Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

MONOOLEFIN AND ACETYLENE COMPLEXES OF NICKEL, PALLADIUM AND PLATINUM

JOHN H. NELSON* AND HANS B. JONASSEN

Richardson Chemical Laboratories, Tulane University, New Orleans, Louisiana 70118 (U.S.A.)

(Received March 5th, 1970)

CONTENTS

---

* Present address: Department of Chemistry, University of Nevada, Reno, Nevada 89507, U.S.A.

ABBREVIATIONS

PR_3	any phosphine	yne	an acetylene
un	unsaturated molecule (olefin or acetylene)	acac	acetylacetonate
		IR	infrared spectroscopy
Q	P, As or Sb	NMR	nuclear magnetic resonance spectroscopy
M	metal	anal.	elemental analyses
Ph	phenyl	M.W.	molecular weight
Et	ethyl	d.p.	decomposition point
Me	methyl	Py	pyridine
X	halogen anion	Pyno	pyridine *N*-oxide
Bu	*n*-butyl	TFE	tetrafluoroethylene
TCNE	tetracyanoethylene	cond.	conductance

A. SCOPE

The organometallic aspects of the coordination of unsaturated molecules to transition metals has received a tremendous amount of attention in recent years. This can be attributed to the use of some of these complexes in homogeneous catalysis, to the recent isolation of oxygen and nitrogen complexes and their relation to the important problems of nitrogen fixation and oxygen carriers and finally to the problems encountered in attempting to describe the bonding in these complexes.

Since the literature has been rather carefully and completely reviewed through 1964[1–28,*], the greatest emphasis in this review will be placed on research published since that time. During the writing of this article a review was published on the same topic[26]. The aspects of the coordination of unsaturated molecules which have recently been reviewed are: Reactions of coordinated ligands[1], zerovalent complexes[2,3], metal carbonyls[4–6], oxidative addition reactions[7,8], catalysis[9–13], and π-complexes[14–26]. Much information useful to researchers in this area is the subject of several recent books[27–32] and the American Chemical Society recently held a symposium dealing with homogeneous catalysis by palladium[33]. This review will deal primarily with monoolefin and acetylene complexes of nickel, palladium and platinum. The chemistry of complexes containing condensed acetylenes or carbon monoxide will not be discussed.

B. PREPARATION

(i) Platinum

1. *Zerovalent platinum complexes*

The preparation of the most useful starting materials for these complexes

---

[*] See also U. Belluco, B. Crociani, R. Pietropaolo and P. Uguagliati, *Inorg. Chim. Acta Rev.*, 3 (1969), 19 and H. W. Quinn and J. H. Tsai, *Advan. Inorg. Chem. Radio Chem.*, 12 (1969), 217.

has been fully reviewed[2,3,21]. Nearly all of the zerovalent platinum complexes contain phosphines as stabilizing ligands and have the stoichiometry $Pt(PR_3)_2(un)$. These complexes are prepared by two general methods; (1) by reduction of divalent complexes and (2) by ligand exchange reactions of zerovalent complexes.

a. Preparation from divalent species.—This method[34] involves reduction of *cis*-$Cl_2Pt(PR_3)_2$ usually with hydrazine in the presence of the unsaturated ligand. Two mechanisms have been proposed[35,36] for this reaction. The first mechanism[34] suggests that the reactive intermediate is bis-(triphenylphosphine)platinum(0) produced by the hydrazine reduction of a platinum hydride, reaction (1), which in turn is the product of the hydrazine reduction of *cis*-$Cl_2Pt(PPh_3)_2$.

$$(Ph_3P)_2PtHCl + N_2H_4 \rightarrow Pt(Ph_3P)_2 \xrightarrow{un} Pt(Ph_3P)_2(un) \qquad (1)$$

It has been shown[37] that the hydrazine reduction of *cis*-$Cl_2Pt(Ph_3P)_2$ eventually leads to $(Ph_3P)_2PtHCl$ and that $(Ph_3P)_2Pt$ reacts with both olefins and acetylenes to form complexes[38]. However, $(Ph_3P)_2Pt$ has only been prepared from a platinum hydride employing oxidizing conditions[38] rather than the reducing conditions of this reaction. The platinum hydride is probably not the intermediate since only in a limited number of cases has the reaction of hydrides with olefins or acetylenes produced olefin or acetylene complexes[39]. The usual products are vinyl complexes[40–44].

The second mechanism is illustrated in Fig. 1. The reaction of 1-bromo-2-propyne with *cis*-$Cl_2Pt(Ph_3P)_2$ and hydrazine to yield hydrazine hydrobromide and tripropynylhydrazine hydrobromide suggests[35] that the hydrazine bridged species (the structure of which has been determined by X-ray crystallography[37]) is the reactive intermediate in these reactions[35].

The hydrazine reduction of platinum phosphine complexes is applicable to a wide variety of olefins and acetylenes but it has been noted to fail[36] for both $(Bu_3P)_2PtCl_2$ and $(Ph_2MeP)_2PtCl_2$ with some acetylenes.

A novel series of presumably zerovalent acetylene complexes of the type

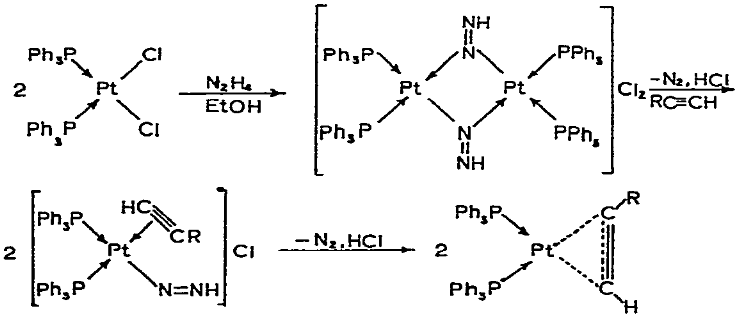


Fig. 1. Proposed mechanism for the reaction of acetylenes with *cis*-$PtCl_2(PPh_3)_2$.

$Pt(yne)_2$ has been prepared[45] directly by adding disubstituted-dihydroxyacetylenes to a solution of $PtCl_4^{2-}$.

b. Preparation from zerovalent species.—Complexes of the type $(R_3Q)_3Pt$ and $(R_3Q)_4Pt$ have served as excellent starting materials for the preparation of both zerovalent and divalent complexes. Much of the chemistry of these species has been reviewed[2,3,9]. The most extensively studied compound $(Ph_3P)_4Pt$ is known to undergo a wide variety of oxidative addition and replacement reactions in solution, which can be attributed to its becoming coordinatively unsaturated, equilibria (2) and (3).

$$(Ph_3P)_4Pt \overset{K_1}{\rightleftharpoons} (Ph_3P)_3Pt + Ph_3P \quad (2)$$

$$(Ph_3P)_3Pt \overset{K_2}{\rightleftharpoons} (Ph_3P)_2Pt + Ph_3P \quad (3)$$

with[46] K_1 large and $K_2 = (1.6 \pm 1) \times 10^{-4}$.

X-ray crystallographic studies have shown that $(Ph_3P)_3Pt$ has a trigonal planar structure[47]. Hydroxyacetylenes react with $(Ph_3P)_4Pt$ to yield two types of complexes[35], $(Ph_3P)_2Pt(un)$ and $(Ph_3P)_2Pt(H)_2(un-H)_2$ and the mechanism proposed for this reaction is shown in Fig. 2.

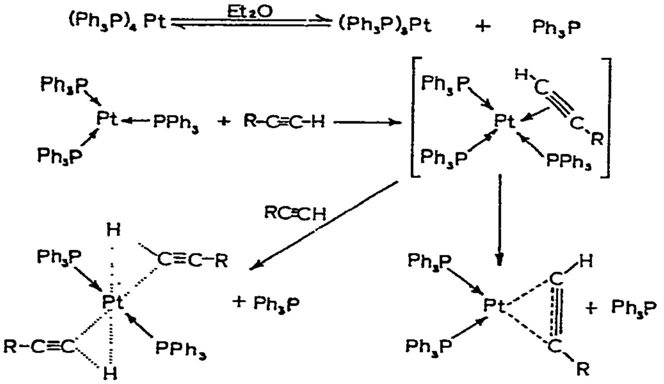


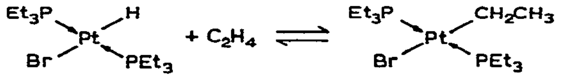
Fig. 2. Proposed mechanism for the reaction of acetylenes with $(Ph_3P)_4Pt$.

In the presence[35] of excess bulky, terminal acetylenes the dihydride diacetylide complexes are formed whereas less bulky acetylenes yield $Pt(Ph_3P)_2(un)$ type complexes. Attempts to prepare the dihydride diacetylide complexes from the monoacetylene complexes have been unsuccessful. The intermediate $(Ph_3P)_3Pt(un)$ could be tetrahedral similar to $(Ph_3P)_3Ni(TFE)$[48,49], $Pt(Ph_3P)_3CO$[50,51] and $(Ph_3P)_4Pt$[3] or square planar similar to divalent platinum complexes such as Zeise's salt. Since hydroxyacetylenes have been shown to be better *trans*-directors than triphenylphosphine[52] and the nature of the reaction product is sterically controlled it is tempting to assume that the $(Ph_3P)_3Pt(un)$ intermediate is square planar.

