Ann. Chem.*, **23**, 12 (1837).
(4) K. Birnbaum, *ibid.*, **145**, 67 (1868).
(5) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).
(6) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).
(7) J. A. Wunderlich and D. P. Mellor, *Acta Crystallogr.*, **8**, 57 (1955).
(8) R. G. Guy and B. L. Shaw, *Advan. Inorg. Chem. Radiochem.*, **4**, 77 (1962).

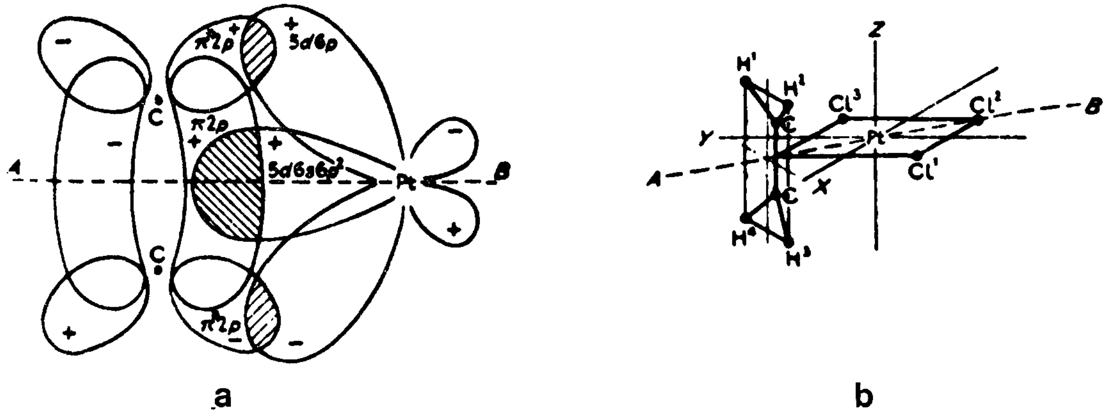

Figure 1.—(a) Orbitals used in the combination of ethylene with platinum. (b) Spatial arrangement of atoms in $[C_2H_4PtCl_3]^-$. (Reproduced from the *Journal of the Chemical Society*, 1953, p 2940, by kind permission.)

The ability of metals to form π complexes with olefinic ligands appears to be confined to the transition series[9] and is usually enhanced when the metal is in a low oxidation state. This is quite reasonable since more electrons are available for back-bonding. For the same reason metals on the right of the transition block tend to form more stable π complexes than those on the left. Furthermore, σ bonds rather than π bonds are invariably formed when olefins react with main group elements (*e.g.*, by inserting into metal–hydrogen bonds) because the energies of the metal orbitals required for possible back-bonding (usually d) are generally incompatible with those on the ligand. Conversely, it is not surprising that alkyl-transition metal σ bonds are not common, since alkyl groups lack low-lying π*-antibonding orbitals necessary for back-bonding.

The investigation of metal–olefin π complexes has been thorough and the quantity of literature considerable, particularly during the last decade. Several review articles[8,11,12] have dealt specifically with this topic. Fischer and Werner are writing a two-volume text on metal π complexes. Part I, already available,[13] describes complexes with di- and oligoolefinic ligands; part II, which is in the course of preparation, will deal with monoolefinic ligands.

Despite the attention given to olefinic ligands, interest in the use of olefins containing functional groups, and their ability to complex with transition metals, has been comparatively recent. The first authoritative[14] report on the characterization of such a complex was by Kharasch and Ashford[18] who in 1936 isolated platinum complexes with styrene, stilbene, and dichloroethylene.

During the last 5 years the literature describing metal-substituted olefin π complexes has proliferated; it is widely scattered, and the purpose of this review is to collect and correlate the relevant articles. It is hoped that this will provide a solid basis for and stimulate interest in a subject that will clearly increase in importance during the next few years.

This review is intended to cover the subject to the end of February 1968. Generally, only monoolefins π-bonded to the metal and containing substituents other than alkyl will be dealt with. When the nature of the bonding in a particular complex is uncertain the compound will be described and the point discussed. In many cases the olefin substituent contains lone-pair electrons in which case bonding both by double-bond participation and by lone-pair donation is possible: complexes for which π bonds are not postulated will only be mentioned to compare and contrast different bonding tendencies of a particular ligand.

One of the aims of this review is to demonstrate the effect of functional group on the properties of the complex; therefore substituted polyolefins and substituted π-allyl ligands, both relatively few in number, will be omitted since they complicate the picture. The effect of substitution on the stability of the complex will be discussed only when it becomes important in the complex as a whole.

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[9] A recent communication[10] reported a complex in which it was thought that propene was π-bonded to aluminum. The evidence, however, was sketchy and the conclusion must be considered tentative.

(10) R. D. Chambers and J. A. Cunningham, *Tetrahedron Lett.*, 3813 (1967).

(11) R. N. Keller, *Chem. Rev.*, **28**, 229 (1941).

(12) M. A. Bennett, *ibid.*, 62, 611 (1962).

(13) E. O. Fischer and H. Werner, "Metal π-Complexes," Vol. I, Elsevier Publishing Co., Amsterdam, 1966.

(14) Earlier attempts to prepare complexes with unsaturated alcohols, acids, and esters[15-17] gave compounds which were formulated with σ-bonding between the metal and olefin. The structure of these compounds remains obscure but the possibility of π-bonding cannot be ignored *a priori*.

(15) E. Biilmann, *Chem. Ber.*, **33**, 2196 (1900).

(16) K. A. Hoffmann and J. Narbutt, *ibid.*, **41**, 1625 (1908).

(17) P. Pfeiffer and H. Hoyer, *Z. Anorg. Allg. Chem.*, 211, 241 (1933); *Chem. Abstr.*, **27**, 5269 (1933).

(18) M. S. Kharasch and T. A. Ashford, *J. Amer. Chem. Soc.*, **58**, 1733 (1936).

Firstly, the metal-substituted olefin π complexes are described in subsections, each dealing with a particular functional group on the ligand. This arrangement emphasizes the correlation between functional group and metal. Sections describing optical isomerism and stability studies follow, and finally the article summarizes the general trends that have appeared.

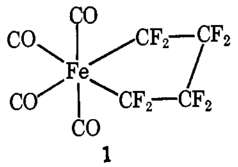
II. THE METAL–OLEFIN π COMPLEXES WITH FUNCTIONALLY SUBSTITUTED OLEFINS

Complexes have been prepared in which most of the common functional groups feature as substituents in the olefinic ligand. In some cases, when the functional group contains an atom with lone-pair electrons, chelation occurs, and there are several examples of multiple substitution. A description of the substituted olefin complexes follows under the heading of the appropriate functional group.

A. HALIDES

The main interest in halogen-substituted olefins as ligands has centered on fluoroolefins. Acceptance of the dual nature of the bonding between olefin and metal (*vide supra*) led to speculation as to whether an electronegative substituent would strengthen or weaken the π bond. One would expect the electron-donating ability of the olefin to decrease but the electron-accepting ability to increase when hydrogen was replaced by fluorine. It was thus difficult to predict the comparative stability of the resulting complexes.

First attempts to obtain a π-bonded fluoroolefin complex were made by Watterson and Wilkinson[19] who isolated colorless stable crystals from the reaction between tetrafluoroethylene (TFE) and iron pentacarbonyl. From elemental analysis results, the presence of three carbonyl stretching bands in the ir, and ^{19}F nmr data, these authors proposed the formula $(C_2F_4)_2$-$Fe(CO)_3$ and implied that two TFE molecules were π-bonded to the metal. However, subsequent work[20,21] showed that the compound was a tetracarbonyl (**1**) in which the metal is σ-bonded to two TFE molecules in a five-membered ring. Structure **1** not only accounts for the presence of three carbonyl ir stretching bands but also for the two aliphatic triplets in the ^{19}F nmr spectrum. The considerable stability, unusual for a compound in which carbon is σ-bonded to a metal, can be ascribed to the electron withdrawal by the fluorine substituents. Several other reports[22–26] of reactions between fluoroolefins and transition metal carbonyls leading to σ-bonded organometallic compounds bear this out. However, Watterson and Wilkinson may have been the first to prepare a π-bonded fluoroolefin complex since they also mention[19] the isolation of an unstable yellow solid formed by treating sodium tetrachloroplatinate(II) with TFE. This product, which they were unable to characterize, gave a ^{19}F nmr spectrum and may well have been a π-bonded species.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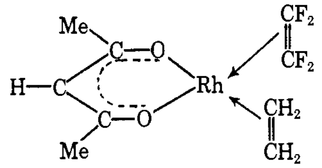
The first convincing description[27] of a fluoroolefin π complex appeared in 1965, when Cramer and Parshall described two rhodium complexes obtained by *displacing* ethylene from 2,4-pentanedionatobis(ethylene)-rhodium(I) or μ-dichloro-tetrakis(ethylene)dirhodium(I) by TFE. Both products (**2** and **3**) were formed by the replacement of one ethylene molecule per metal atom.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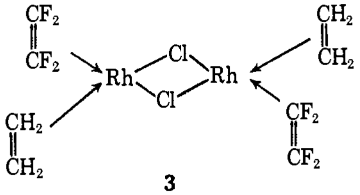
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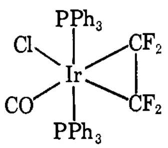
Ethylene, but not TFE, in **2** and **3** could be displaced by phosphines, amines, nitriles, and the cyanide ion. Both ethylene and TFE were displaced by 1,5-cyclooctadiene or carbon monoxide, and this led the authors to postulate π-bonding between TFE and metal. In contrast TFE *added* to chlorocarbonylbis(triphenylphosphine)iridium(I), forming the σ-bonded octahedral heterocyclic complex **4**, in a manner analogous to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[19] K. F. Watterson and G. Wilkinson, *Chem. Ind.* (London), 991 (1959).

[20] K. F. Watterson and G. Wilkinson, *ibid.*, 1358 (1960).

[21] T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 249 (1961).

[22] R. B. King, P. M. Treichel, and F. G. A. Stone, *Proc. Chem. Soc.*, 69 (1961).

[23] T. D. Coyle, R. B. King, E. Pitcher, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **20**, 172 (1961).

[24] P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

[25] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 93 (1965).

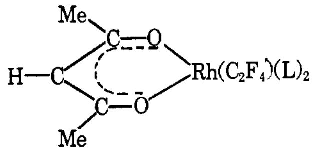
[26] P. W. Jolly, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.*, 5830 (1965).

[27] R. Cramer and G. W. Parshall, *J. Amer. Chem. Soc.*, **87**, 1392 (1965).

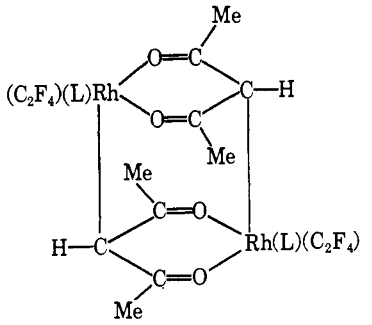
[28] L. Vaska, *Science*, **140**, 809 (1963).

the formation[28] of the oxygen complex $(Ph_3P)_2(CO)IrCl(O_2)$.

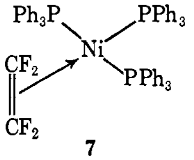
A further more comprehensive account from the same laboratories[29] described five types of complexes (**2** and **4–7**) formed by the treatment of some group VIII metals with fluorinated olefins. The properties of the



5, L = *trans*-$(n\text{-}C_4H_9)_3P$, *cis*-$(Me)_2SO$, *cis*-C_5H_5N, *cis*-$^1/_2(Me_2NCH_2\text{–})_2$, or *cis*-$^1/_2(Ph_2PCH_2\text{–})_2$



6, L = CH_3CN, PhCN, $HOCH_2CH_2CN$, $C_5H_{11}CN$, $C_6H_{13}CN$, or $HCON(Me)_2$



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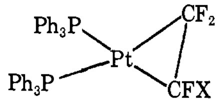
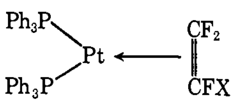
complexes together with nmr and ir data suggest that bonding between olefin and metal is intermediate between π and σ. Infrared spectroscopy showed a clear distinction between the bonding in **2** and **7**, on the one hand, and **4–6**, on the other. In support of this the ^{19}F nmr spectra of **2** and **7** had fine structure, all fluorine nuclei absorbing in the same region, in contrast to separations of 7–18 ppm in the spectra of **4–6**. These observations suggest that **2** and **7** more nearly resemble π complexes (in which the fluorine atoms are equivalent) than do **4–6**. The rhodium complexes **5** and **6** as well as the iridium complex (**4**) can best be considered as distorted octahedra in which the carbon–metal bonds are mainly σ.

Platinum(0) appears reluctant to form π bonds with fluoroolefins. Treatment of tetrakis(triphenylphosphine)platinum(0) with either TFE, hexafluoropropene, or chlorotrifluoroethylene produced[30] colorless stable crystals of composition $(Ph_3P)_2Pt$(fluoroolefin). On the basis of the ^{19}F nmr spectrum and chemical behavior of the compound, it was postulated to be a square-planar platinum(II) complex with two platinum–carbon σ bonds (**8**), rather than a π-bonded platinum(0) derivative (**9**).

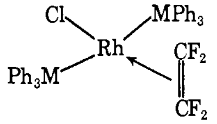


8, X = CF_3, F, or Cl



9, X = CF_3, F, or Cl

Mays and Wilkinson[31] proposed a π-bonded complex for the product of the reaction between chlorotris(triphenylphosphine)rhodium(I) and TFE. The yellow crystals obtained were very stable and did not decompose in benzene at 37°. Analysis figures were correct for the formula $(Ph_3P)_2RhCl(C_2F_4)$ and molecular weight determination showed the species to be monomeric. The ^{19}F nmr spectrum consisted of a triplet of doublets, with separations which were independent of field frequency, showing that all four fluorine atoms are equivalent. The structure most consistent with this is one in which the TFE molecule is π-bonded to the metal at right angles to the plane of the complex, and *trans* to the chlorine ligand (**10a**).



10a, M = P
b, M = As

The ^{19}F nmr spectrum of a solution of **10a** containing excess TFE showed no line broadening at −80°. Therefore, at that temperature TFE exchange was slower than 10^{-2} sec^{-1}. This behavior is in contrast with other ethylene complexes[32,33] and with the rapid exchange found[34] in the corresponding ethylene complex $(Ph_3P)_2Rh(C_2H_4)Cl$. When chlorotris(triphenylphosphine)rhodium(I) was treated with chlorotrifluoroethylene, an analogous complex formed slowly. The same compound was more readily obtained by ligand exchange in the ethylene complex. The nature of bonding in this complex has not been elucidated because the ^{19}F nmr spectrum is complicated due to the presence of three nonequivalent fluorine atoms and their associated coupling, but it is probably similar to **10a**. The triphenylarsine analog (**10b**) has recently been reported,[35] its ^{19}F nmr spectrum consisting of a sharp doublet (33.5 ppm upfield from benzotrifluoride), which is insensitive to an excess of TFE, so that ligand exchange is again slow.

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(29) G. W. Parshall and F. N. Jones, *J. Amer. Chem. Soc.*, **87**, 5356 (1965).

(30) M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *Chem. Commun.*, 502 (1966).

(31) M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, 6629 (1965).

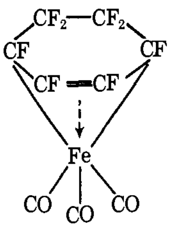
(32) R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964).

(33) R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).

(34) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, *A*, 1711 (1966).

(35) J. T. Mague and G. Wilkinson, *ibid.*, 1736 (1966).

Several fluoroolefin complexes have been isolated for which both σ- and π-bonding between the olefin and metal were postulated. The reaction between octafluoro-1,4-cyclohexadiene and $Fe_3(CO)_{12}$ gives[36] an air-stable compound of molecular formula $C_6F_8Fe(CO)_3$. The authors interpreted the ir spectrum in terms of a wholly π-bonded structure, but Treichel and Stone[37] proposed structure **11** in which the olefin is attached by two σ bonds and one π bond. This structure is in keeping with X-ray data from similar dieneiron tricarbonyl complexes[38] and the ^{19}F nmr spectrum.[36]



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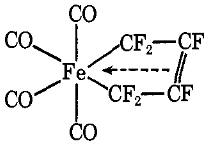
A similar compound was formed in the reaction between hexafluoro-1,4-butadiene and iron pentacarbonyl. An X-ray structure determination of the resultant iron tetracarbonyl derivative (**12**) showed the fluorocarbon ligand to be σ-bonded to the metal, with some double-bond interaction.[39]



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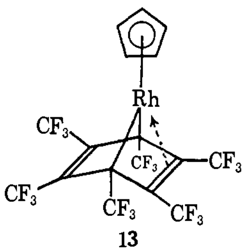
One of the products from the reaction between cyclopentadienylrhodium(I) dicarbonyl and hexafluoro-2-butyne was identified as the 1,4 adduct of hexakis(trifluoromethyl)benzene. This interesting compound (**13**), for which two σ bonds and one π bond were proposed,[40] is a derivative of "Dewar benzene." The structure was subsequently confirmed by an X-ray determination.[41]



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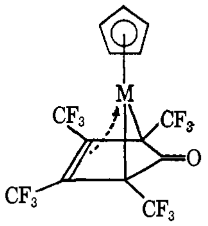
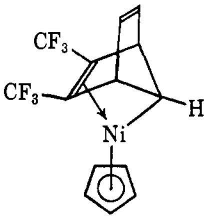
The other product from the reaction[40] was shown spectroscopically to have structure **14a**. The cyclopentenone carbon skeleton, which is bonded to rhodium by two σ bonds and one π bond, must have originated from two hexafluoro-2-butyne and one carbon monoxide molecules. Similarly, treatment of cyclopentadienylcobalt(I) dicarbonyl with hexafluoro-2-butyne produced a complex containing two σ bonds and a single π bond.[42] However, the cyclobutadiene structure originally postulated[42] was shown[43] by X-ray measurements to be incorrect; the complex actually has structure **14b**. One of the products of the reaction between hexafluoro-2-butyne and nickelocene was reported[44] to be a nickel complex (**15**) with one cyclopentadienyl and one 2,3-bis(trifluoromethyl)-2,5-norbornadiene ligand, the latter being coordinated by one σ and one π bond.



14a, M = Rh
b, M = Co



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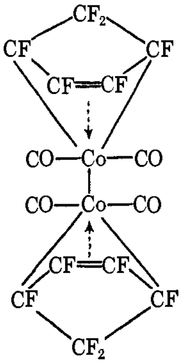
Treatment of hexafluorocyclopentadiene with cobalt carbonyl was shown to yield a dinuclear complex. The structure proposed (**16**) was in agreement with ir and



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[36] H. H. Hoehn, L. Pratt, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.*, 2738 (1961).

[37] P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964).

[38] D. L. Smith and L. F. Dahl, *J. Amer. Chem. Soc.*, **84**, 1743 (1962).

[39] P. B. Hitchcock and R. Mason, *Chem. Commun.*, 242 (1967).

[40] R. S. Dickson and G. Wilkinson, *Chem. Ind.* (London), 1432 (1963).

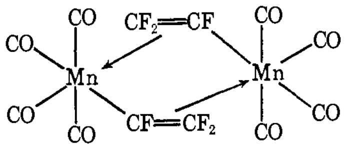
[41] M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 365 (1963).

[42] J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).

[43] M. Gerloch and R. Mason, *Proc. Roy. Soc.*, **A279**, 170 (1964).

[44] D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1752 (1964).

^{19}F nmr data.[45] Finally, a recent communication[46] mentioned a dimeric manganese carbonyl compound with bridging perfluoroethylene groups (**17**), as one of the products obtained when $Me_3SnMn(CO)_5$ was treated with TFE. The main product was $Me_3SnCF_2CF_2Mn(CO)_5$.



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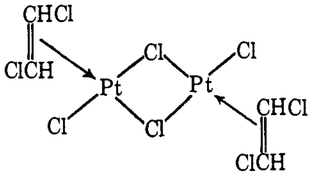
There are few examples of π complexes containing olefins substituted with halogens other than fluorine. In 1936 Kharasch and Ashford[18] succeeded in isolating a bridged platinum complex by refluxing platinum(II) chloride with *trans*-dichloroethylene. Although no evidence was given, structure **18** was proposed. No



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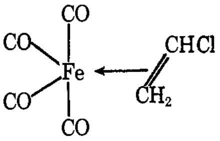
solid products were isolated from similar reactions with *cis*-dichloroethylene, allyl chloride, allyl bromide, or vinyl chloride. However, Gustorf, Henry, and Pietro[47] recently isolated vinyl chloride–iron(0) tetracarbonyl (**19**) from the photochemical reaction between vinyl chloride and iron pentacarbonyl. The ir spectrum of the complex indicated π-bonding, and it is probable that the olefinic ligand is equatorial (*cf.* the fumaric acid and acrylonitrile analogs described in sections II.C and II.E, respectively).



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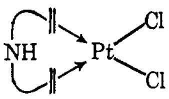
A σ-bonded structure was proposed[48] for a compound formed in the reaction between tetrachloroethylene and tetrakis(triphenylphosphine)platinum(0), and recently[49] it has been reported that in a similar reaction palladium can be inserted into the carbon–chlorine bond of some chloroolefins.

The preponderance of fluoroolefin complexes in this section is quite marked and can be attributed to four factors. Firstly, by choosing fluorine as a substituent, use can be made of the well-established ^{19}F nmr method. The fluorine nucleus is often a better molecular "probe" than the proton since ^{19}F chemical shifts are more sensitive to electronic effects in the molecule. Secondly, fluorine is particularly interesting because it is the most electronegative halogen producing the greatest substituent effect. Thirdly, fluorine is much smaller than the other halogens so that fluoroolefins form more stable complexes because steric interactions are minimized. Finally, fluoro compounds in general are more stable than their chloro, bromo, or iodo analogs.

B. AMINES

The first attempts to prepare complexes of unsaturated amines were reported by Liebermann and Paal,[50] who boiled solutions of a hexachloroplatinate(IV) with allylamine and several substituted allylamines and obtained compounds with the empirical formula (amine-H)$PtCl_3$. Similar compounds were more recently reported by Rubinshtein and Derbisher[51] and by Gelman and Essen.[52] Rubinshtein and Derbisher[51] showed that the reaction between diallylamine and ammonium tetrachloroplatinate(II) gave two compounds, $PtLCl_2$ and $(PtLCl_2)_2$, where L = diallylamine. For the monomer they proposed a structure (**20**) with a chelating π-bonded ligand. The dimer was formulated as $[Pt(diallylamine)_2]PtCl_4$.



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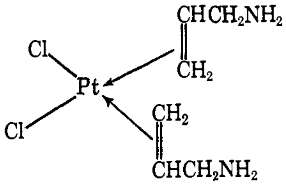
Gelman and Essen[52] obtained different products at different pH values. In neutral solution treatment of potassium tetrachloroplatinate(II) with allylamine gave yellow crystals of a compound for which structure **21** was proposed. The participation of the double



21

bond was indicated, according to these authors, by the appearance of a metallic mirror when the complex was heated with water. In strongly acidic solutions a dimer, $[Cl_2Pt(allylamine)HCl]_2$, was obtained which was formulated as the σ complex **22**.

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(45) R. E. Banks, T. Harrison, R. N. Haszeldine, A. B. P. Lever, T. F. Smith, and J. B. Walton, *Chem. Commun.*, 30 (1965).

(46) H. C. Clark and J. H. Tsai, *ibid.*, 111 (1965).

(47) E. K. Gustorf, M. C. Henry, and C. D. Pietro, *Z. Naturforsch.*, *B*, **21**, 42 (1966).

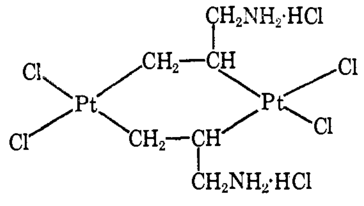
(48) W. J. Bland and R. D. W. Kemmitt, *Nature*, 211, 963 (1966).

(49) P. Fitton and J. E. McKeon, *Chem. Commun.*, 4 (1968).

(50) C. Liebermann and C. Paal, *Chem. Ber.*, **16**, 530 (1883).

(51) A. M. Rubinshtein and G. V. Derbisher, *Dokl. Akad. Nauk SSSR*, **74**, 283 (1950); *Chem. Abstr.*, **45**, 3280*b* (1951).

(52) A. D. Gelman and L. N. Essen, *Dokl. Akad. Nauk SSSR*, **77**, 273 (1951); *Chem. Abstr.*, **45**, 6117*g* (1951).