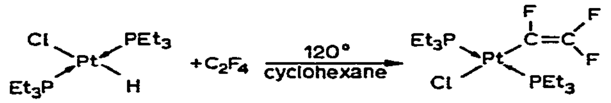
2. *Divalent platinum complexes*

Platinum hydrides react with olefins and acetylenes[16,39–44,53] to yield olefin[39], acetylene[16], or vinyl complexes[40–44] as illustrated in reactions(4), (5), and (6).

$$(Et_3P)_2PtHCl + TCNE \rightarrow (Et_3P)_2Pt(TCNE) + HCl \quad (4)$$



(5)



(6)

In the reverse of reaction (5) the hydride can come from either ethyl carbon as shown by deuterium labeling studies[53]. The rate of reaction (4) has been studied and the proposed mechanisms for reactions (4) and (5) are presented in Fig. 3.

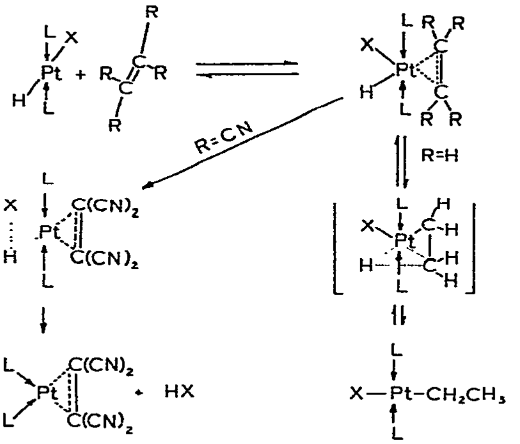
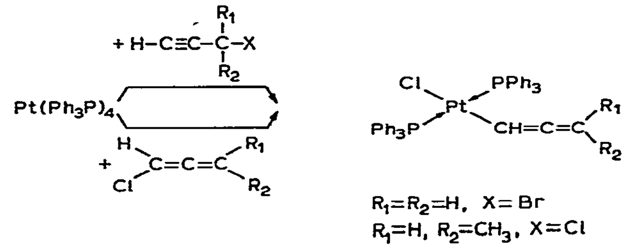


Fig. 3. Proposed mechanism for the reaction of olefins with platinum hydrides.

The intermediate *trans*-(H)CNPt(PEt$_3$)$_2$(TCNE)[16] has been isolated and characterized. However, the complex first thought[44] to be [Pt(H)Cl(PEt$_3$)$_2$(C$_2$F$_4$)] has since been shown by X-ray and chemical analyses to be *trans*-[PtCl(CO)(PEt$_3$)$_2$]$^+$SiF$_5^-$ formed by reaction with the glass vessel[54].

Dicyanoacetylene reacts[16,55] similarly to tetracyanoethylene, reaction (4), in tetrahydrofuran to give an acetylene complex but in benzene a vinyl complex is formed similar to reaction (6). Solvent assistance has been suggested as the discriminating factor for the difference in the nature of the products formed.

Chloroallenes and α-chloroacetylenes have been found to react[56] with Pt(Ph$_3$P)$_4$ by oxidative addition to yield σ-bonded allene complexes as illustrated in reaction (7).



(7)

This reaction is undoubtedly complex as $Pt(Ph_3P)_4$ reacts with allene[57,58] to form the zerovalent complex $Pt(Ph_3P)_2(CH_2{=}C{=}CH_2)$ and the allene is displaced in the presence of excess triphenylphosphine. Thus, a π-bonded complex is probably first formed which undergoes internal rearrangement to form the σ-bonded complex.

The isolation[59] of a divalent platinum olefin complex, which can best be formed by bubbling ethylene through a saturated solution of potassium tetrachloroplatinate(II), has proven to be a general route to a variety of olefin and acetylene complexes of platinum(II). Zeise's salt and Zeise's dimer (Fig. 4) react with a variety of Lewis bases (this involves bridge breaking in the case of the dimer) to form complexes of the type *trans*-(base) $PtCl_2$(olefin).

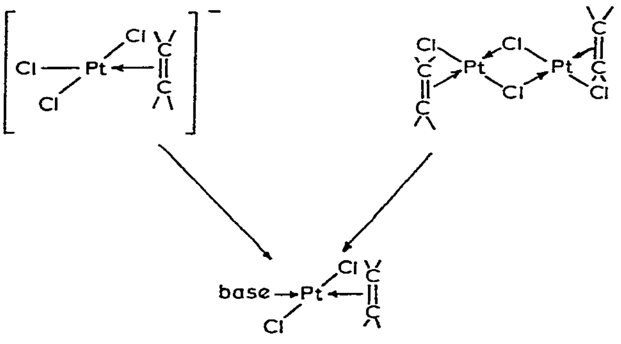
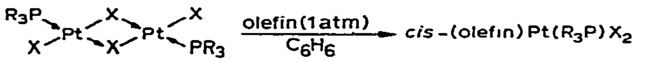


Fig. 4. Structures of Zeise's salt, Zeise's dimer and complexes derived from these by substitution reactions.

The *trans*-base($PtCl_2$(olefin)) complexes have been reviewed for the bases pyridine or a substituted pyridine[18] and pyridine N-oxides[17].

The platinum dimer $Pt_2X_4(R_3P)_2$ reacts with olefins, reaction (8), by bridge breaking to form *cis*-monomer complexes[60] rather than the more usual *trans*-complexes.



(8)

The ethylene in both Zeise's salt and Zeise's dimer exchanges with other olefins and the base in the complexes *trans*-(base)$PtCl_2$(olefin) may be exchanged by other bases. The rates of some of these reactions will be discussed later.

(ii) Palladium

1. *Zerovalent palladium complexes*

The zerovalent palladium phosphine complexes which have been found to be more reactive and consequently less stable than their platinum analogues have not been as extensively studied. Some isolable acetylene and olefin complexes of the type $(R_3Q)_2Pd(un)$ prepared by reaction of the species $(R_3Q)_4Pd$ or $(R_3Q)_3Pd$ have been reported[36,61–63]. Several reducing agents fail[36,64] to yield acetylene or olefin complexes from divalent palladium complexes in the presence of olefins and acetylenes in contrast to the reactions of *cis*-$Pt(R_3Q)_2Cl_2$. Palladium complexes[37] analogous to the platinum hydrazine species (Fig. 7) have been briefly reported with no follow-up however. One of the few zerovalent palladium olefin complexes is formed by the reaction of TCNE with bis-(*t*-butylisocyanide)palladium(0) to yield Pd(TCNE) $(t\text{-BuNC})_2$[65]. Although the phosphite complexes $Pd[(RO)_3P]_4$ have been prepared[66], studies of the reactions of these complexes have not yet appeared.

2. *Divalent palladium complexes*

Palladium complexes analogous to Zeise's dimer have been prepared[67] from dichlorobis(benzonitrile)palladium(II). Although the palladium dimer is less stable than the platinum analogue it undergoes many of the same reactions.

No reports of isolable palladium complexes analogous to Zeise's or Buckhovet's salts have appeared as the measured heats of formation of several palladium(II) complexes are very close to zero[68–73] but they have been postulated to exist temporarily in solution as intermediates in many catalytic reactions involving palladium chloride[9–12].

(iii) Nickel

1. *Zerovalent nickel complexes*

Nickel has yielded the smallest number of isolable complexes of the triad because of the reactivity of its zerovalent state and its noted catalytic ability, a stable example being the $Ni(Ph_3P)_2(CO)_2$ species[74–76]. The fairly stable ethylene complex $(Ph_3P)_2Ni(C_2H_4)$, however, is a good starting material for the preparation of olefin and acetylene complexes[36,77,78]. The ethylene complex is prepared by reaction (9).

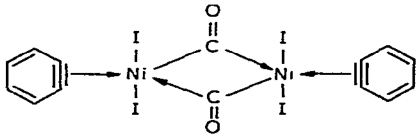
$$Ni(acac)_2 + Ph_3P + AlEt_3 + C_2H_4 \xrightarrow[N_2,\ 0°C]{ether} Ni(Ph_3P)_2(C_2H_4) \qquad (9)$$

and the ethylene exchanges readily, reaction (10)

$$Ni(Ph_3P)_2(C_2H_4) + un \xrightarrow[hexane]{C_6H_6} Ni(Ph_3P)_2(un) + C_2H_4 \qquad (10)$$

The ethylene complex must be thoroughly washed free of the aluminum alkyl with ether before exchange reactions are carried out since otherwise it serves as an excellent polymerization catalyst[36]. Tetrafluoroethylene reacts with the nickel ethylene complex[49] *via* an unusual coordinative disproportionation to yield the fluorocarbon complex $Ni(Ph_3P)_3(C_2F_4)$ containing three phosphines rather than the usual two. Similarly, TCNE reacts with $Ni(t\text{-}BuNC)_2(O_2)$ to yield both $Ni(t\text{-}BuNC)_2(TCNE)$ and $Ni(t\text{-}BuNC)_3(TCNE)$ with the latter being formed only in the presence of excess isocyanide[65].

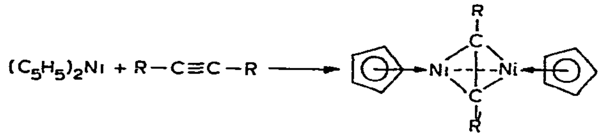
A carbonyl bridged structure has been proposed[79] for the first complex of benzyne and apparently the only acetylene complex of nickel(II) which is formed by reaction of *o*-di-iodobenzene and nickel carbonyl.



Similar attempts to prepare platinum benzyne complexes resulted in complexes of the benzyne precursors[80,81].

Vinyl complexes which can be formed directly by reacting $M(QR_3)_4$ with α-chloroalkenes are also prepared by reactions involving Grignard or lithium compounds[224]. Thus, treatment of $(Et_3P)_2NiCl_2$ with perfluorovinyl magnesium bromide affords *trans*-$(Et_3P)_2Ni(CF{=}CF_2)Br$ and *trans*-$(Et_3P)_2Ni(CF{=}CF_2)_2$. Similarly, from *cis*-$(Et_3P)_2PtCl_2$ a mixture of the compounds *cis*- and *trans*-$(Et_3P)_2Pt(CF{=}CF_2)Br$ is obtained. Perfluorovinyl-lithium reacts with *cis*-$(Et_3P)_2PtCl_2$ to give *cis*-$(Et_3P)_2Pt(CF{=}CF_2)_2$ and with *trans*-$(Et_3P)_2PdCl_2$ to give *trans*-$(Et_3P)_2Pd(CF{=}CF_2)_2$.

Nickelocene reacts with several acetylenes to yield[27,82–84] dimeric acetylene bridged species, reaction (11), and the structures of two of these complexes have been determined by X-ray crystallography[85,86].



(11)

The complexes $(R_3Q)_4Ni$[87] as well as the phopshite complexes $M[(RO)_3P]_4$ (Refs. 88–91) have been prepared. An investigation of the reactions of these complexes should lead to important information for theoretical comparisons among the members of this triad. An interesting reaction[92] along these lines is reaction (12)

$$Ni(Ph_3P)_4 + 1/2\, X_2 \rightarrow Ni(Ph_3P)_3X \qquad (12)$$

giving one of the very few examples of monovalent nickel complexes.

(iv) Complex acetylides

A large number of acetylide complexes have been prepared from terminal acetylenes, metal acetylides or alkynyl halides[27,35,93–99,204], *via* the following synthetic routes, reactions (13–16).

$$(QR_3)_2MX_2 + 2\ R'\text{–}C{\equiv}CMgBr \rightarrow cis\text{- and } trans\text{-}[(QR_3)_2M(C{\equiv}CR')_2] + cis\text{- and } trans\text{-}[(QR_3)_2M(C{\equiv}CR')X] \quad (13)$$

$$(QR_3)_2MX_2 + 2\ R\text{–}C{\equiv}C\text{–}Li \xrightarrow{NH_3} cis\text{- and } trans\text{-}[(QR_3)_2M(C{\equiv}CR')_2] + cis\text{- and } trans\text{-}[(QR_3)_2M(C{\equiv}CR')X] \quad (14)$$

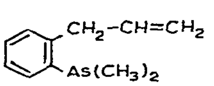
$$(QR_3)_4M + 2\ H\text{–}C{\equiv}C\text{–}R' \rightarrow (QR_3)_2M(H)_2(C{\equiv}C\text{–}R')_2 \quad (15)$$

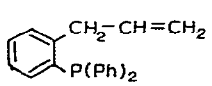
$$(QR_3)_4M + 2\ X\text{–}C{\equiv}C\text{–}X \rightarrow (QR_3)_2M(C{\equiv}C\text{–}X)_2 + (QR_3)_2M(C{\equiv}C\text{–}X)X \quad (16)$$

The nature of the complex formed depends upon the solvent, the reaction conditions and the reagents employed in the reactions. The alkynyl complexes are more stable than the corresponding alkyls or aryls[93] due to the greater possibility of π-bonding in the alkynyl complexes. For analogous complexes the stability[95] increases in the series Ni < Pd < Pt and for $(R_3Q)_2M(C{\equiv}CR')_2$ it increases in the series $R'{=}H{<}CH_3{<}Ph$. These complexes are all square planar, diamagnetic and the *trans*-complexes have very small dipole moments. The crystal structure[100] of $(PEt_3)_2Ni(C{\equiv}C\text{–}Ph)_2$ shows the expected *trans*-planar geometry with bond lengths Ni–C = 1.88Å and Ni–P = 2.22Å and the bond angles about the central nickel are very nearly 90°. In all of these complexes the $C \equiv C$ stretching frequency $\nu_{C\equiv C}$ appears in the region 2000–2100 cm^{-1}, a value slightly lower than that generally found for disubstituted acetylenes[101].

(v) Complexes of olefins containing other donor sites

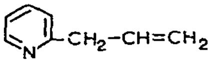
Several complexes of the nickel triad having the general formula MX_2L have been formed[102,108] with ligands (L) such as:





$R\text{–}S\text{–}(CH_2)_n\,CH{=}CH_2$
$n = 2,3,\ R = n\text{–butyl}$

$H_3C\text{–}CH{=}CH\text{–}CH_2PR_2$



In these complexes both the olefin and the Lewis base act as donors to give chelating ligands. The olefinic stretching frequency $\nu_{C=C}$ in these complexes is shifted to lower energy relative to the free ligand by about 140–180 cm^{-1} for the platinum and about 100 cm^{-1} for the palladium complexes[103,105,107]. The complexes are diamagnetic and nonconducting in nitrobenzene and can best be formulated as monomeric square planar complexes. Both zerovalent and divalent platinum and palladium complexes have been prepared[109,110] from the ligands $Ph_2P{-}C{\equiv}C{-}PPh_2$ and $Ph_2P{-}C{\equiv}C{-}CH_3$. The phosphorus atom is the donor site with no participation of the acetylenic moiety in the bonding. This likely arises as a consequence of the rigid stereochemistry of the ligands.

C. REACTIONS

(i) Dissociation

Complexes of the type $(R_3Q)_2M(un)$ dissociate in solution[37,46,77,111,112] according to the general reaction (17).

$$(R_3Q)_2M(un) + \text{solvent} \rightarrow (R_3Q)_2M(\text{solvent}) + un \qquad (17)$$

In at least two cases[36,113] the solvent adds by oxidative addition to form the complexes $(Ph_3P)_2PtCl(CCl_3)$ and $(Ph_3P)_2PtCl(CHCl_2)$. These two complexes have been isolated and it has been shown unequivocally that the carbon halogen bond has been broken. These reactions (at least in halocarbon solvents) are thus oxidative addition reactions rather than dissociation reactions.

The simplified mechanism presented in Fig. 3 for the reaction of $(Ph_3P)_4Pt$ with acetylenes is consistent with the experimental evidence. The system is, however, much more complex as is illustrated in Fig. 5.

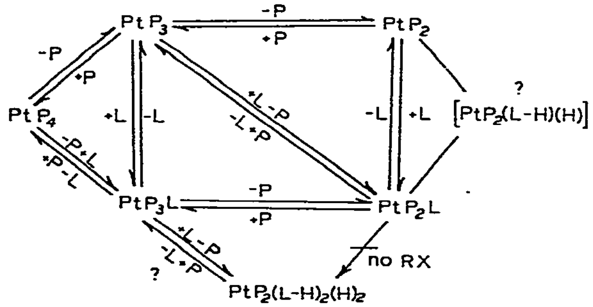
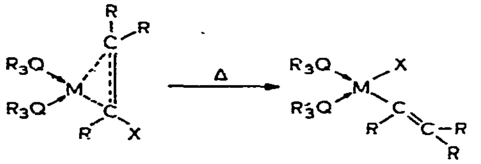


Fig. 5. Equilibria for platinum phosphine, olefin and acetylene complexes. P, tertiary phosphine; L, an olefin or acetylene; I—H, is a vinyl or acetylide group formed by loss of a hydrogen from the olefin or acetylene L; reactions marked with a question mark are still in doubt.

The platinum phosphines and phosphine acetylene complexes are involved in multistage equilibria. The relative importance of these has not yet been established and will necessarily depend upon such factors as the nature of the various ligands, the metals, the solvents, and the reaction conditions. These equilibria can be further complicated by the direct participation of the solvent, *e.g.* reaction (17).

(ii) Oxidative addition reactions

The platinum and palladium olefin complexes formed from bromo- or chloro-substituted olefins undergo rearrangement reactions by oxidative additation of the coordinated olefin when heated [61, 113–116] to form vinyl complexes reaction (18).



(18)

Since this reaction can be, and generally is, carried out in the solid state, dissociation is not necessarily involved. Some of the compounds prepared in this manner are listed in Table 1.