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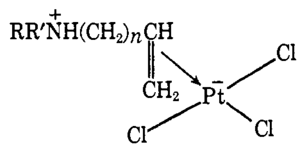
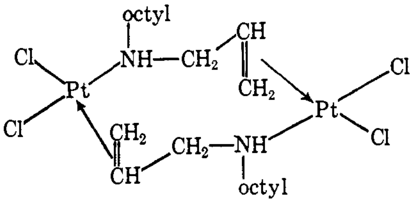


23a, R = R' = H, C_2H_5, $CH_2{=}CHCH_2$, or C_8H_{17}; *n* = 1
b, R = H; R' = H or C_8H_{17}; *n* = 2, 3
c, R = H; R' = CH_3, C_3H_7, or C_4H_9; *n* = 1
d, R = H; R' = C_2H_5; *n* = 2



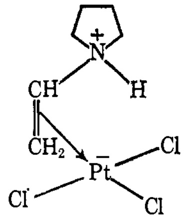
24

More recently there has been considerable activity in this field largely due to the efforts of Venanzi who has isolated several series of compounds and studied their relative stabilities. Preparatively (stability studies will be described in section V) Denning and Venanzi[53] described compounds obtained from the treatment of potassium tetrachloroplatinate(II) with a series of primary and tertiary allylamines. Irrespective of whether the reaction was in neutral or acidic solutions, a series of monomers with zwitterionic character was produced. Formulation of the complexes as **23a** was based on several lines of reasoning. Firstly, ir results confirmed the presence of π-bonding and a quaternary ammonium group. Secondly, the compounds are nonelectrolytes and insoluble in both water and organic solvents, a characteristic of zwitterions (*cf.* amino acids). Thirdly, when potassium tetrachloroplatinate(II) was treated with an N,N-diethylallylammonium salt, the same type of complex was obtained. Finally, the ir and uv spectra were similar to those measured for Zeise's salt. Secondary allylamines gave polymeric complexes with the exception of the N-octyl derivative which was shown by ir to be dimeric and coordinated to platinum through the double bond and the nitrogen lone pair (**24**). Aqueous acid solutions of the complexes did not obey Beer's law,[53] and the concentration of complex showed a strong dependence on chloride ion concentration presumably due to the following equilibria

$$[PtCl_3(allylNHRR')] + H_2O \rightleftharpoons [PtCl_2(H_2O)(allylNHRR')]^+ + Cl^- \quad (1)$$

$$[PtCl_3(allylNHRR')] + Cl^- \rightleftharpoons [PtCl_4]^{2-} + (allylNHRR')^+ \quad (2)$$

Further studies[54] have shown that the reaction between unsaturated amines containing two or three methylene groups between the double bond and nitrogen atom leads to similar zwitterionic complexes (**23b**). Insoluble compounds of the formula $PtCl_2[NHR(CH_2)_n\,CH{=}CH_2]$ are produced when the complexes are neutralized, with the exception of $[PtCl_2$(N-octyl-4-pentenylamine)] which is dimeric. A subsequent paper,[55] concerned mainly with thermodynamics, describes the preparation and isolation of several additional compounds (**23c**, **23d**, **25**, and **26**), but their properties were not discussed. Several analogous C-substituted allylamine complexes have also been mentioned.[56]



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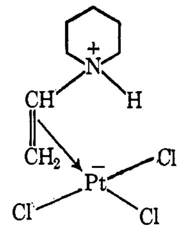
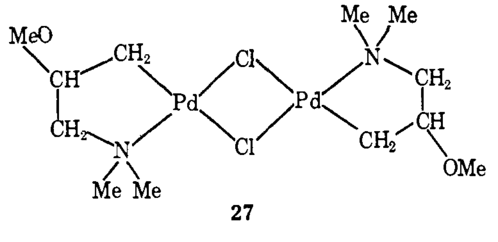


26

In contrast to the unsaturated amine complexes in which π-bonding to platinum is important, it has recently been shown that allylamine will react with palladium(II) chloride in the presence of methanol to give a σ complex.[57] The methoxyl ion attacks the double bond at the internal unsaturated carbon atom, producing a ligand which chelates to the palladium so that the dimer **27** is formed. A similar reaction occurs between diolefins and both palladium and platinum in the presence of alcohols (see section II.G).



27

Ultraviolet spectroscopy was used[58] to predict the relative d-orbital energies in the complexes formed between allylamine, N,N,N-triethylallylammonium chloride, allyl alcohol, and P,P,P-triethylallylphosphonium

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[53] R. G. Denning and L. M. Venanzi, *J. Chem. Soc.*, 3241 (1963).

[54] D. V. Claridge and L. M. Venanzi, *ibid.*, 3419 (1964).

[55] R. G. Denning, F. R. Hartley, and L. M. Venanzi, *ibid.*, *A*, 324 (1967).

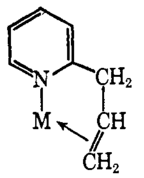
[56] R. G. Denning, F. R. Hartley, and L. M. Venanzi, *ibid.*, 328 (1967).

[57] A. C. Cope, J. M. Kliegman, and E. C. Friedrich, *J. Amer. Chem. Soc.*, 89, 287 (1967).

[58] R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J Chem. Soc.*, *A*, 1322 (1967)

chloride and potassium tetrachloroplatinate(II). For each complex the energies of the orbitals were in the order $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} > d_{x^2}$.

Complexes of 2-allylpyridine with Cu(I), Ag(I), and Pt(II) have been characterized by Yingst and Douglas.[59] Infrared spectroscopy indicated that the ligand chelates to form complexes of type **28**.



28, M = Cu, Ag, or Pt

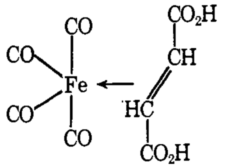
C. ACIDS, ANHYDRIDES, AND ESTERS

The majority of complexes with unsaturated acids, anhydrides, and esters have been made from iron pentacarbonyl. A series of compounds $Fe(CO)_4L$ was isolated[60] from the reaction between iron pentacarbonyl and a series of olefinic acids, anhydrides, and esters (L); several other olefins substituted with different groups are reported under the appropriate headings. Details of the ligands (L) together with yields and melting points of the complexes are collected in Table I. All the products were 1:1 yellow crystalline materials whose stability increased with the electron-withdrawing ability of the substituent, a phenomenon which is discussed later. Bonding between L and the metal was thought to be π in nature, the olefinic double bond behaving as the donor in each case. Evidence for this was from ir (no discernible carbon–carbon double-bond stretch) and the nmr spectrum, in which the olefinic protons were displaced some 2.4–3.4 ppm upfield relative to the position of the signal in the corresponding uncomplexed olefin. Confirmation for the structure of the fumaric acid derivative (and by implication the whole series) was provided by a recent X-ray structure determination.[61] The complex is trigonal bipyramidal (**29**) and the fumaric acid is situated equatorially. Each carboxyl group is bent out of the H—C═C—H plane away from the iron atom to the extent of 18°.

Table I

Iron Tetracarbonyl Complexes of Unsaturated Acids, Anhydrides, and Esters[60]

Ligand (L)	Yield, %	Mp, °C
Maleic anhydride	60	92
Maleic acid	93	150
Monomethyl maleate	70	93
Dimethyl maleate	68	36
Methylmaleic acid	80	~90
Fumaric acid	79	~155
Dimethyl fumarate	86	137
Acrylic acid	68	104
Methyl acrylate	71	28
Ethyl acrylate	64	~−2
Cinnamic acid	64	63
Methacrylic acid	15	70



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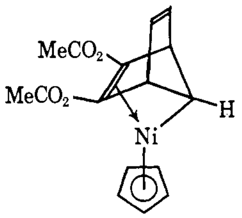
A similar tetracarbonyl complex was prepared in good yield by photochemical irradiation of iron pentacarbonyl and maleic anhydride in benzene at room temperature.[62] A π-bonded structure was postulated on the basis of ir and nmr data. Hydrolysis of the complex with dilute sulfuric acid gave a precipitate of the acid, whereas boiling hydrobromic acid induced degradation to ferrous ion and succinic acid. One carbonyl group was displaced by triphenylphosphine to give (maleic anhydride)$(Ph_3P)Fe(CO)_3$. Similar tetracarbonyl derivatives were formed with maleic and fumaric acids, ethyl fumarate, methyl methacrylate, and vinyl acetate.[63] The methyl methacrylate–iron(0) tetracarbonyl was quite unstable and decomposed under argon in a few hours at room temperature, but more slowly (several days) at −20°. γ-Radiation from a ^{60}Co source was also used successfully in the preparation of similar compounds.[64]

A nickel complex of 2,5-norbornadiene-2,3-dicarboxylic acid dimethyl ester, in which bonding between the bicyclic diene and nickel is by means of one σ and one π bond, has been described.[65] The complex is formed as a Diels–Alder adduct from nickelocene and acetylenedicarboxylic acid dimethyl ester. Convincing evidence for structure **30** was obtained from the nmr spectrum which consisted of a singlet at −5.24 ppm (5 H) due to the π-bonded cyclopentadienyl group, a triplet at −6.55 ppm (2 H) correct for olefinic



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[59] R. E. Yingst and B. E. Douglas, *Inorg. Chem.*, **3**, 1177 (1964).

[60] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

[61] P. Corradini, C. Pedone, and A. Sirigu, *Chem. Commun.*, 341 (1966).

[62] G. O. Schenck, E. K. Gustorf, and M. J. Jun, *Tetrahedron Lett.*, 1059 (1962).

[63] E. K. Gustorf, M. J. Jun, and G. O. Schenck, *Z. Naturforsch.*, *B*, **18**, 503 (1963).

[64] E. K. Gustorf, M. J. Jun, and G. O. Schenck, *ibid.*, **18**, 767 (1963).

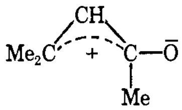
[65] M. Dubeck, *J. Amer. Chem. Soc.*, **82**, 6193 (1960).

protons, a multiplet centered at −3.7 ppm containing a singlet (6 H) assigned to the methoxyl groups and further resonance (2 H) due to the tertiary bridgehead hydrogens, and finally a triplet at −2.18 ppm (1 H) attributable to the remaining methine proton. This spectrum is quite consistent with the structure proposed (**30**). Further evidence came from the observation that **30** was diamagnetic and decomposed on hydrogenation to nickel metal, cyclopentane, and 2,5-norbornadiene-*endo,cis*-2,3-dicarboxylic acid dimethyl ester.

Lastly, but indeed first chronologically, Cuta and Vydra[66] provide the only examples of unsaturated acids coordinated to a metal other than iron. Treatment of aqueous solutions of oleic and elaidic acids with palladium(II) chloride gave dimeric complexes which were not isolated, but, on the basis of the ir spectrum, it was concluded that bonding was through the carbon–carbon double bond and that there was extensive intramolecular hydrogen bonding.

D. ALDEHYDES AND KETONES

One of the earliest coordination compounds known was the complex ($C_6H_{10}O \cdot PtCl_2$) formed between mesityl oxide and platinum(II) chloride.[67,68] A similar palladium compound was described in 1959 by Russian workers[69,70] who suggested that it was bonded *via* the π-allylic system **31**. In fact, ir and nmr spectroscopy showed[71] the complex to be a bridged dimer with π-allylic ligands (**32**). The nmr spectrum of the platinum complex was quite different and not consistent with an allylic structure. The ir spectrum indicated that the ketone group was involved in bonding since the band found at 1685 cm^{-1} in the spectrum of mesityl oxide was absent. From this evidence, together with its chemical properties, a polymeric structure (**33**) was postulated[71] for the compound in which the metal atoms are linked through the double bond and carbonyl groups of separate mesityl oxide molecules.



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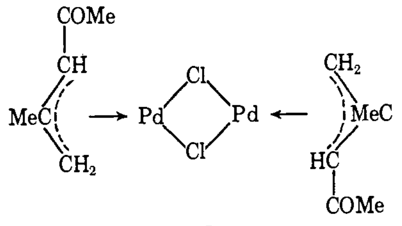

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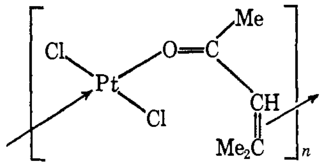
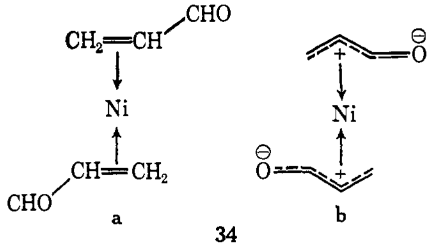


33

Schrauzer, during a comprehensive study of acrylonitrile complexes of nickel and other group VIII metals (see section II.E), prepared bis(acrolein)nickel(0). On the basis of ir data the carbonyl group was thought to be highly polarized. Of the two possible alternatives considered (**34a** and **b**) the π-allylic structure **34b** was preferred.[72] Involvement of the carbon–carbon double bond and the carbonyl group in the bonding satisfies the coordination requirements of the metal. The reaction between iron pentacarbonyl and acrolein afforded[73] acroleiniron(0) tetracarbonyl; the nmr and ir spectra of this complex showed that only the carbon–carbon double bond was involved in bonding (structure **35a**). The olefinic protons absorbed at higher field than those in the free ligands, whereas the aldehyde proton was shifted upfield by only 0.13 ppm. Furthermore, a strong carbonyl band was seen in the ir spectrum of **35a** at frequencies similar to those found for the free aldehyde.



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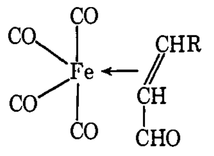

35a, R = H
b, R = Ph

Acrolein chelates to molybdenum[74] to form bis(acrolein)molybdenum(0) dicarbonyl. This complex, which is formed by displacing acetonitrile from tris(acetonitrile)molybdenum(0) tricarbonyl, was shown to be diamagnetic, and its nmr and ir spectra were compatible

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[66] F. Cuta and F. Vydra, *Collect. Czech. Chem. Commun.*, **25**, 967 (1960); *Chem. Abstr.*, **54**, 12872*d* (1960).

[67] H. Zeise, *J. Prakt. Chem.*, **20**, 193 (1840).

[68] W. Prandtl and K. A. Hofmann, *Chem. Ber.*, **33**, 2981 (1900).

[69] I. I. Moiseev, E. A. Feodorovskaya, and Y. K. Syrkin, *Zh. Neorg. Khim.*, **4**, 2641 (1959); *Chem. Abstr.*, **54**, 13933*g* (1960).

[70] I. I. Moiseev, E. A. Feodorovskaya, and Y. K. Syrkin, *Russ. J. Inorg. Chem.*, **4**, 1218 (1959).

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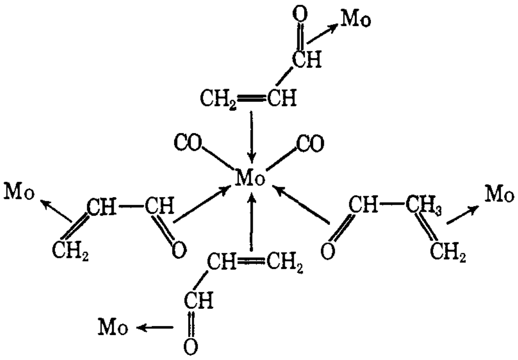
[74] D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, **4**, 1323 (1965).

with a structure in which both the carbon–carbon double bond and the carbonyl group take part in bonding. The large upfield nmr shift (1.27 ppm) of the aldehyde proton indicated a change from free to complexed acrolein and led to the suggestion[74] that π electrons in the carbonyl group were involved in the bonding. Coordination through the oxygen lone pair should, by an inductive effect, lead to a downfield shift of the aldehyde proton. When initially formed, the complex is soluble in benzene and chloroform but precipitates irreversibly from solution on standing. Polymerization to give a compound having structure **36**, in which intermolecular chelation occurs, was suggested to account for this. Analogous complexes of methyl vinyl ketone and crotonaldehyde were described and similar structures proposed. It has also been demonstrated[75] that methyl vinyl ketone will chelate to tungsten; three ligands, each bonding through both the carbon–carbon double bond and carbonyl group, satisfy the octahedral requirement of the metal (structure **37**).



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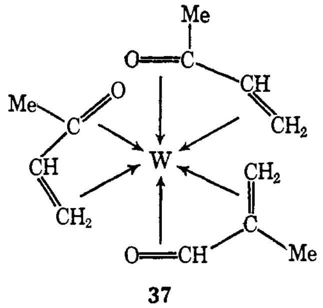
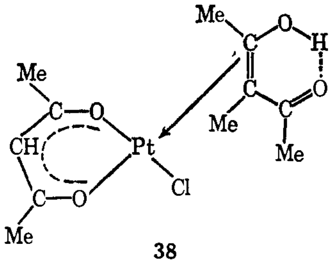


37

A complex formed between cuprous chloride and acrolein has been reported.[76] The yellow crystals of $(CH_2{=}CHCHO)CuCl$ decomposed in air but were quite stable *in vacuo*. Shifts of 90 and 30 cm⁻¹ in the positions of the carbon–carbon double bond and carbonyl stretching frequencies, respectively, led to the suggestion that bonding occurred mainly through the double bond.

When $K[Pt(acac)_2Cl]$ was treated with acid (unspecified), a yellow complex formed which was shown to contain one acetylacetone ligand "frozen" in the enol form.[77] Thus the compound, which was insoluble in water but dissolved in organic solvents, gave an nmr spectrum with three different methyl resonances in the ratio of 2:1:1. Further evidence was the presence of a characteristic broad OH band in the ir spectrum consistent with structure **38**.

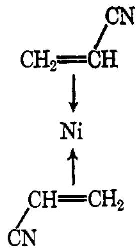


38

E. NITRILES

Since the discovery of bis(acrylonitrile)nickel(0) by Schrauzer,[78] the predominant interest has been with the use of acrylonitrile (AN) as a ligand. The number of different metals with which this ligand coordinates is considerable.

The structure and properties of bis(acrylonitrile)-nickel(0) and related compounds have been comprehensively studied by Schrauzer and his group. When nickel carbonyl was refluxed with acrylonitrile, the four carbonyl groups were replaced by two AN molecules[78] to give red, nonvolatile, pyrophoric crystals of bis-(acrylonitrile)nickel(0). The ir spectrum of this compound contained no absorption in the vinylic proton or carbon–carbon double-bond regions. A band at 2200 cm^{-1} attributable to nitrile stretching was shifted very little from the corresponding band in the spectrum of AN (2245 cm^{-1}). Since nitrile absorption in the ir spectrum of complexes in which the nitrogen lone-pair electrons are involved in the bonding shifts to higher frequencies,[79–81] it was concluded that only the carbon–carbon double bond of AN takes part in the bonding. Structure **39** was therefore proposed, with the proviso that the complex is undoubtedly associated in the solid



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[75] R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).

[76] S. Kawaguchi and T. Ogura, *ibid.*, **5**, 844 (1966).

[77] G. Allen, J. Lewis, R. F. Long, and C. Oldham, *Nature*, **202**, 589 (1964).

[78] G. N. Schrauzer, *J. Amer. Chem. Soc.*, **81**, 5310 (1959).

[79] H. J. Coerver and C. Curran, *ibid.*, **80**, 3522 (1958).

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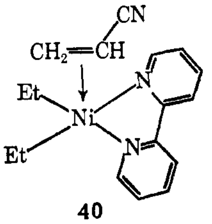
[81] H. A. Brune and W. Zeil, *Z. Naturforsch.*, *A*, **16**, 1251 (1961).

state.[82] The complex can be hydrogenated[82] with a rhodium catalyst at normal pressure (the product was not described) and will readily form 1:1 and 1:2 adducts with triphenylphosphine.[78,83,84] A bispyridine adduct, which was unstable in air and decomposed to metallic nickel at room temperature, was also isolated.[84] Another nickel complex containing pyridine and AN ligands has recently been described.[85] Treatment of diethyl-2,2′-(dipyridyl)nickel(II) with AN at −78° gave an unstable orange solid of composition (2,2′-dipyridyl)-(AN)Et_2Ni, the ir spectrum of which was consistent with structure **40**. The complex catalyzed the polymerization of AN. 1,1-Dicyano- and 1,1,2-tricyanoethylene do not form isolable complexes with nickel carbonyl, which is an extremely powerful polymerization catalyst for these compounds.[86] Phenyl-substituted derivatives of these nitriles gave complexes which are described in section II.H.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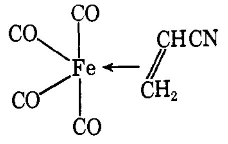
The bonding in bis(acrylonitrile)nickel(0) was explained by recourse to molecular orbital theory.[87] The positions of highest σ-donating and π-accepting strength are localized at the olefinic carbon atoms, and consequently bonding will be more favorable at the carbon–carbon double bond than at the nitrile group.

Bis(acrylonitrile)nickel(0) has been used to catalyze the dimerization of 2,5-norbornadiene,[88] polymerization of various alkynes,[89] and the trimerization of hexafluoro-2-butyne.[42] It was also shown[90] that bis-(acrylonitrile)nickel(0) would catalyze the Meerwein[91] reaction; thus bis(acrylonitrile)nickel(0) reacted with *p*-chlorobenzenediazonium chloride to give α,4-dichlorohydrocinnamic acid. Experiments also indicated the importance of copper(I) chloride–olefin π complexes, and unstable copper(I) chloride and bromide complexes with AN were isolated.[90]

Other group VIII metals which coordinate with AN are iron, ruthenium, and rhodium. Shortly after the discovery that AN would complex with nickel,[78] the unstable acrylonitrileiron(0) tetracarbonyl (**41**) was prepared[92] in low yield (2–3%) by reacting iron pentacarbonyl with AN. It was concluded from nmr and ir measurements that the double bond interacted strongly with the metal, but that the nitrile group did not coordinate; this was subsequently verified by an X-ray structure determination,[93,94] which also showed that the AN ligand assumes an equatorial configuration. Recently two other products were isolated[95] from the treatment of iron pentacarbonyl with AN. One, a volatile oil, was believed, on the basis of ir analysis, to have the ligand bonded to iron *via* the nitrogen atom. The other compound was a very stable bridged dimer (structure **42**) in which π- and σ-bonding were postulated from ir and nmr data. Ethylene in μ-dichlorotetrakis(ethylene)dirhodium(I) could be replaced by acrylonitrile, but the product was not characterized.[96] The complex $(AN)_3RuCl_2$ was formed by refluxing ruthenium(III) chloride with excess AN in ethanol;[97] bonding through the nitrogen was indicated from ir data. On the other hand, a polymeric product, which was tentatively formulated as **43** on the basis of ir measurements, has also been obtained[98] from the reaction between rhodium(III) chloride and AN. Treat-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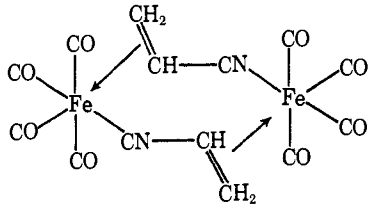
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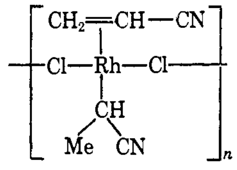
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(89) G. N. Schrauzer, *ibid.*, **94**, 1403 (1961).

(90) G. N. Schrauzer, *ibid.*, **94**, 1891 (1961).

(91) H. Meerwein, E. Buchner, and K. Emster, *J. Prakt. Chem.*, **152**, 237 (1939).

(92) S. F. A. Kettle and L. E. Orgel, *Chem. Ind.* (London), 49 (1960).

(93) A. R. Luxmoore and M. R. Truter, *Proc. Chem. Soc.*, 466 (1961).

(94) A. R. Luxmoore and M. R. Truter, *Acta Crystallogr.*, **15**, 1117 (1962).

(95) E. H. Schubert and R. K. Sheline, *Inorg. Chem.*, **5**, 1071 (1966).

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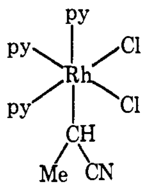
(97) A. Misono, Y. Uchida, M. Hidai, and H. Kanai, *Chem. Commun.*, 357 (1967).

(98) K. C. Dewhirst, *Inorg. Chem.*, **5**, 319 (1966).

ment with pyridine broke down the polymer chain to give (1-cyanoethyl)trispyridinerhodium(III) dichloride (**44**).



44, py = pyridine

Only one group VII metal, namely manganese, has been shown to complex with AN. Two AN–manganese complexes have been reported.[99,100] Photochemical reaction between cyclopentadienylmanganese(0) tricarbonyl and AN yielded a complex with the formula $(AN)(C_5H_5)Mn(CO)_2$ in which the acrylonitrile ligand is π-bonded through the double bond.[99] Evidence leading to this hypothesis was (a) the stability of the complex, (b) carbonyl ir stretching frequencies, (c) the nitrile stretching frequency, and (d) the nmr spectrum. In contrast, the bonding between AN and manganese in the complex $(AN)Mn_2(CO)_9$, prepared by direct interaction of $Mn_2(CO)_{10}$ and AN, was found to be through the nitrogen atom.[100]

Complexes of AN with all the group VI metals have been isolated. Bonding through the nitrogen occurs in acrylonitriletungsten(0) pentacarbonyl, though this is not surprising since complexes of group VI metals with acetonitrile are well known. Massey,[101] who first reported this complex as a product from the reaction between a large excess of AN and tungsten hexacarbonyl, noted "normal" carbon–carbon double-bond absorption in the ir spectrum. Furthermore, the nitrile band was unusually high, indicative of nitrogen lone-pair donation,[79–81] and the nmr spectrum was remarkably similar to uncomplexed AN. A spectroscopic study (ir and nmr) of complexes $(AN)_nM(CO)_{6-n}$ (M = Cr, Mo, or W; n = 1, 2, or 3) has been reported.[102] These compounds were prepared by substituting AN into the appropriate acetonitrile analog. Elemental analysis figures, when M = W and n = 1 or 3, were given[103] but the remaining members of the series were not adequately characterized. Spectral data led the authors[102] to the conclusion that the mono- and disubstituted complexes (n = 1 or 2) were bonded through the nitrogen atom, while carbon–carbon double-bond participation was indicated for the $(AN)_3M(CO)_3$ series. When molybdenum hexacarbonyl was refluxed in excess of acrylonitrile, 4 moles of carbon monoxide was liberated and a complex with analysis consistent with $(AN)_2Mo(CO)_2$ was obtained. Bonding through the double bond was suggested on the basis of ir results, but the possibility that the complex could be a polymer was not ruled out.[104]

A complex of the formula $(AN)_2VCl_3$, which was formed at −70°, proved to be a useful polymerization cocatalyst for ethylene.[105] No details of bonding were proffered. Complexes formed by reacting anhydrous halides of every metal in the first transition series with acrylonitrile have been isolated;[106] some compounds were nonstoichiometric and the formulas given by elemental analyses were $TiCl_3 \cdot 3AN$, $VCl_3 \cdot 3AN$, $CrCl_3 \cdot 3AN$, $MnCl_2 \cdot AN$, $FeCl_2 \cdot AN$, $FeCl_2(FeCl_3)_2 \cdot 6AN$, $CoCl_2 \cdot AN$, $NiCl(AN)_{2.2}$, $NiCl_2 \cdot 3AN$, $NiCl_2(AN)_{1.1}$, $CuCl_2(AN)_{0.5}$, and $ZnCl_2 \cdot 2AN$. No details of the structures of these complexes were given.

Recently an acrylonitrile complex of platinum(0) was isolated by treating bis(triphenylphosphine)-platinum(0) with AN under very mild conditions. Colorless crystals, stable in air, were obtained and thought to be a π-bonded complex since the carbon–carbon double-bond absorption was 100 cm^{-1} lower than that for the free ligand; also the olefinic protons appeared at unusually high frequency in the nmr spectrum.[107] Elemental analysis was correct for the formula $(AN)(Ph_3P)_2Pt$.

The most interesting aspect of the acrylonitrile ligand is that five modes of bonding can be visualized. These are: (a) π-bonding through the carbon–carbon double bond, (b) π-bonding through the nitrile triple bond, (c) σ-bonding from the nitrogen lone pair, (d) chelation involving (a) and (b), and (e) chelation involving (a) and (c).