TABLE 1

PLATINUM CHLORO VINYL COMPLEXES

Compound	*D.p.*	*Ref.*	*Physical methods*
trans-$(Ph_3P)_2Pt(CF{=}CF_2)Cl$	269–270°	115, 116	NMR, anal., IR, M.W.
trans-$(Ph_3P)_2Pt(CF{=}CF_2)Br$	276°		
trans-$(Ph_2MeP)_2Pt(CF{=}CF_2)Cl$	167°		
trans-$(Ph_3P)_2Pt(CCl{=}CCl_2)Cl$	289°	114	IR, anal., M.W.
cis-$(Ph_3P)_2Pt(CH{=}CCl_2)Cl$	260°	114	IR, anal., M.W.
$(Et_3P)_2Pt[C(CF_2H){=}CF_2]Cl$	59°	40, 44, 132	IR, anal., NMR, cond.
$(Et_3P)_2Pt[CF_3{-}CF{=}CF]Cl$	—		
$(Et_3P)_2Pt$(perfluorocyclobut-1-ene)Cl	67–68°		
$(Et_3P)_2Pt(CF{=}CF_2)Cl$	61°		
cis- and *trans*-$(Et_3P)_2Pt(CF{=}CFH)Cl$	69–71°		
$(Et_3P)_2Pt(CF_3{-}C{=}C(CF_3)H)Cl$	90–91°		
$(Ph_3P)_2Pt(C_2HBr_2)Br$	220°	114	

It is interesting to note that the complex[225] $(Ph_3P)_2Pt(C_2Cl_4)$ does not rearrange by reaction (18) in refluxing benzene, dichloromethane or acetone but does rearrange in ethanol. Presumably the more polar solvent facilitates C–Cl bond cleavage[113]. This suggestion is supported by kinetic studies[117,118] on the isomerization of this complex which indicate that the rate determining step is close to the S_N1 (lim) solvolysis of the coordinated tetrachloroethylene involving the ionic intermediate $[Pt(CCl{=}CCl_2)(PPh_3)_2]^+$.

With certain haloolefins halogenation of the metal leads to $(R_3Q)_2PtX_2$ complexes (Table 2) with no π-olefin complexes being isolated. Reaction of $(Ph_3P)_4Pt$ with TCNE yields[119] $(Ph_3P)_2Pt(CN)_2$ and even though $(Ph_3P)_2Pt$(TCNE) has been prepared, attempts to isomerize it have been unsuccessful[113]. The compounds that react with $(Ph_3P)_4Pt$ to yield $(Ph_3P)_2PtX_2$ type complexes are listed in Table 2.

TABLE 2

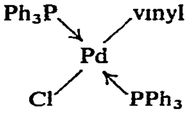
COMPOUNDS WHICH REACT WITH $(Ph_3P)_4Pt$ TO GIVE $(Ph_3P)_2PtX_2$

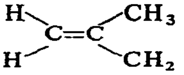
Compound	*Ref.*
Tetracyanoethylene	119
trans-Dichloroethylene	113
cis-Dichloroethylene	113
Hexachloroethane	113
Chloroform	113
Bromotrichloromethane	113

Vinyl complexes are produced exclusively (Table 3) from the reaction of tetrakis (triphenylphosphine)palladium(0) with chloroolefins[61].

TABLE 3

COMPLEXES OF THE TYPE



Vinyl	*D.p.*	*Ref.*	*Analytical methods*
C_2Cl_3	259–262°	61	IR, NMR, anal., M.W.
C_2HCl_2	>300°	61	
trans-C_2H_2Cl	272–277°	61	
cis-C_2H_2Cl	279–283°	61	
	121–143°	120	

Hexachloropropene reacts[114] with Pt(*trans*-stilbene) $(Ph_3P)_2$ to give $Pt(Ph_3P)_2Cl_2$ while 1,1,2-trichloro-3,3,3-trifluoropropene gives the platinum(IV) compound $Pt(Ph_3P)_2Cl_2F_2$ and tribromoethylene gives $PtBr(C_2HBr_2)(PPh_3)_2$. Both the *cis*- and *trans*-isomers of $(Ph_3P)_2PtCl(C_2HCl_2)$ have been isolated from the reaction of $Pt(Ph_3P)_4$ with trichloroethylene. *Cis* → *trans*-isomerization readily occurs in benzene at 110 °C and in ethanol in the presence of hydrazine but not in ethanol alone. In some *cis*- and *trans*- bis(triphenylphosphine) metal complexes[114]*, a relation seems to exist between the stereochemistry of the metal phosphines and the relative intensities of the two phenyl bands observed in the infrared spectra at *ca.* 1586 and 1572 cm^{-1}. The 1586 cm^{-1} band is more intense than the 1572 cm^{-1} band in *cis*-complexes and less intense in *trans*-complexes. (It would be of interest to check the generality of this observation).

---

* For recent references of vinyl complexes see D. R. FAHEY, *J. Amer. Chem. Soc.*, 92 (1970) 402; J. ASHLEY-SMITH, M. GREEN AND F. G. A. STONE, *J. Chem. Soc., (A)*, (1969) 3019; A. J. MUKHEDKAR, M. GREEN AND F. G. A. STONE, *J. Chem. Soc. (A)*, (1969) 3023; R. G. MILLER, R. D. STAUFFER, D. R. FAHEY AND D. R. PARNELL, *J. Amer. Chem. Soc.*, 92 (1970) 1511.

The reactions that $Pd(Ph_3P)_4$ and $Pt(Ph_3P)_4$ undergo with various olefins are summarized in Fig. 6.

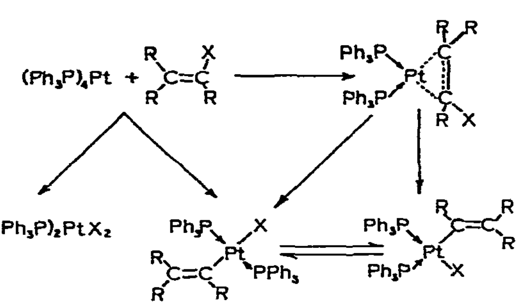
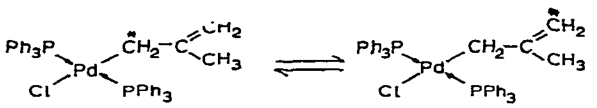


Fig. 6. Reactions observed for various halo-olefins with $(Ph_3P)_4Pt$ and $(Ph_3P)_4Pd$.

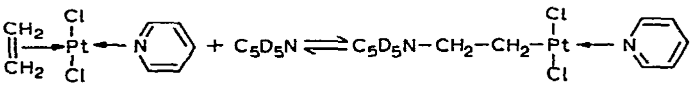
Figs. 5 and 6 show that the number of species present in any one of these reactions may be very large.

Two interesting reactions related to oxidative addition have been proposed solely on the basis of NMR spectral data. Tautomerization, reaction (19), has been suggested[120] to explain the NMR equivalence of the methylene protons of *trans*-$Cl(Ph_3P)_2Pd(CH_2=C(CH_3)CH_2)$,



(19)

and π → σ conversion, reaction (20), has been suggested[121] as an explanation for the coupling in the NMR spectrum of *trans*-$Cl_2Pt(C_2H_4)(Py)$ at −50 °C.



(20)

Similar σ-bonded complexes have been postulated[122] as intermediates in the reactions of amines with platinum(II) olefin complexes of the type *cis*-(olefin)Pt-$(PR_3)Cl_2$.

(iii) Ligand exchange

The complexes $(R_3Q)_2M(un)$ undergo exchange reactions with other unsaturated molecules[17,25,36,77,78,113,114,117,118,123,125].

$$(R_3Q)_2M(un)+un' \rightleftharpoons (R_3Q)_2M(un')+un \qquad (21)$$

The complexes $(R_3Q)_2M$ are thought to be the reactive intermediates in these reactions[46,124,223]. Reaction (21) has been extensively used as a preparative route to complexes of reactive olefins and acetylenes and the reaction rates of some of these have been studied[46,124]. It was found that acetylenes with deactivating substituents formed more stable complexes than those bearing activating substituents and that the stability increases[126] in the order $C_2H_2 < \text{alk–C}\equiv\text{C–H} < C_2(\text{alk})_2 \sim \text{PhC}\equiv\text{C–H} < C_2Ph_2 < C_2(NO_2p\text{–}C_6H_4)_2$.

The kinetics of diethylamine exchange reaction[52] for complexes of the type *trans*-$LPtCl_2[^{14}C]NHEt_2$ have been studied and the decreasing *trans*-effect for the ligand "L" was found to be $C_2H_4 \sim i\text{-PrCH}=\text{CHCH}_3 \sim (CH_3)_2C(OH)C\equiv C\,C(OH)\,(CH_3)_2 \gg Et_3Sb > Ph_3Sb > (CH_3)_3P > Et_3P > i\text{-}Pr_3P > Ph_3P > Et_3As > Ph_3As \gg n\text{-}Pr_2S$. Again the properties of the third member of a periodic group are not intermediate between the second and the fourth: Sb > P > As.

The rates of halide exchange so important in a variety of exchange and/or dissociation reactions of Zeise's salts and Zeise's dimer have been measured[127,128]. This exchange, already extensively reviewed[16,18,19], has been used almost exclusively for the preparation of olefin and acetylene complexes of platinum(II) and derivatives of the palladium analogue to Zeise's dimer.

The stability of the metal ethylene bond has been measured[27] for complexes of the type $K[PtX_3(C_2H_4)]$ and falls in the order $X = Cl > Br > I > NO_2 > SCN > CN$ and L = quinoline > pyridine > ammonia > thiourea > ethylene for *trans*-$(C_2H_4)PtCl_2L$ complexes. Stability constant data[129–131] for reaction (22)

$$\text{Olefin} + [PtX_4]^{2-} \rightleftharpoons [\text{olefin } PtX_3]^- + X^- \qquad (22)$$

have been obtained where olefin is an olefinic ammonium ion or alcohol and X is chloride or bromide.