Participation of the nitrile triple bond has not been postulated for any acrylonitrile complex so that modes b and d are eliminated. The bonding situation for the compounds described is shown in Table II. Unfortunately, no clear picture emerges except that chelation (e) is rare. Some metals, particularly those in group VI, are versatile and will bond by methods a and c. All three modes of bonding have been postulated for $(AN)Fe(CO)_4$. Carbon–carbon double-bond participation only has been observed for nickel(0), manganese(I), and platinum(0). σ-Bonding through the nitrogen atom is the only type observed for ruthenium(II).

Tetracyanoethylene (TCNE) is a very efficient electron acceptor and forms colored complexes with a wide variety of organic molecules particularly hydrocarbons.

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(100) M. L. Ziegler, H. Hass, and R. K. Sheline, *Chem. Ber.*, **98**, 2454 (1965).

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(102) B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, **2**, 1023 (1963).

(103) D. P. Tate, J. M. Augl, and A. Buss, *ibid.*, **2**, 427 (1963).

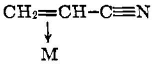
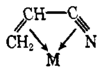
(104) A. G. Massey and L. E. Orgel, *Chem. Ind.* (London), 436 (1961).

(105) L. K. Case, British Patent 822,091 (1959); *Chem. Abstr.*, **54**, 15247*d* (1960).

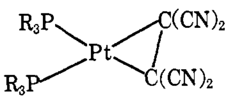
(106) R. J. Kern, *J. Inorg. Nucl. Chem.*, **25**, 5 (1963).

(107) S. Cenini, R. Ugo, F. Bonati, and G. L. Monica, *Inorg. Nucl. Chem. Lett.*, **3**, 191 (1967).

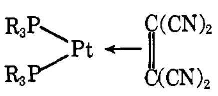
TABLE II
BONDING IN ACRYLONITRILE METAL COMPLEXES

π-Bonding through the double bond			σ-Bonding from the nitrogen atom			Chelation		
 $\underset{\displaystyle M}{\overset{\downarrow}{CH_2{=}CH{-}C{\equiv}N}}$			$CH_2{=}CH{-}C{\equiv}N{\rightarrow}M$					
Complex	Evidence for bonding	Ref	Complex	Evidence for bonding	Ref	Complex	Evidence for bonding	Ref
$(AN)_2Ni$	Ir	78	$(AN)Fe(CO)_4$	Ir	95	$[(AN)Fe(CO)_4]_2$	Ir and nmr	95
$(AN)Et_2(2,2'\text{-dipyridyl})Ni$	Ir	85	$(AN)_3RuCl_2$	Ir	97			
$(AN)Fe(CO)_4$	Ir, nmr, and X-ray	92–94	$(AN)Mn_2(CO)_9$	Ir	100			
$(AN)(C_5H_5)Mn(CO)_2$	Ir and nmr	99	$(AN)W(CO)_5$	Ir and nmr	101			
$(AN)_3Cr(CO)_3$	Ir	102	$(AN)Cr(CO)_5$	Ir	102			
$(AN)_3Mo(CO)_3$	Ir	102	$(AN)Mo(CO)_5$	Ir	102			
$(AN)_3W(CO)_3$	Ir and nmr	102	$(AN)_2Cr(CO)_4$	Ir	102			
$(AN)_2Mo(CO)_2$	Ir	104	$(AN)_2Mo(CO)_4$	Ir	102			
$(AN)(Ph_3P)_2Pt$	Ir and nmr	107	$(AN)_2W(CO)_4$	Ir and nmr	102			

Indeed, it has been reported to form a complex with ferrocene, by interaction with the π electrons of one of the cyclopentadienyl rings.[108] Thus one would expect that TCNE would complex with transition metals, particularly those to the right of the periodic table and in low valency states, since these metals can often be stabilized by ligands capable of accepting charge. Accordingly, compounds of the type $(R_3P)_2(TCNE)$-$Pt(0)$ were prepared in two ways.[109] This was accomplished either by replacing the phenylacetylene in (R_3P)(phenylacetylene)Pt(0) by TCNE, or by reacting TCNE with $[H(R_3P)Pt]Cl$ where $R = Ph$ or Et in both cases. The resulting compounds can be regarded either as σ-bonded square-planar Pt(II) (**45**) or π-bonded trigonal Pt(0) (**46**) complexes. The authors preferred structure **45** since $(Ph_3P)_4Pt(0)$ is oxidized to Pt(II) by TCNE.



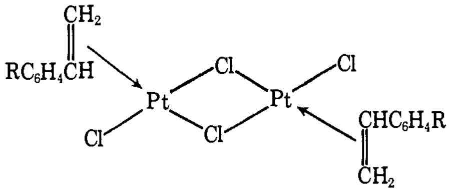
45, R = Ph or Et



46, R = Ph or Et

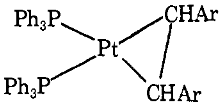
F. PHENYL AND SUBSTITUTED-PHENYL COMPOUNDS

Complexes derived from the ligands styrene and stilbene have received much attention. First efforts in this field were by Anderson,[110] who studied the effect of replacing ethylene in Zeise's salt by various substituted olefins. With styrene he obtained a product whose elemental analysis was consistent with $PtCl_2$-(styrene)$_2$. Although the compound could not be purified, Anderson prepared a pure salt from it which he formulated as $[Pt(NH_3)_4]^{2+}[PtCl_3(\text{styrene})]_2^-$. The 1,1-diphenylethylene and 1-phenyl-1-methylethylene analogs could not be obtained, although both compounds liberated ethylene from Zeise's salt.[110] As part of an investigation into the relative stability of platinum complexes, a series of substituted styreneplatinum(II) compounds (**47**) was prepared[111] by substituting the appropriate styrene derivative for ethylene in tetrachlorobis(ethylene)diplatinum(II). The structure–stability correlation of this series together with some pyridine N-oxide analogs will be discussed in section IV.



47, R = H, 3-OMe, 4-OMe, 3-NO$_2$, 4-NO$_2$, 3-Cl, 4-Cl, or 4-Me

Two stilbeneplatinum complexes (**48**) were isolated by reacting stilbene, and separately 4,4′-dinitrostilbene, with *cis*-dichlorobis(triphenylphosphine)platinum(II) in the presence of hydrazine.[112] The products, which were initially obtained pure, deteriorated on standing.



48, Ar = Ph or p-NO$_2$C$_6$H$_4$

It was thought that the olefin took up two coordination sites, such that a square-planar platinum(II) complex was formed. Recently nmr was used[113] to investigate

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(108) E. Adam, M. Rosenblum, S. Sullivan, and T. N. Margulis, *J. Amer. Chem. Soc.*, **89**, 4540 (1967).

(109) W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

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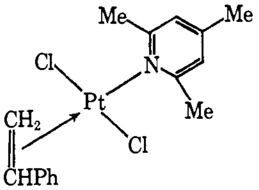
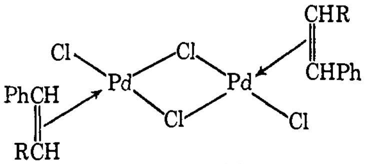
the rotation of styrene about the platinum–styrene bond axis in *trans*-dichloro(styrene)(2,4,6-trimethylpyridine)platinum(II) (**49**). Molecular models show that the 2- and 6-methyl groups on the pyridine ring favor a geometry in which this ring is perpendicular to the square plane. Assuming that the styrene carbon–carbon double bond is also at right angles to the square plane, the 2- and 6-methyl protons will be nonequivalent. At room temperature only one signal attributable to both these methyl groups was observed, showing that either the styrene ligand is rotating rapidly, or the pyridine, or both. The "fixed pyridine–rotating styrene" model was preferred.[113] Rapid exchange of either styrene or pyridine molecules could also be ruled out since coupling between platinum and both ligands was observed. At −60°, however, separate signals were seen for the 2- and 6-methyl groups showing that rotation had been arrested. The nmr spectrum of potassium trichloro(styrene)platinum(II) was found[114] to be first order. Coupling between the two β protons was very small, but coupling between platinum and the olefinic protons was clearly visible.



49

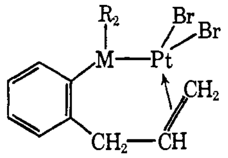
Two palladium complexes have been reported, one with a styrene ligand and one with stilbene. The styrene compound, tetrachlorobis(styrene)dipalladium(II) (**50a**) was prepared from bis(benzonitrile)palladium(II) dichloride.[115] Treatment of palladium(II) chloride with styrene did not lead to **50a**. A subsequent X-ray structure determination[116] showed that the four chlorine and two palladium atoms are coplanar, and that the angle between this plane and the carbon–carbon double bond is 74°. The stilbene analog, (stilbene)$_2$Pd$_2$Cl$_4$, was prepared[117] in a manner similar to that employed for **50**; its X-ray structure[118] showed a similar π-bonded complex (**50b**) with the two phenyl groups equidistant from the metal.



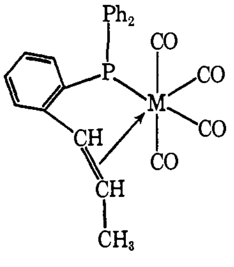
50a, R = H
b, R = Ph

Styrene and derived styrene complexes of iron, nickel, and tungsten have also been described. Styrene, α-methylstyrene, and *trans*-stilbene complexes of nickel were obtained[119] in good yield by replacing ethylene in ethylenebis(triphenylphosphine)nickel(0). By treating acetonitriletungsten(0) pentacarbonyl with *trans*-stilbene, an orange solid formulated as (PhCH=CHPh)W(CO)$_5$ was obtained.[120] The iron complex, styreneiron(0) tetracarbonyl, was prepared photochemically from iron pentacarbonyl and styrene.[47]

Finally, several olefinic phenylphosphine (and related arsine) complexes have recently been reported. When the ligand, *o*-allylphenyldiphenylphosphine, was mixed with a solution of platinum(II) bromide, colorless crystals of **51a** were isolated.[121,122] Double-bond participation was indicated by the shift from 1642 to 1495 cm^{-1} in the carbon–carbon double-bond stretching frequency in the free and complexed ligand, respectively. The same ligand formed similar compounds when reacted with 2,5-norbornadienemolydenum(0) tetracarbonyl and the chromium and tungsten analogs. The products were thought to have structure **52** because the nmr spectrum showed that the allyl group had isomerized. Support for structure **52** was provided when similar compounds were prepared from *o*-vinylphenyldiphenylphosphine and the tetracarbonyls of



51a, M = P; R = Ph
b, M = As; R = Me



52, M = Mo, Cr, or W

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(114) H. P. Fritz, K. E. Schwarzhans, and D. Sellmann, *J. Organometal. Chem.*, **6**, 551 (1966).

(115) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Amer. Chem. Soc.*, **60**, 882 (1938).

(116) J. R. Holden and N. C. Baenziger, *ibid.*, **77**, 4987 (1955).

(117) N. C. Baenziger and J. R. Doyle, U. S. Department of Commerce, Office of Technical Services, PB Report 156075, 1961; *Chem. Abstr.*, **58**, 5241*b* (1963).

(118) N. C. Baenziger and J. R. Doyle, U. S. Department of Commerce, Office of Technical Services, PB Report 156074, 1961; *ibid.*, **58**, 5241*d* (1963).

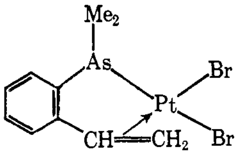
(119) G. Wilke and G. Herrmann, *Angew. Chem.*, **74**, 693 (1962).

(120) D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross, and J. G. Grasselli, *J. Amer. Chem. Soc.*, **86**, 3261 (1964).

(121) M. A. Bennett, L. V. Interante, and R. S. Nyholm, *Z. Naturforsch.*, *B*, **20**, 633 (1965).

(122) M. A. Bennett, L. V. Interante, and R. S. Nyholm, *Inorg. Chem.*, **5**, 2212 (1966).

the same three metals;[123] X-ray crystallography has recently confirmed it.[124] The ligands *o*-allylphenyldimethylarsine and *o*-vinylphenyldimethylarsine also chelate to platinum(II) bromide (**51b**) and **53**, respectively).[125] Double-bond participation was indicated by the fact that the carbon–carbon double-bond stretching absorption appeared at 1500 cm^{-1}. Complexes of formulas L_2PtBr_2 (L = *o*-allylphenyldimethylarsine or *o*-vinylphenyldimethylarsine) with no double-bond participation were also isolated. Bromine oxidized **51b** and **53** to products containing 1 extra mole of bromine; dimeric octahedral platinum(IV) complexes were proposed for the brominated products in which the allyl (or vinyl) side chain was σ-bonded to the platinum. Treatment of the bromo derivatives with methanol regenerates methoxy derivatives of the original complexes, by elimination of hydrogen bromide.[126]

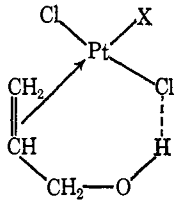


53

G. ALCOHOLS AND ETHERS

There are very few examples of reactions between unsaturated alcohols and metals leading to π complexes. However, allyl alcohol was found[127] to react with chloro-bridged $(Et_3P)_2Pt_2Cl_4$ to give the mononuclear complex $(Et_3P)Pt(\text{allyl alcohol})Cl_2$. The olefin ligand was assumed to be π-bonded to platinum because the carbon–carbon double-bond stretching frequency was lowered 140 cm^{-1} by coordination. A series of allyl alcohol and methyl allyl ether platinum amine complexes, $(CH_2{=}CHCH_2OR)AmPtCl_2$ (R = H or Me; Am = *p*-toluidine, piperidine, or pyridine), as well as $(CH_2{=}CHCH_2OR)PtCl_3$ (R = H or Me), have been isolated.[128] On the basis of ir data, the series was shown to have π-bonded allyl ligands; in the case of the nonmethylated complexes there was extensive hydrogen bonding between the chlorine and hydroxyl groups (**54**).

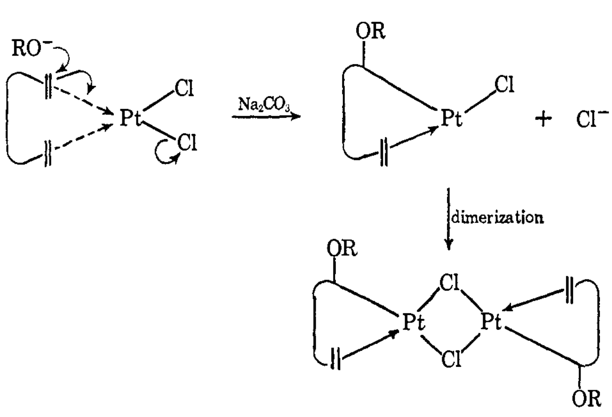
A colorless complex of allyl alcohol and copper(I) was obtained[129] from allyl alcohol and cuprous chloride in a vacuum system; ΔH for the reaction was found to be −12 kcal/mol. The complex, which is dimeric at 23–43° but monomeric at 97°, gave an ir spectrum in which carbon–oxygen bands occurred at normal frequencies whereas the carbon–carbon double-bond stretching absorption shifted to a frequency 95 cm^{-1} lower than that for allyl alcohol. Consequently, the ligand was assumed to be π-bonded to the metal.



54, X = Cl, *p*-toluidine, piperidine, or pyridine

A complex, which was formed by the interaction of diallyl ether with potassium chloroplatinate(II), has been described.[130] The compound was found to be monomeric and possess a large dipole moment: on this basis ligand chelation was proposed such that both carbon–carbon double bonds occupied coordination sites. Ethyl vinyl ether was reported to form a π-bonded complex with iron pentacarbonyl.[47] The product fits elemental analysis figures for $(CH_2{=}CHOC_2H_5)Fe(CO)_4$, and, since it did not absorb in the carbon–carbon double-bond stretching region of the ir, double-bond participation was assumed.

An interesting reaction between diolefin complexes of platinum[131] or palladium[132] and alcohols in the presence of weak base was shown to lead to hydroxy-olefin chloro-bridged dimeric complexes. The reaction appears to be quite general and can be visualized as nucleophilic attack of the alkoxide ion at one of the unsaturated carbon atoms. Formation of a carbon–platinum σ bond and expulsion of a chloride ion gives the observed product. The reaction sequence is depicted in eq 3 for a platinum–diolefin complex.



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[123] M. A. Bennett, R. S. Nyholm, and J. D. Saxby, *J. Organometal. Chem.*, **10**, 301 (1967).

[124] H. Luth, M. R. Truter, and A. Robson, *Chem. Commun.*, 738 (1967).

[125] M. A. Bennett, J. Chatt, G. J. Erskine, J. Lewis, R. F. Long, and R. S. Nyholm, *J. Chem. Soc., A*, 501 (1967).

[126] M. A. Bennett, G. J. Erskine, and R. S. Nyholm, *ibid.*, 1260 (1967).

[127] J. Chatt, N. P. Johnson, and B. L. Shaw, *ibid.*, 1662 (1964).

[128] J. Chatt, R. G. Guy, L. A. Duncanson, and D. T. Thompson, *ibid.*, 5170 (1963).

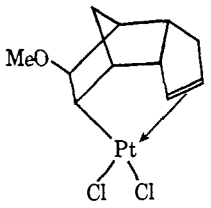
[129] T. Ogura, N. Furuno, and S. Kawaguchi, *Bull. Chem. Soc. Jap.*, **40**, 1171 (1967).

[130] K. A. Jensen, *Acta Chem. Scand.*, **7**, 866 (1953).

[131] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 2496 (1957).

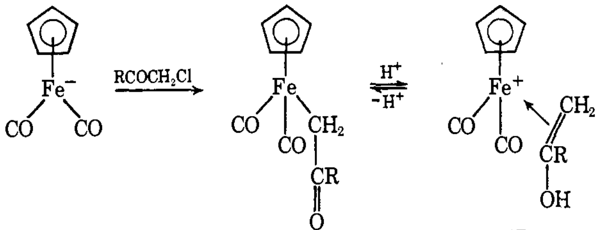
[132] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *ibid.*, 3413 (1957).

It was shown that, with dicyclopentadieneplatinum(II) dichloride in the presence of methyl and ethyl alcohols,[131] the products were the same as those originally reported by Hoffmann and Narbutt[16] in 1908. The reaction (eq 3) on platinum and palladium derivatives of dipentene and 1,5-cyclooctadiene[131,132] gave hydroxyolefin complexes. In an elegant piece of work Stille and Morgan unravelled the stereochemistry of these compounds and extended the series by preparing the platinum and palladium 2,5-norbornadiene analogs.[133] Structural assignments were made by reduction of the complexes to known, or independently synthesized, ethers and by nmr studies. Subsequently an X-ray structure determination of the (methoxydicyclopentadiene)platinum(II) derivative[134] confirmed the structure (**55**) proposed by Stille and Morgan.[133]



55

The reaction between sodium cyclopentadienyliron(II) dicarbonyl and either chloroacetone or chloroacetaldehyde gave[135] substituted alkyliron(II) derivatives (**56**) which reversibly enolized when treated with dry hydrogen bromide (eq 4, R = H or Me). On the basis of ir and nmr measurements, the π-bonded structure **57** was postulated. This compound (R = H) is particularly interesting because it is a derivative of vinyl alcohol,[136] and it is surprising that this stabilization of the unusually labile enol form was not emphasized.



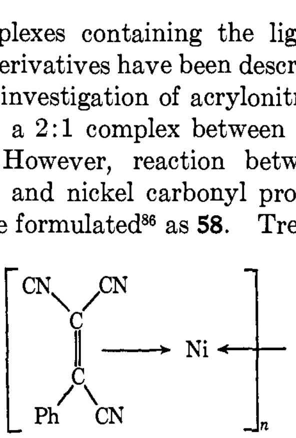
(4)

56 **57**

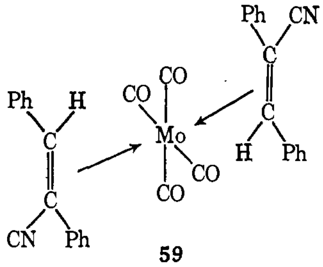
H. LIGANDS WITH MORE THAN ONE FUNCTIONAL GROUP

There are several examples of olefinic ligands, having two or more different functional groups, and which complex to a metal. Because of the complicating effect that different groups have upon each other, they are discussed in a separate section.

Several complexes containing the ligand cinnamonitrile and its derivatives have been described. Schrauzer, during his investigation of acrylonitrilenickel complexes, isolated a 2:1 complex between cinnamonitrile and nickel.[73] However, reaction between tricyanophenylethylene and nickel carbonyl produced a polymeric substance formulated[86] as **58**. Treatment of this complex with tributylphosphine afforded bis(tributylphosphine)(tricyanophenylethylene)nickel(0), which was shown to be diamagnetic and monomeric in benzene.[86] Red unstable crystals of **59** were isolated from the reaction between 1,2-diphenylcyanoethylene and molybdenum hexacarbonyl.[137] Attachment to the metal *via* the olefinic double bond was indicated from the ir spectrum. Double-bond participation was also proposed for complexes obtained from the reaction of copper(I) salts with 1,1-dicyanophenylethylene and 1,1-dicyano-2,2-diphenylethylene.[138] The ir spectra of these intensely colored complexes showed normal nitrile bands, but carbon–carbon double-bond stretching frequencies 100 cm^{-1} lower than those of the free ligands.



58



59

The complex cinnamaldehydeiron(0) tetracarbonyl (**35b**) was prepared from diiron nonacarbonyl.[73] The nmr and ir spectra showed that only the carbon–carbon double bond was involved in bonding. Thus the olefinic but not the aldehyde protons absorbed at higher field in the nmr spectrum of the complex, and a strong carbon–oxygen double-bond absorption was apparent in the ir spectrum. When **35b** was heated in benzene at 60°, 1 mole of carbon monoxide was lost to produce cinnamaldehydeiron(0) tricarbonyl. Disappearance of the carbon–oxygen double-bond absorption in the ir spectrum and a marked upfield shift (2 ppm) in the aldehyde proton, together with loss of coupling between the aldehyde and olefinic protons in the nmr spectrum,

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(133) J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, **88**, 5135 (1966).

(134) W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966).

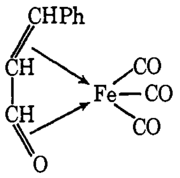
(135) J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 1 (1964).

(136) Vinyl alcohol *per se* is unknown because the keto form (acetaldehyde) is much more stable.

(137) G. N. Schrauzer and S. Eichler, *Chem. Ind.* (London), 1270 (1961).

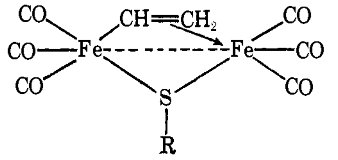
(138) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 260 (1962).

led the authors to propose structure **60**, in which the unsaturated aldehyde is chelated to the metal. The *p*-methoxycinnamaldehyde complex was similar.[73]



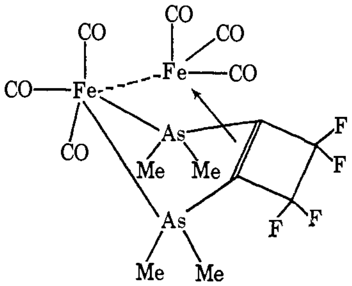
60

The reaction between several vinyl thioethers and diiron nonacarbonyl was reported[139] to yield dinuclear complexes of structure **61**. The products were red oils (except where R = Me, when an orange solid was isolated) and fairly stable. Their ir spectra contained no absorption in the carbon–carbon double-bond region (except in the case where R = vinyl, when absorption due to the uncomplexed vinyl residue was recognized), and showed that no bridging carbonyl groups were present. The nmr spectrum of each complex could be analyzed and was consistent with the proposed structures. Sharp lines showed that the compounds (**61**) are diamagnetic and therefore contain metal–metal bonds. Cleavage of the sp^2 carbon–sulfur bond by iron carbonyl is reasonable since precedent for it exists[140] in the desulfurization of thiophen with iron pentacarbonyl.



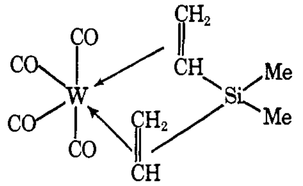
61, R = Me, Et, isopropyl, or vinyl

An interesting π complex was isolated during an investigation[141] of the ligand 1,2-bis(dimethylarsino)-tetrafluorocyclobutene. Treatment of this ligand with iron pentacarbonyl gave a tricyclic complex which was shown by X-ray crystal analysis to have structure **62**, which also contains a metal–metal bond. This same ligand was subsequently shown[142] to form 1:1 complexes with palladium(II), platinum(II), and mercury(II). Chelation through the two arsenic atoms occurred (no double-bond participation) with these metals.



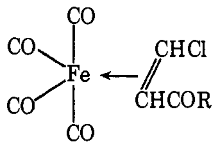
62

A diolefin–metal complex in which the two double bonds of the olefin are separated by silicon was prepared by refluxing tungsten hexacarbonyl with dimethyldivinylsilane.[143] Yellow crystals analyzed correctly for $(CH_3)_2Si(CH{=}CH_2)_2(CO)_4$ and gave an ir spectrum consistent with structure **63**. A similar complex was obtained when molybdenum hexacarbonyl was used.



63

Recently a series of (β-chlorovinyl ketone)iron(0) tetracarbonyl π complexes have been reported by Nesmeyanov's group.[144] From the ir and nmr spectra it was deduced that the carbon–carbon double bonds form metal π bonds, and that carbonyl participation is negligible. This and other chemical evidence led the authors to propose structure **64**. The organic ligand is probably equatorial by analogy with the similar complexes **29** and **41** for which X-ray structure determinations have been carried out.[61,93] Derivatives of phenyl β-aminovinyl ketone chelate to tin(IV) through the nitrogen and oxygen atoms thus completing a six-membered ring (most favorable stereochemically); no double bond participation occurs.[145]



64, R = Me, Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, or *p*-BrC_6H_4

I. MISCELLANEOUS

Olefins containing several types of substituent not already dealt with have been shown to form metal π complexes. These are collected below for the sake of convenience.

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(139) R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 3600 (1961).

(140) H. D. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols, and F. G. A. Stone, *ibid.*, **82**, 4749 (1960).

(141) F. W. B. Einstein, W. R. Cullen, and J. Trotter, *ibid.*, **88**, 5670 (1966).

(142) W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *Inorg. Chem.*, **6**, 2256 (1967).