The olefin complexes were found to have stability constants comparable to the heavier halogens. A very recent review discusses the stability data in great detail[26]. These stability data indicate that the π-acceptor capacity of the olefin is more important than its σ-donor capacity in determining the strength of the metal olefin or acetylene bond (see *The metal–ligand bond* section).

D. PHYSICAL PROPERTIES

(i) X-ray results

The X-ray crystal structures of several olefin and acetylene complexes of the nickel triad have been reported and the pertinent data for zerovalent complexes are summarized in Table 4.

Some general observations can be made regarding these data. Although there should be a considerable difference in the bonding properties of the various ligands (σ-donor and π-acceptor ability) and the various metals (σ-acceptor and π-donor ability) the metal–carbon (M–C) bond lengths vary by only 0.13 Å. Moreover, the metal–oxygen bond lengths (M–O) vary by only 0.09 Å and are

TABLE 4

X-RAY CRYSTALLOGRAPHIC DATA OF ZEROVALENT AND MONOVALENT COMPLEXES

Compound	*M–C distance (Å)*[a]	*C–C distance (Å)*[b]	*Dihedral angle*[c]	*Ref.*
$Pt(PPh_3)_2(Ph_2C_2)$	2.06	1.32	14°	133
$Pt(PPh_3)_2(TCNE)$	2.11	1.52	10°	134
$Ni(PPh_3)_2(C_2H_4)$	1.94	1.41	—	135
	2.02	—	14°	136
$IrH(CO)(FUMN)(Ph_3P)_2$[d]	2.10	1.43	—	137
$IrBr(CO)(TCNE)(Ph_3P)_2$	2.15	1.51	—	138
$Pt(PPh_3)_2[(CN)_2C_2]$	2.1?	1.40	8°	139
$Pt(PPh_3)_2O_2$	2.01[f]	1.45[e]	—	140
$Ir(O_2)(diphos)_2^+$	1.98[f]	1.66[e]	—	138
$IrI(O_2)(PPh_3)_2(CO)$	2.06[f]	1.51[e]	—	141
$IrCl(O_2)(PPh_3)_2(CO)$	2.07[f]	1.30[e]	—	142
Ni(*t*–BuNC)$_2$(TCNE)	1.954	1.476	23.9	228

[a] The M–C distance is the distance from the metal atom to the coordinated olefin or acetylene. [b] The C–C distance is the bond distance of the coordinated C–C double or triple bond of the olefin or acetylene. [c] The dihedral angle is as defined in Fig. 6. [d] FUMN, fumaronitrile. [e] O–O distance. [f] M–O distance.

extraordinarily close to the metal–carbon bond lengths. The size of the atomic radii[143] (neutral atoms) indicates that what differences there are, are due primarily to the metal (Ni, 1.14 Å; Ir, 1.26 Å; Pt, 1.29 Å). Furthermore, the metal–carbon (M–C) distances in TCNE, $C_2(CN)_2$, and Ph_2C_2 complexes of platinum differ by only 0.05 Å and the M–C distances in TCNE complexes of platinum and iridium differ by only 0.04 Å, differences which are close to the uncertainty of the determinations. The M–C and M–O bond distances, therefore, seem to be the same for a given metal in analogous complexes, reflecting the synergistic nature of the bonding. The extent of π-back donation is reflected in the difference in both the C–C and O–O bond distances of the coordinated ligand relative to the free ligand as there is a considerable variance in these bond lengths. This is due to the donation of electron density from the π-bonding orbitals and acceptance of electron density into the π^* orbitals both of which would serve to lengthen the C–C and O–O bonds.

In all the zerovalent complexes the substituents on the olefin or acetylene are bent away from the metal atom, an effect which has been ascribed to steric and/or electronic interactions.

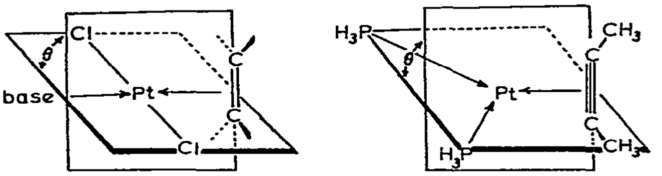


Fig. 7. Definition of the dihedral angle θ formed between the plane containing the PtCC atoms and that containing the Pt and other donor atoms for divalent and zerovalent platinum olefin and acetylene complexes.

The zerovalent complexes are not rigidly planar. Steric interactions lead to the dihedral angle θ (defined in Fig. 7) formed by the plane containing the M,P,P and that containing the MCC atoms which varies from 6° to 14°. This has been taken as an indication of a low barrier to rotation (see *The metal–ligand bond* section).

X-ray structural data has also been obtained for several palladium(II) and platinum(II) olefin and acetylene complexes (Table 5).

TABLE 5

X-RAY CRYSTALLOGRAPHIC DATA ON DIVALENT COMPLEXES

Compound	*M–C distance (Å)*[a]	*C–C distance (Å)*[b]	*Dihedral angle*[c]	*Ref.*
$[PdCl_2(C_2H_4)]_2$	2.28	—	90°	144
trans-$[PtCl_2(t\text{-}Bu)C{\equiv}C(t\text{-}Bu))$ (*p*-toluidine)]	—	1.27	90°	145
trans-$[(C_2H_4)PtCl_2(CH_3)_2NH]$	2.09	1.47	90°	146
[Pt(Codome)PyCl][d]	2.16	—	—	147
$[RhI(Ph_3P)_2(C_3H_4)]$	2.17, 2.04	1.35	76°	148
(−)*cis*-Cl_2(*trans*-2-butene) [(S)-α-phenethylamine]Pt	2.16	1.36	77°	149
$[PtCl(OCH_3)$ (dicyclopentadiene)]	2.11	1.37	—	150
$[Rh(Ph_3P)_2(C_2F_4)Cl]$	2.00	1.41	—	151
$K[PtCl_3(C_2H_4)] \cdot H_2O$	—	1.354	—	229
	—	1.44	—	230

[a] The M–C distance is the metal–carbon bond distance for the coordinated olefin or acetylene. [b] The C–C distance is the carbon–carbon bond distance for the double or triple bond of the coordinated olefin or acetylene. [c] The dihedral angle is defined in Fig. 6. [d] Codome = methoxy-cycloocta-1,5-diene.

The metal–carbon bond distances for the divalent complexes are dependent upon the *trans*-substituent and probably reflect the ease of substitution. The implications of this in terms of the *trans*-effect have been discussed in a recent review[26]. The interpretation in terms of π-bonding is supported by recent molecular orbital calculations[152]. The carbon–carbon bond distances of the complexed ligand are longer than those of the free ligands but less so than for the zerovalent compounds. This seems to indicate greater π-back donation from the zerovalent metal with a consequent greater population of the ligand's π* orbitals. This would be expected from comparisons of the first and the third ionization potentials of the metal[153]. In all cases the dihedral angle (Θ) is 90° or very nearly so (see *The metal–ligand bond* section).

(ii) Infrared results

Since the stretching frequencies $\nu_{C=C}$ and $\nu_{C\equiv C}$ are shifted to lower energies upon coordination, the magnitude in this shift has generally been used as a measure of metal olefin and/or acetylene bond strength. Normal coordinate analyses were performed for Zeise's dimer and similar complexes[154–156] and for acetylacetonato olefin complexes[157] and the IR and Raman spectra assigned. The change in the C=C stretching frequency $\Delta\nu_{C=C}$ was found to range from 97 to 106 cm^{-1} and in Zeise's dimer the C=C stretching frequency is coupled to the CH_2 bending mode[155]. Thus, the magnitude of the shift in $\nu_{C=C}$ cannot strictly be used as a measure of the metal–olefin bond strength, although the metal olefin stretching force constant can[154]. IR data on the complexes (un)X_2PtPy and (un)X_2PtPyno have been summarized by Orchin and Schmidt[18,19].

TABLE 6

REPRESENTATIVE IR DATA FOR ACETYLENE COMPLEXES

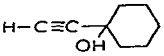
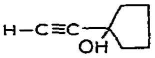
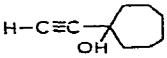
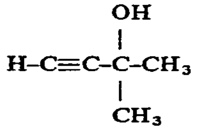
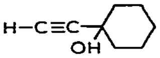
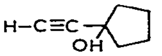
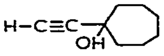
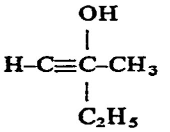
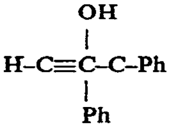
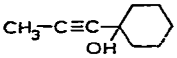
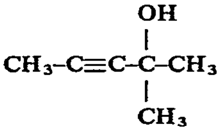
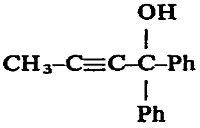
Compound	$\nu_{C\equiv C}(cm^{-1})$	$\Delta\nu_{C\equiv C}(cm^{-1})$	*Ref.*
K[PtCl$_3$(yne)]			
yne =			
$HOCMe_2$–C≡C–CMe_2OH	2010	−38	164
$HOCMe_2$–C≡C–CMe_2OMe	2004	−44	164
$MeOCMe_2$C≡C–CMe_2OMe	1994	—	164
HOCMeEt–C≡C–CMeEtOH	2010	—	164
$HOCMe_2$–C≡C–CMePhOH	2004	—	164
t-Bu–C≡C–CMe_2OH	2008	−65	164
t-Bu–C≡C–CMePhOH	2009	−50	164
($Ph_3P)_2$Pt(yne)			
yne =			
H–C≡C–CMe_2OH	1681	−433	35
	1686	−431	35
	1681	−439	35
	1668	−452	35
H–C≡C–CMeEtOH	1670	−455	35
H–C≡C–CPh_2OH	1678	−440	35
CF_3–C≡C–CF_3	1775	−425	36, 125
Ph–C≡C–H	1675	−445	36, 125
Ph–C≡C–Ph	1768, 1740	—	36
Ph–C≡C–CH_3	1756	—	36
MeOOC–C≡C–COOMe	1782, 1765(sh)	—	36
NC–C≡C–CN	1683	−535	17
$(Ph_3As)_2$Pt(CF_3–C≡C–CF_3)	1775	−425	36, 125
$(Ph_3P)_2$Ni(Ph–C≡CPh)	1800	—	36
$(Ph_3P)_2$Ni(Ph–C≡C–Me)	1795	—	36
$(Ph_3P)_2$Ni(CF_3–C≡C–CF_3)	1790	−410	36
$(Ph_3P)_2$Pd(MeOOC–C≡C–COOMe)	1845, 1830	—	36
$(Ph_3P)_2$Pd(CF_3–C≡C–CF_3)	1838, 1811	−462	36
$(PhMe_2P)_2$Pd(CF_3–C≡C–CF_3)	1837, 1800	−463	36
(*n*-$Bu_3P)_2$Pd(CF_3–C≡C–CF_3)	1837, 1795	−463	36
$(PhMe_2P)_2$Pt(CF_3–C≡C–CF_3)	1767	−533	36
(*n*-$Bu_3P)_2$Pt(CF_3–C≡C–CF_3)	1758	−542	36

TABLE 7

TYPICAL NMR DATA FOR $CDCl_3$ SOLUTION OF COMPLEXES OF THE TYPE $(Ph_3P)_2M(un)$
τ values relative to TMS internal standard.

M	*un*	τ_{Ph}	τ_{CH_3}	τ_{CH_2}	$\tau_{C\equiv C-H}$	τ_{OH}	*Ref.*
Pt	$PhC\equiv CCH_3$	2.7	7.88^a	—	—	—	36, 166
Ni	$PhC\equiv CCH_3$	2.7	7.86^b	—	—	—	36, 166
Pt	$CH_3OOCC\equiv CCOOCH_3$	2.9	6.75	—	—	—	36, 166
Pd	$CH_3OOCC\equiv CCOOCH_3$	2.9	6.80	—	—	—	36, 166
Pt	 $\mathrm{H{-}C{\equiv}C{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}{-}CH_3}$	2.70	8.68^c	—	3.76^d	8.34	35, 112
Pt		2.68	—	8.50	3.74^e	8.75	35, 112
Pt		2.70	—	8.32	3.72^f	8.75	35, 112
Pt		2.70	—	8.49	3.78^g	8.98	35, 112
Pt	 $\mathrm{H{-}C{\equiv}\overset{\displaystyle OH}{\underset{\displaystyle C_2H_5}{C}}{-}CH_3}$	2.70	8.75^c 9.17^j	8.46^j	3.78^h	9.20	35, 112
Pt	 $\mathrm{H{-}C{\equiv}C{-}\overset{\displaystyle OH}{\underset{\displaystyle Ph}{C}}{-}Ph}$	2.80	—	—	3.55^k	8.80	35, 112
Pt		2.75	8.09^m	8.60	—	9.09	35, 112
Pt	 $\mathrm{CH_3{-}C{\equiv}C{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}{-}CH_3}$	2.74	8.72 9.23^m	—	—	8.91	35, 112
Pt	 $\mathrm{CH_3{-}C{\equiv}C{-}\overset{\displaystyle OH}{\underset{\displaystyle Ph}{C}}{-}Ph}$	2.83	8.71^m	—	—	8.16	35, 112

[a] $J_{P-trans-H} = 6.2H_z$, $J_{P-cis-H} \cong 1.2H_z$, $J_{Pt-H} = 41.5H_z$. [b] $J_{P-trans-H} = 4.5H_z$, $J_{P-cis-H} \cong 1H_z$. [c] $J_{Pt-CH_3} = 2H_z$. [d] $J_{P-trans-H} = 22H_z$, $J_{P-cis-H} = 10H_z$, $J_{Pt-H} = 59.5H_z$. [e] $J_{P-trans-H} = 22.8H_z$, $J_{P-cis-H} = 10H_z$, $J_{Pt-H} = 63H_z$. [f] $J_{P-trans-H} = 22H_z$, $J_{P-cis-H} = +10H_z$, $J_{P-H} = 60H_z$. [g] $J_{P-trans-H} = 22H_z$, $J_{P-cis-H} = 10H_z$, $J_{Pt-H} = 62H_z$. [h] $J_{P-trans-H} = 23.3H_z$, $J_{P-cis-H} = 10.3H_z$, $J_{Pt-H} = 63.5H_z$. [j] $J_{Pt-CH_2} \cong 1H_z$. [k] $J_{P-trans-H} = 22.3H_z$, $J_{P-cis-H} = 10H_z$, $J_{Pt-H} = 58H_z$. [m] $J_{P-trans-CH_3} = 6\text{–}8H_z$, $J_{P-cis-CH_3} = 0.5\text{–}1.5H_z$, $J_{Pt-H} = 36\text{–}40.5H_z$.

Since the complexes $M(R_3Q)_2$ (olefin) do not show any band in the infrared attributable to $\nu_{C=C}$ it has been concluded that the double bond of the olefin in these complexes has been reduced in bond order essentially to that of an alkane[62,115,116]. Similarly the $\nu_{C\equiv C}$ stretching frequency for the complexes $M(R_3Q)_2$ (acetylene) is found in the region of $\nu_{C=C}$ and the complexed acetylene is spectroscopically equivalent to an olefin[35,36]. For the divalent complexes of platinum and palladium[158–161] $\Delta\nu_{C=C}$ and $\Delta\nu_{C\equiv C}$ are in the range -50 to -250 cm^{-1} while for the zerovalent complexes[35,36,125,162], $\Delta\nu_{C\equiv C}$ is in the range -400 to -550 cm^{-1} indicating a much stronger metal ligand interaction with zerovalent complexes. The larger magnitude of change for the zerovalent complexes is in accord with the X-ray data suggesting a greater population of the olefin and acetylene π^* orbitals in these complexes. The far infrared spectra of several zerovalent phosphite complexes of the nickel triad have also been recorded and assigned[163]. Some representative infrared data are summarized in Table 6.

TABLE 8

NMR DATA FOR Pt(acac)Cl (OLEFIN) COMPLEXES IN $CDCl_3$
τ values relative to TMS internal standard.

Olefin		*Olefin*		*acac*		*Ref.*
		=CH	*-CH_3*	*=CH*	*-CH_3*	
Ethylene		5.48[a]	—	4.40	7.85	184
		5.53			8.03	
Propylene	*gem*	—w				
		4.55				
	cis	5.44	8.4		7.91	184
		5.57		4.47		
	trans	5.53	8.35		8.10	
		5.76				
cis-But-2-ene		—w	8.27w	4.52	7.95	184
		4.68	8.49		8.10	
trans-But-2-ene		5.11	8.23	4.47	7.94	184
		4.86	8.42		8.10	
Tetramethylethylene		—	8.15	4.50	7.96	184
			8.44		8.08	

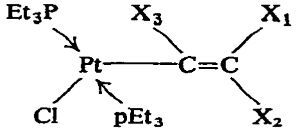
[a] Most intense lines of AA′BB′ multiplet.

(iii) Nuclear magnetic resonance

Nuclear magnetic resonance has been particularly useful in the structural assignment of these complexes. The platinum complexes have been the most thoroughly investigated due to the presence of ^{195}Pt($I = 1/2$, 34% natural abundance) coupling in both the proton and fluorine NMR. The NMR investigations have been especially fruitful because the coupling constants J and chemical shifts τ of the various nuclei are such that many of the spectra can be interpreted by simple first order analyses.