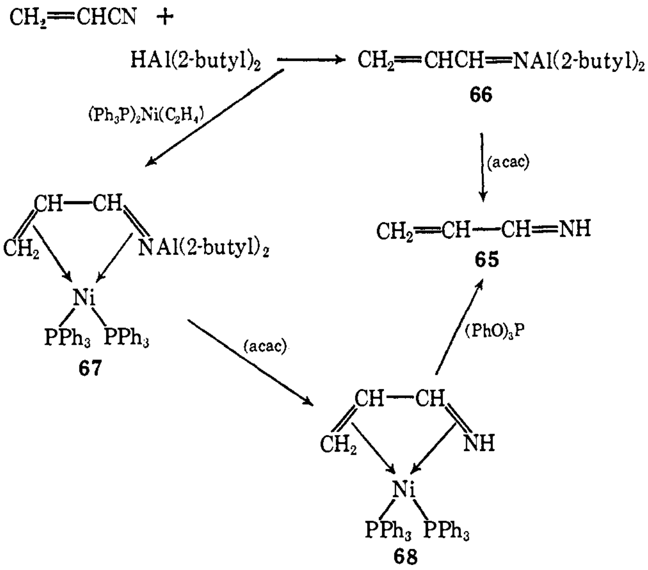
(143) T. A. Manuel and F. G. A. Stone, *Chem. Ind.* (London), 231 (1960).

(144) A. N. Nesmeyanov, K. Ahmed, L. V. Rybin, M. I. Rybinskaya, and Y. A. Ustynyuk, *J. Organometal. Chem.*, **10**, 121 (1967).

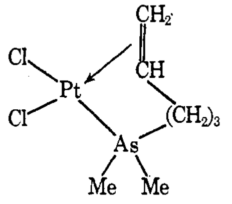
(145) V. T. Panyushkin, V. P. Kurbatov, A. D. Garnovskii, O. A. Asipov, V. I. Minkin, and K. N. Kovalenko, *Zh. Neorg. Khim.*, **12**, 819 (1967); *Chem. Abstr.*, **67**, 121897*q* (1967).

An improved synthesis of acraldehydeimine **65** has led to the isolation of a π complex containing both nickel and aluminum.[146] It had previously been shown[147] that acrylonitrile would add to bis(2-butyl)-aluminum hydride to give the N-aluminum-substituted acraldehydeimine **66**. Treatment of **66** with acetylacetone gave **65** which was difficult to separate. The isolation of **65** was greatly facilitated by complexing **66** with bis(diphenylphosphine)ethylenenickel(0) to give the complex **67** from which the required imine (**65**) could readily be obtained by successive treatments with acetylacetone and triphenyl phosphite. These reactions are set out in Scheme I. Complex **67** could be isolated as a sparingly soluble orange solid but its structure was not discussed. Treatment of **67** with acetylacetone gave deep red crystals of the acraldehydeimine-nickel(0) complex (**68**) which again was not described further.

SCHEME I



There are several examples of complexes containing ligands which consist of tertiary phosphines or arsines with an alkenyl group. Such ligands contain two potential coordination sites, the double bond and the phosphorus (arsenic) donor atom, and the interesting possibility that either or both will form bonds was recognized by Kouwenhoven, Lewis, and Nyholm. These authors first studied the reaction of the ligand dimethyl-4-pentenylarsine with platinum and mercuric salts.[148] The ligand reacted readily with sodium chloroplatinate(II) to form a colorless complex which contained one arsine molecule per platinum atom. It was therefore concluded that the ligand had taken up two coordination sites, and structure **69** was proposed. The corresponding bromide and iodide were formed by adding the appropriate lithium salt to the reaction mixture. Evidence for double-bond participation was the presence of a band at 1505 cm^{-1} in the ir spectrum of **69**, which appeared at 1637 cm^{-1} in the uncomplexed ligand. Further proof was the reappearance of the 1637-cm^{-1} band when **69** was treated with diphenylarsine; the carbon–carbon double bond was displaced, leaving the original ligand attached solely by the arsenic lone pair. In contrast to platinum, mercuric salts gave dimeric complexes in which there was no double-bond participation. The study was extended[149] to the ligand dimethyl-4-pentenylphosphine, and phosphorus complexes analogous to **69** were formed between the phosphine and potassium chloroplatinate(II). Again chelation was adduced and the double bond could be displaced by tertiary arsines, *p*-toluidine, and thiocyanate ion. Palladium complexes, like the mercury compounds, were shown to be dimeric.[149] It has also been shown that allyldiphenylphosphine does not chelate to nickel, since complexes of the type $(allylPh_2P)_2NiX_2$ were isolated.[150]



69

Colorless stable 1:1 and 2:1 complexes were isolated from the reaction between vinyldiphenylphosphine and silver(I) salts.[151] On the basis of ir and nmr spectroscopy, it was postulated that both the phosphorus atom and the carbon–carbon double bond took part in the bonding.

As might be expected olefins which are disubstituted with phosphorus or arsenic do not form π-bonded complexes. Chelation by these group V donors is preferred especially if five-membered rings result. Thus bis-1,2-(diphenylphosphine)ethylene chelates[152] to nickel(II) and cobalt(II), and bis-1,2-(dimethylarsine)ethylene chelates[153] to titanium(IV) with no double-bond participation in either case. In the latter case, when the ligand is in the *trans* configuration, chelation is prevented and a polymer is produced.[153]

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(146) R. Bogdanovic and M. Velic, *Angew. Chem. Int. Ed. Engl.*, **6**, 803 (1967).

(147) B. Bogdanovic, *Angew. Chem.*, **77**, 1010 (1965).

(148) H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *Proc. Chem. Soc.*, 220 (1961).

(149) M. A. Bennett, H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 4570 (1964).

(150) M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. J. Pratt, L. E. Sutton, and L. M. Venanzi, *ibid.*, 693 (1962).

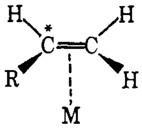
(151) C. Wu and F. J. Welch, *J. Org. Chem.*, **30**, 1229 (1965).

(152) H. N. Ramaswamy, H. B. Jonassen, and A. M. Aguiar, *Inorg. Chim. Acta*, **1**, 141 (1967).

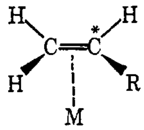
(153) R. J. H. Clark and R. H. U. Negrotti, *Chem. Ind.* (London), 154 (1968).

III. OPTICAL ISOMERISM

This section is devoted to the work of Paiaro and Panunzi who realized[154] that if an unsymmetrically substituted olefin was π-bonded to any center, the resulting molecule would be disymmetric;[155] *i.e.*, it would have a nonsuperimposable mirror image. When such a condition obtains, the mirror images are enantiomorphs, and the compound is optically active. In the case of the unsymmetrical olefin $CH_2{=}CHR$, the two enantiomorphs are **70** and **71** (R = any group except H; M = coordinating center). In accordance with the nomenclature proposed by Cahn, Ingold, and Prelog[156] the asymmetric olefinic carbon atom in **70** (designated C*) can be defined as (*S*) while C* in **71** is (*R*). Rotation of the olefin about the olefin–M axis does not effect racemization.



70

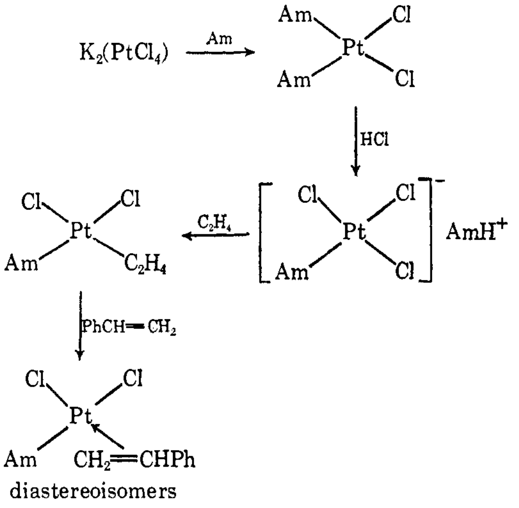


71

Racemic modifications of a number of olefin complexes were resolved by separating diastereoisomers formed when another asymmetric ligand was incorporated in the molecule. Thus by crystallizing solutions of *trans*-dichloro(olefin)[(*R* or *S*)-α-phenylethylamine]platinum(II), in which the olefin was propylene, styrene, or *trans*-2-butene, one diastereoisomer could be isolated. In the case of *trans*-2-butene[157] the type of diastereoisomer obtained depended upon the solvent used. By treatment of the unique diastereoisomers with hydrochloric acid followed by $[(NH_3)_4Pt]Cl_2$, it was possible to separate optically active $[PtCl_3($*trans*-2-butene$)]^-$ as the tetraammineplatinum(II) salt. The diastereoisomeric mixtures were prepared by olefin exchange in *trans*-(C_2H_4)(amine)$PtCl_2$. Subsequently *cis*-dichloro(styrene)[(*S*)-α-phenylethylamine]platinum(II) was prepared and the diastereoisomers were separated.[158]

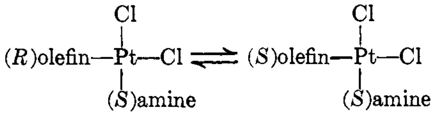
The reaction sequence leading to the *cis* isomer is shown in Scheme II.

SCHEME II



Am = (*S*)-α-phenylethylamine

In the case of 1,2-disubstituted olefins oriented *cis* to phenylethylamine, the diastereoisomeric mixture did not contain equal quantities of (*R*) and (*S*) olefin; *i.e.*, the equilibrium constant of eq 5 was not unity as was found in the case of the *trans*-olefin(amine)platinum(II) series.[159] A study of the optical properties of products formed from a number of differently substituted olefins showed that the origin of the asymmetric induction lay in the steric interaction of the olefin and the adjacent amine (whose configuration remains constant).[160]



$$(R)\text{olefin}-\underset{\underset{(S)\text{amine}}{|}}{\overset{\overset{\text{Cl}}{|}}{\text{Pt}}}-\text{Cl} \rightleftharpoons (S)\text{olefin}-\underset{\underset{(S)\text{amine}}{|}}{\overset{\overset{\text{Cl}}{|}}{\text{Pt}}}-\text{Cl} \qquad (5)$$

Paiaro, Palumbo, Musco, and Panunzi[161] also reported the resolution of diastereoisomers formed in the reaction between fumaric acid–iron(0) tetracarbonyl and optically active brucine. The brucine complex, without being characterized, was successfully decomposed to yield optically active fumaric acid–iron(0) tetracarbonyl. As expected, when the corresponding maleic acid (*cf. cis*-butene[157]) complex was treated in a similar manner, the decomposition product was optically inactive.

IV. STABILITY STUDIES

Since the general acceptance of the dual nature of olefin–metal bonding put forward by Dewar,[5] and by Chatt and Duncanson,[6] the effect of olefinic functional groups on the nature of the π bond has remained largely obscure. The presence of electron-withdrawing groups on the olefinic carbon atoms can influence the π bond in two opposing ways. Firstly the σ bond formed by donation of the olefinic π electrons to the metal would be weakened. Secondly the energy of the olefin π*-antibonding orbital would be lowered with the result that the back-bond from the metal would be strengthened. Consequently there is uncertainty about the

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[154] G. Paiaro and A. Panunzi, *J. Amer. Chem. Soc.*, **86**, 5148 (1964).

[155] For the full implications of this term see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co. Inc., New York, N. Y., 1962, p 9.

[156] R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).

[157] Note that, when *cis*-butene, which itself possesses a plane of symmetry, is coordinated to a metal, the product has no disymmetry. Diastereoisomers were not formed with this olefin.[154]

[158] G. Paiaro and A. Panunzi, *Tetrahedron Lett.*, 441 (1965).

[159] P. Corradini, G. Paiaro, A. Panunzi, S. F. Mason, and G. H. Searle, *J. Amer. Chem. Soc.*, **88**, 2863 (1966).

[160] A. Panunzi and G. Paiaro, *ibid.*, **88**, 4843 (1966).

[161] G. Paiaro, R. Palumbo, A. Musco, and A. Panunzi, *Tetrahedron Lett.*, 1067 (1965).

over-all effect of substitution since it cannot readily be predicted which of these two factors will predominate.