TABLE 9

COMPLEXES OF THE TYPE $(Et_3P)_2PtCl$ (FLUOROVINYL)*



		A	*B*	*C (cis)*	*D (trans)*	*E (cis)*	*F (trans)*	*G*
	X_1	*F*	*F*	*F*	CF_3	*F*	*H*	CF_3
	X_2	*F*	*F*	CF_3	*F*	*H*	*F*	*H*
	X_3	*F*	CF_2H	*F*	*F*	*F*	*F*	CF_3
^1H *NMR*	δCF_3	−1.21	−0.58	−1.7	−1.7	−1.23	−1.23	−1.8
	δCF_2	−1.95	−1.31	−2.5	−2.5	−1.97	−1.97	−2.4
	δ_1	—	—	—	—	—	−7.58	−6.50
	δ_2	—	—	—	—	−5.54	—	—
	δ_3	—	−4.58 for CF_2H	—	—	—	—	—
	J_{12}	—	—	—	—	82.3	84	9.62
	J_{13}	—	—	—	—	—	7.8	—
	J_{14}	—	—	—	—	—	4.2	—
	J_{23}	—	—	—	—	24	—	—
	J_{24}	—	—	—	—	4	—	—
	J_{HCF_2}	—	57	—	—	—	—	—
	J_{CF_2H-Pt}	—	7.5	—	—	—	—	—
^{19}F *NMR*	δ_1	24	46.4	75.1	−12.22			−20.7
	δ_2	58.7	47.7	−13.2	97.1			—
	δ_3	77	47.0	8.27	22.8			−25.7
	J_{12}	120	26.5	15.3	13.3			9.6
	J_{13}	35.6	—	12.8	21.3			12.2
	J_{14}	59.7	—	12.8	5.82			5.82
	J_{15}	4.8	—	—	—			—
	J_{23}	120	—	9.29	124			0
	J_{24}	62.4	—	13.45	186			—
	J_{34}	574	240	479	501			142.3
	J_{CF_2-H}	—	55	—	—			—
	J_{25}	—	—	3.17	3.5			—

* Data from Ref. 132 spectra recorded in $CDCl_3$ solution, chemical shift values are in p.p.m. relative to TMS external reference (^1H) and trifluoroacetic acid external reference (^{19}F spectra).
A = $(Et_3P)_2PtCl(CF{=}CF_2)$, B = $(Et_3P)_2PtCl[C(CH_2F){=}CF_2]$, C = $(Et_3P)_2PtCl$ *cis*-$CF{=}CFCF_3$), D = *trans*-isomer of C, E = $(Et_3P)_2PtCl($*cis*-$CF{=}CFH)$, F = *trans*-isomer of E, G = $(Et_3P)_2PtCl[C(CF_3){=}C(CF_3)H]$.

Since no source contains a compilation of various nuclei interacting with ^{195}Pt, and since NMR is of such great value in this field, a rather comprehensive list of data is given in Tables 7–10.

The NMR data for complexes of the type *trans*-$PtCl_2$(un)Py and *trans*-$PtCl_2$(un) (Pyno) have been reviewed[18,19]. Significantly, the *trans* labilizing effect of unsaturated ligands can be evaluated by observing the temperature at which coupling occurs between platinum and the α-pyridine hydrogens for complexes of the type[165]:

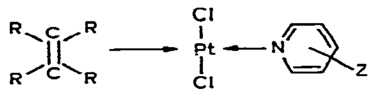


TABLE 10

NMR DATA FOR FLUOROVINYL COMPLEXES*

Compound	δ_1	δ_2	δ_3	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$
trans-$(Et_3P)_2Ni(CF{=}CF_2)Br$[a]	89.9	132.2	158.8	107	36	107
trans-$(Et_3P)_2Ni(CF{=}CF_2)_2$	91.4	134.1	170.8	112	32	112
trans-$(Et_3P)_2Pd(CF{=}CF_2)$[b]	95.8	133.6	166.1	109	40	104
trans-$(Et_3P)_2Pt(CF{=}CF_2)Br$	99.8	129.5	145.5	107	34	107
cis-$(Et_3P)_2Pt(CF{=}CF_2)Br$[c]	98.6	127.0	155.1	104	34	104
cis-$(Et_3P)_2Pt(CF{=}CF_2)_2$[d]	101.1	131.8	161.4	104	33	104
cis-$(Et_3P)_2Pt(CCl{=}CF_2)_2$[g]	92.2	80.0	—	65	—	
trans-$(Et_3P)_2Pt_2(CCl{=}CF_2)_2Br_2$[h]	91.1	80.6	—	64	—	
$(Et_3P)PyPt(CCl{=}CF_2)Br$[i]	96.3	81.3	—	66	—	
trans-$(Et_3P)_2Pd_2(CCl{=}CF_2)_2Br_2$[j]	93.9	80.4	—	69	—	

* Data taken from Ref. 224. ^{19}F chemical shifts (p.p.m.) in C_6H_6 relative to CCl_3F and coupling constants (c.p.s.). [a] J_{P-F}: F_1, 7.0; F_2, 7.0; F_3, 5.5 c.p.s. [b] J_{P-F}: F_1, 6.0; F_2, 4.5; F_3, 1.0 c.p.s. [c] J_{P-F}: F_1, 23; F_2, 0; F_3, 34 c.p.s.; J_{Pt-F}: F_1, 188; F_2, 51; F_3, 348 c.p.s. [d] J_{P-F}: F_1, 17; F_2, 0; F_3, 33 c.p.s.; J_{Pt-F}: F_1, 167; F_2, 42; F_3, 395 c.p.s. [g] J_{Pt-F}: F_1, 140 c.p.s. [h] J_{Pt-F}: F_1, 145; F_2, 90 c.p.s.; J_{P-F}, 1 c.p.s. [i] J_{Pt-F}: F_1, 145; F_2, 87 c.p.s.; J_{P-F}: F_1, 1; F_2, 2 c.p.s. [j] J_{P-F}: F_1, 4; F_2, 4 c.p.s.

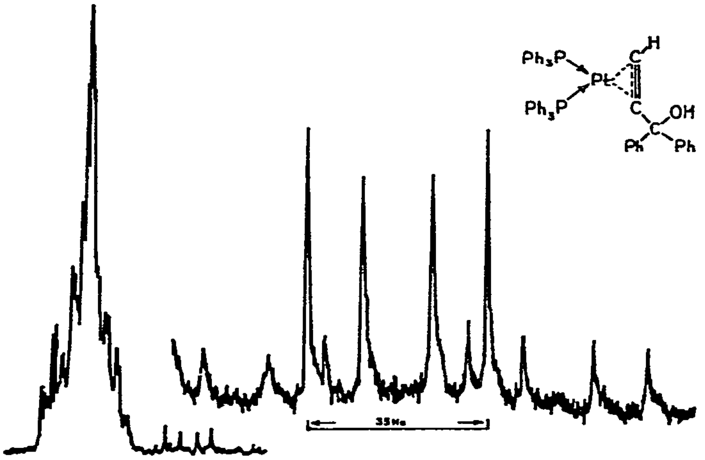


Fig. 8. 100 MHz NMR spectrum of $(Ph_3P)_2Pt[H{-}C{\equiv}C{-}C(OH)(Ph)_2]$ in $CDCL_3$ solution at 32°. The inset is the expanded acetylene hydrogen C≡C–H resonance showing the AMXX′ multiplet. The large resonance is the unresolved multiplet of the phenyl groups.

Very interesting conclusions can be drawn from the NMR spectra[35,36,112,166] of complexes of the type $(R_3P)_2Pt(yne)$. Typical spectra are shown in Figs. 8–11.

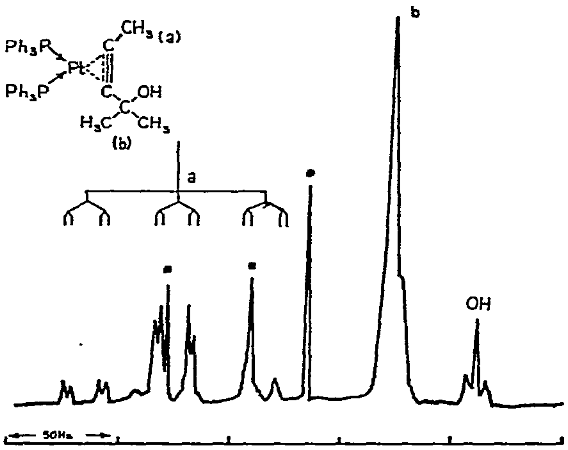


Fig. 9. 100 MHz NMR spectrum of the methyl region for the complex $(Ph_3P)_2Pt[CH_3{-}C{\equiv}C{-}C(OH)(CH_3)_2]$ in $CDCl_3$ at 32°. The starred resonances are due to uncomplexed acetylene. The coupling scheme of the AMXX′ multiplet of the CH_3(a) group is indicated.

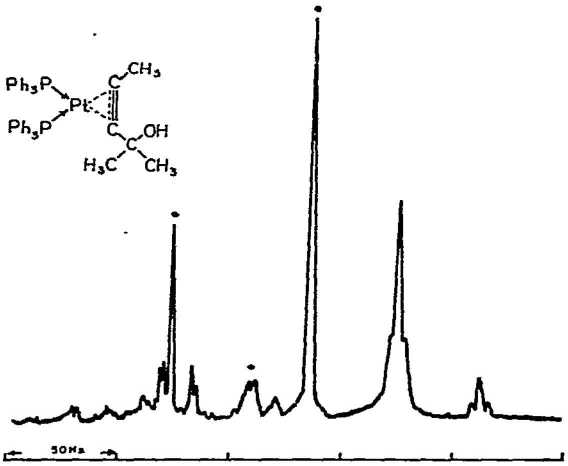
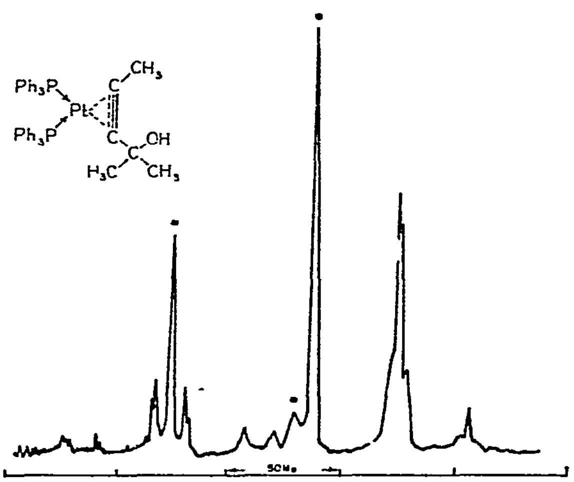


Fig. 10. 100 MHz NMR spectrum of the methyl region for the complex $(Ph_3P)_2Pt[CH_3{-}C{\equiv}C{-}C(OH)(CH_3)_2]$ in $CDCl_3$ at 60°. The starred resonances are due to uncomplexed acetylene. The AMXX′ multiplet for the CH_3 group is as in Fig. 9.