The main contribution to these studies has been made by Venanzi who has been particularly interested in the stability of olefinic amines, phosphines, arsines, and alcohols. Stability constants together with entropies and enthalpies of formation were determined[55] for a number of platinum(II) olefin complexes of the type $[\mathrm{CH_2{=}CH(CH_2)}_n\mathrm{LHRR'}]^+\mathrm{PtCl_3}^-$ (L = N, P, or As; n = 1 or 2; R, R′ = H or alkyl). Relative stabilities of the complexes were expressed as the equilibrium constant (K_1) for the reaction

$$\mathrm{PtCl_4^{2-} + (ol)^+ \overset{K_1}{\rightleftharpoons} (ol)^+PtCl_3^- + Cl^-} \qquad (6)$$

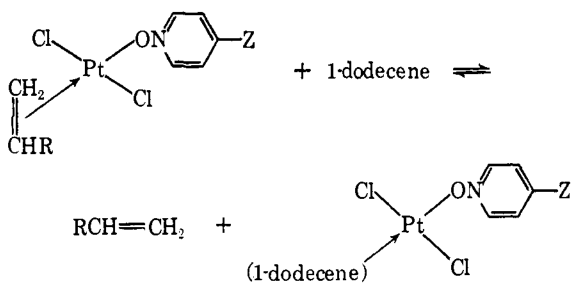
The term (ol)$^+$ refers to the various olefins described above. The equilibrium was studied spectrophotometrically, and additional equilibria involving hydrolysis of the chloroplatinate(II) and the complexes were considered. Entropy and enthalpy values were obtained by determining K_1 at three temperatures. Results showed that the olefins had affinities for platinum greater than water, lower than neutral amines, and comparable with heavy halide ions. The enthalpy and entropy changes indicated that the π-acceptor capacity of the olefin is more important than its σ-donor capacity in platinum–olefin bonding. Investigation of a series of C-substituted allylammonium cations showed[56] that replacement of hydrogen in the allylammonium cation by methyl or phenyl lowered the stability of the complex. The effect is greater at C_1 than at C_2. Therefore steric and electronic effects are important in determining the stability of members of this series of compounds.[56]

On extending the investigations to unsaturated alcohol–platinum complexes, it was found[162] that unsaturated alcohols formed more stable complexes with platinum than did the corresponding ammonium salts. This was attributed mainly to solvation effects. The determination[163] of stability constants for the formation of silver(I)–olefin complexes [AgL$^+$ (L = allylX or *trans*-2-butenylX; X = OH or $\mathrm{NH_2}$)] showed them to be much less stable than the platinum complexes which is due almost certainly to the reduced accepting ability of silver compared with platinum.[164]

Dependence of the platinum–olefin bond strength on other ligands attached to the metal was investigated by determining the equilibrium constant for the reaction between potassium tetrabromoplatinate(II) and several unsaturated ammonium cations.[165] A procedure similar to that employed for investigating the thermodynamics of eq 6 showed that the bromo compounds were less stable than the corresponding chloro derivatives, but that the olefin–platinum bond is stronger in the former. Since $\mathrm{PtBr_4^{2-}}$ is a weaker σ accepter, but stronger π donor, than $\mathrm{PtCl_4^{2-}}$, the π-accepting ability of the olefin is more important in these compounds than its σ-donating ability.

In a further study of platinum complexes, equilibrium constants were obtained[111] for the reaction shown in eq 7. Results for various substituents (X = H, 3-Cl, 3-OMe, 4-OMe, 3-$\mathrm{NO_2}$, 4-$\mathrm{NO_2}$, or 4-Me) were obtained spectrophotometrically. All substituents had a stabilizing effect relative to styrene (X = H). A Hammett plot of the logarithms of the equilibrium constants *vs.* the substituent σ values gave a U-shaped curve rather than a straight line. This served to emphasize that the stability of the complexes does not depend solely upon the electron-withdrawing ability of the ligand. Since steric effects could be ruled out (the substituent being varied is far removed from the metal), it was thought that the accepting and donating abilities of the ligand were affected equally, but in opposite directions by the substituent. In a further study a similar equilibrium (eq 8) was studied[166] by uv spectroscopy. The equilibrium was affected by the styrene (R= p-$\mathrm{C_6H_4X}$ or m-$\mathrm{C_6H_4X}$; X = OMe, Me, H, Cl, or $\mathrm{NO_2}$) and to an even greater extent by the substituents on the pyridine N-oxide ring (Z = OMe, Me, H, Cl, $\mathrm{CO_2Me}$, or $\mathrm{NO_2}$). Electron-withdrawing groups on the styrene decreased the equilibrium constant which showed that back-bonding from platinum to the olefin must be important. In contrast electron-releasing groups on the pyridine N-oxide increased the equilibrium constant, a surprising result since styrene should dissipate excess negative charge more readily than dodecene.

$$\mathrm{X{-}C_6H_4CH{=}CH_2 + (1\text{-}dodecene)PtCl_3 \rightleftharpoons (X{-}C_6H_4CH{=}CH_2)PtCl_3 + 1\text{-}dodecene} \qquad (7)$$



(8)

The effect of deuteration on the bonding of ethylene, propylene, and 2-butene to silver(I) has been investigated[167] by a glpc technique.[168] The second-order iso-

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[162] F. R. Hartley and L. M. Venanzi, *J. Chem. Soc., A*, 330 (1967).

[163] F. R. Hartley and L. M. Venanzi, *ibid.*, 333 (1967).

[164] J. Chatt, in "Cationic Polymerization and Related Complexes," P. H. Plesch, Ed., Heffer, Cambridge, England, 1953, p 40, points out that the decrease in $\nu_{\mathrm{C=C}}$ which occurs on complex formation is much less for silver (65 cm^{-1}) than for platinum (140 cm^{-1}).

[165] R. G. Denning and L. M. Venanzi, *J. Chem. Soc., A*, 336 (1967).

[166] S. I. Shupack and M. Orchin, *J. Amer. Chem. Soc.*, **86**, 586 (1964).

[167] R. J. Cvetanović, F. J. Duncan, W. E. Falconer, and R. S. Irwin, *ibid.*, **87**, 1827 (1965).

[168] M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962).

tope effect was to increase stability in every case and olefinic deuterium stabilized more effectively than deuterium in the methyl groups. Since it is known that deuterium behaves as an electron-releasing group relative to hydrogen,[169] it was concluded that stabilization in the deuterated series was due to stronger olefin–silver σ bonds. It would seem, therefore, that back-bonding is more important in the platinum(II) than in silver(I) complexes.

Cramer[170] examined the effect of olefinic substitution on the stability of rhodium(I) complexes by determining the equilibrium constant (K_2) for eq 9 by ir spectroscopy.

$$\text{olefin} + (\text{acac})(C_2H_4)_2\text{Rh} \underset{}{\overset{K_2}{\rightleftharpoons}} (\text{acac})(C_2H_4)(\text{olefin})\text{Rh} + C_2H_4 \quad (9)$$

Values of K_2 greater than unity (*i.e.*, favoring the substituted ethylene) were found when electronegative substituents (Cl, F, or $COCH_3$) were present. Alkyl substituents gave values of K_2 less than unity.

Mass spectrometry has been used to obtain information about the stability of a number of substituted olefin–iron(0) tetracarbonyl complexes.[171] By using the relative abundance of the ligand ion in the mass spectrum as a measure of its coordinating strength, a qualitative picture of the stabilities of some halogen olefins and olefinic anhydrides, esters, and one ether was obtained. It was found that halogen olefins had slightly better coordinating power than ethylene, but anhydrides and acids were better still.

Finally, the formation of complexes between 2-butene-1,4-dicarboxylic, vinylacetic, crotonic, fumaric, and maleic acids with copper(I), copper(II), and silver(I) was studied by polarographic and potentiometric methods.[172] Vinylacetic acid was found to be the only acid which stabilizes copper(I). Furthermore, all the copper(II) complexes were less stable than their copper(I) analogs, while silver(I) had very little tendency to coordinate with any ligand.

V. CONCLUSIONS

In this review π complexes between many substituted olefins and most of the transition metals have been described. Three basic conditions must be fulfilled in order that a stable complex will form. Firstly, the orbitals involved in π-bond formation must be energetically compatible. Thus the metal, its oxidation state, and the substituent effect all are important. Secondly, orbitals will only interact strongly if overlap is significant. The size and directional properties of the relevant atomic and molecular orbitals govern overlap, and thus the effects of other ligands as well as the oxidation state of the metal itself are important. Third, and perhaps somewhat neglected, is the question of steric hindrance. An X-ray structure determination[61] of fumaric acid–iron(0) tetracarbonyl (**29**) showed that the carboxyl groups interact with the iron atom so that they are bent out of the double-bond plane to the extent of 18°. Also in the styrene–palladium(II) complex (**50a**), where an angle of 90° between the carbon–carbon double bond and the square plane is required for maximum overlap, the actual angle was shown[116] to be 74°. Clearly, the large diffuse atomic orbitals which are characteristic of the transition metals may sterically interact with any substituent on the olefin, and the properties of the complex will be correspondingly perturbed.

TABLE III
ETHYLENE SUBSTITUENT EFFECT ON THE STABILITY[a] OF π COMPLEXES

Stability of complex increased Functional group			Stability of complex decreased Functional group		
	Metal	Ref		Metal	Ref
D	Ag(I)	167	CD_3	Ag(I)	167
Cl	Rh(I)	170	CH_3	Ag(I)	168
F	Rh(I)	170	CH_3	Rh(I)	170
$COCH_3$	Rh(I)	170	C_2H_5	Rh(I)	170
Cl	Fe(O)	171	OCH_3	Rh(I)	170
Br	Fe(O)	171			
CO_2H	Fe(O)	171			
CO_2R	Fe(O)	171			
$(CO)_2O$	Fe(O)	171			
CN	Pt(O)[b,c]	109			
Cl	Pt(O)[b,c]	48			
Ph	Pt(O)[b,c]	112			

[a] For method used in measuring stability see corresponding reference. [b] The unsubstituted ethylene complex was reported[173] to be too unstable for isolation. [c] It is uncertain whether the olefin is σ- or π-bonded to the metal.

The stability of the complexes formed covers a wide range from the highly reactive pyrophoric[78] bis(acrylonitrile)nickel(0) to quite stable complexes such as[31] bis(triphenylphosphine)tetrafluoroethylenerhodium(I) chloride (**10a**). The real interest in these complexes is incorporated in the effect that the substituent exerts on the strength of the π bond. Although accounts of stability measurement have been few, a number of substituent effects can be recognized and a qualitative picture is emerging. Table III separates functional groups into those which increase and those which decrease the strength of the π bond between ethylene and various metals. Olefin complexes of Rh(I), Fe(0), and Pt(0) are stabilized (see Table III) by electron-withdrawing (−E) groups on the olefin. In these cases the importance of back-bonding must be considerable since it can be argued that −E groups might destabilize the complex in two ways, *i.e.*, by steric interaction (*vide supra*) and by weakening the metal–donor bond. The resultant stabilization by −E group substitution shows that the energy gained by enhanced back-bonding

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(172) R. K. Resnik, and B. E. Douglas, *Inorg. Chem.*, **2**, 1246 (1963).

is greater than that lost due to the steric hindrance and a weaker donor bond.

Electron-releasing (+E) groups (alkyl and alkoxide) decrease the stability of Rh(I) and Ag(I) ethylene complexes. In these cases both suppression of back-bond and steric interaction of the substituent by the +E group will weaken the π bond; the relative magnitude of these effects cannot be estimated *a priori.*

The fact that the ethylenesilver(I) complex is stabilized by deuteration is particularly interesting, because in this case the steric factor has been eliminated. Since deuterium is a +E group,[169] the olefin–silver donor bond is more important than the back-bond. The over-all effect of olefin substitution therefore depends not only on the olefin but also on the electronic configuration of the metal ion.

The theory of π-bonding between metal and olefin[5,6] seems to be generally applicable to substituted olefin complexes. However, in many cases the decision as to whether σ- or π-bonding should be proposed is not clear-cut. In the formal sense, a metal–olefin complex can be considered either as a π complex, in which the olefin occupies one coordination site, or a complex with two σ bonds between the metal and (initially) olefinic carbon atoms. In the latter case two coordination sites are required and the metal oxidation state is increased by two. Interaction with the lone pair on a substituent offers a further range of complications.

Sometimes the coordination requirement of the metal serves as a clue in structure elucidation. Although the unequivocal technique of X-ray structure determination has been much used, it is laborious, and great reliance has been placed on the position of the carbon–carbon stretching frequency in the ir spectrum. In particular, for platinum complexes, which are most readily accessible, a shift to lower frequencies of 140 cm^{-1} is good evidence for double-bond participation.[173] Furthermore, metal–olefin π complexes which have been shown, by X-ray methods, to contain π-bonded ligands, generally absorb near 1500 cm^{-1}. And yet several other classes of compound absorb[174] strongly at or near the C=C stretching region. All aromatic compounds absorb strongly at 1500 cm^{-1}, so that styrene– (or stilbene–) olefin complexes, and any complex with a triphenylphosphine ligand, will interfere. The amide-(II) band due to NH deformation is also strong[175] and appears at 1510–1550 cm^{-1} and could interfere in some cases. Similarly the CH_2 deformation at 1465 cm^{-1} is usually very strong[176] and could easily mask a weak band at 1500 cm^{-1} unless the resolution of the spectrophotometer is good.

Nuclear magnetic resonance has provided valuable evidence, and, as spectral correlations are accumulating, the applications to structural problems are becoming widespread. Yet care must be exercised since the magnetic anisotropy effects of transition metals in various oxidation states are largely unknown.

Only one application of the use of mass spectrometry[171] for structural studies in substituted olefin complexes has been found, and clearly a valuable untapped source of information awaits future workers in this field. In particular, reports of structures[19,42] of novel compounds, which have later been shown to be incorrect by one CO group, probably could have been prevented by use of this technique, since the complexes frequently give a parent peak in the mass spectrometer together with large peaks for loss of successive carbon monoxide ligands.

It is well established that otherwise inaccessible compounds with donor properties can be fixed as metal complexes. In favorable circumstances the properties and reactions of the elusive compound can then be studied. Pettit's elegant investigations[177–180] of the reactions of cyclobutadiene by obtaining it *in situ* from the iron(0) tricarbonyl complex provide one example. On our present topic metal complexes of vinyl alcohol and α-methylvinyl alcohol provide[135] another.

Finally it is certain that interest in substituted olefin complexes is rapidly expanding. They provide an increased range of stabilities as compared with unsubstituted analogs, and this leads one to the prediction that such complexes may find use in tailor-making of catalysts of specific activity (or instability). Indeed, several examples of catalysis by these complexes have already been mentioned above, and a sustained effort in this direction could well lead to some interesting and industrially important discoveries in the next few years.

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