The chemical shift values of the acetylenic protons (Table 7) demonstrate that the complexed acetylene has been reduced essentially to an olefin, these protons appearing in the region where olefinic protons are normally found[167]. This fact is in agreement with the X-ray data and with the spectral shifts observed in the IR data. The coupling scheme for the acetylenic and methylacetylenic protons can be analyzed as follows: the protons are the A part of AMXX′ and A_3MXX' multiplets respectively which should contain twelve lines as shown in Fig. 12.



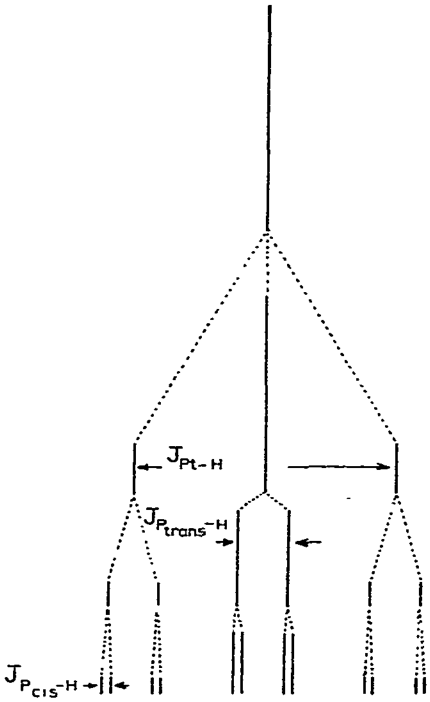


Fig. 11. 100 MHz NMR spectrum of the methyl region for the complex $(Ph_3P)_2Pt[CH_3-C\equiv C-C(OH)(CH_3)_2]$ in $CDCl_3$ at 32° after being heated to 60° for 1/2 h. The starred resonances are due to uncomplexed acetylene. The AMXX′ multiplet for the CH_3 group is as in Fig. 9.

Fig. 12. Representation of the coupling scheme for C≡C–H and $C\equiv C-CH_3$ protons of platinum complexes of the type $(PPh_3)_2Pt(R-C\equiv C-H)$ and $(PPh_3)_2Pt(R-C\equiv C-CH_3)$.

There are two satellite lines due to coupling with platinum and one line due to the uncoupled resonance in the relative intensity ratio of 1: 4:1. The three lines are then further split by the non-equivalent *cis*- and *trans*- phosphorus atoms to give an apparent triplet of double doublets or twelve lines with relative intensities 1,1,1,1,4,4,4,4,1,1,1,1. The observation of non-equivalent coupling[35,36,112,166] to the *cis*- and *trans*-phosphorus atoms implies the same structure (essentially square planar) in solution as in the solid state. Distinctive *cis* and *trans* coupling to the phosphorus atoms implies that the rate of rotation of the acetylene is very slow on the NMR time scale (with an upper limit of about 1.2 sec^{-1}) based upon the magnitude of J_{Pt-H}.

The presence of free acetylene in solutions of the complex $(Ph_3P)_2Pt[(CH_3)_2C(OH)C\equiv C-CH_3]$ further complicates the spectra (Figs. 9, 10 and 11, the starred resonances are due to free acetylene). The observation of separate resonances for the free and complexed acetylene implies a slow rate of acetylene exchange. Furthermore, the concentration of free acetylene increases with an increase in temperature (compare the relative magnitudes of the starred peaks to the unstarred peaks in Figs. 9 and 10), demonstrating that the exchange is temperature dependent. The spectra presented in Figs. 9 and 11 show that the reaction is not a simple dissociation reaction for the spectrum of a sample after a temperature cycle does not appear the same as that of one before a temperature cycle. Rather, an irreversible oxidative addition reaction, reaction (23), involving the solvent has occurred[36,112].

$$(R_3P)_2Pt(yne)+CDCl_3 \rightarrow (R_3P)_2PtCl(CDCl_2)+yne \qquad (23)$$

The NMR spectra of the complexes $[(Me_2Ph)_3P]_2MX_2$ show a 1:2:1 triplet for the methyl resonance in the *trans*-complexes due to virtual coupling and a symmetrical doublet for the *cis*-complexes. The proton NMR thus reveals the geometrical arrangement of the phosphines[168–170]. It is now generally accepted that phosphorus *trans* to the organic moiety displays greater coupling constants than phosphorus atoms in the *cis*-position[168–171]. The ranges for coupling constants J_{Pt-H} (Table 11) have been reported[19,166,112,169–184].

Much of the ^{195}Pt–H coupling data has been interpreted in terms of the Fermi contact contribution established through a platinum orbital containing some s-character and σ–π mixing in the olefin moiety[171,177,185,186]. However, it has been found that J_{Pt-CH} and $J_{Pt-C-C-H}$ have opposite signs[179] in platinum(II) olefin complexes; similar behaviour was found for the sigma bonded complex $PtCl(C_2H_5)_3$[174]. This suggests that contributions from terms other than the Fermi contact term are important. The molecular orbital calculations (section E, i) furthermore, showed that the platinum 6s orbital does not make a significant bonding contribution in these complexes. Thus caution is necessary in interpreting this coupling in terms of the s-character of the atomic orbitals involved in bonding.

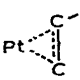
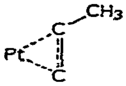
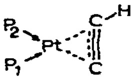
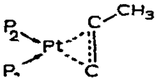
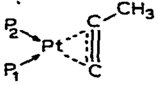
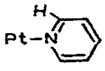
(iv) Electronic spectra

The electronic spectra of platinum(II) complexes has been rather extensively studied and the transitions have been assigned for Zeise's salt[187–191] and a number of its analogs containing different olefins[189–191]. The electronic spectra are composed of d–d transitions and metal–olefin π^* charge transfer transitions. From the spectral shifts observed upon changing the solvent and the *trans*-ligand for complexes of the type *trans*-$LPtCl_2$(olefin) the relative order of the platinum d-orbitals has been assessed[191].

Complexes of the type *cis*- or *trans*-(amine)$PtCl_2$(olefin) derived from Zeise's

TABLE 11

COUPLING CONSTANT RANGES FOR VARIOUS COMBINATIONS INVOLVING PLATINUM COUPLING

	J_{Pt-H}(Hz)	J_{P-H}(Hz)	J_{P_1-H}(Hz)	J_{P_2-H}(Hz)
P–Pt–H	700–1350	10–17		
Pt–P–C–H	27–36			
Pt–As–C–H	20–24			
Pt–C–H	70–120			
Pt–P–C–C–H	0–72			
	34–75			
	38–39			
	58–65		20–24	10–11
	28–40		7–8	1–3
	35–40		7–8	1–3
	60–70			
Pt–N–C–H	32–42			
Pt–S–C–H	45–56			

salt possess optical isomers if the amine is optically active and the circular dichroism of several of these complexes has been studied[149,192–198]. The sign of the circular dichroism band depends solely on the optical activity of the olefin and is independent of both the optical activity of the amine and the relative positions of the olefin and the amine[198]. A general quadrant rule has been developed to predict the absolute configuration from the sign of the C.D. maxima near 400 mμ[198]. As shown in Fig. 13 the chirality of the complexed olefinic centers is related to the location of substituents or ring residues in quadrants of alternating sign formed by the intersection of the platinum square plane normally corresponding to the olefinic C=C bond viewed along the platinum X-axis. The X-ray crystal structure[149] of one of these complexes has been determined and can be used as a reference compound for the assignment of the absolute configuration of olefinic complexes.

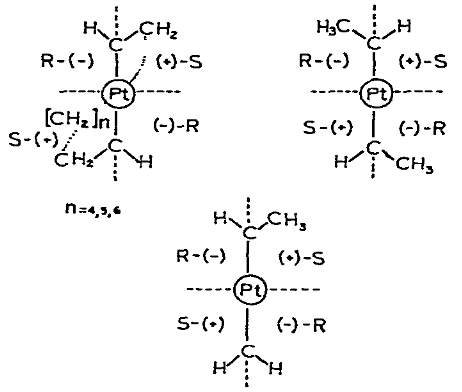


Fig. 13. Quadrant rule for predicting the absolute configuration of divalent platinum olefin amine complexes.

E. THE METAL LIGAND BOND

(i) *Molecular orbital calculations*

Because the number of orbitals involved in complete calculations is very large only a few molecular orbital calculations on molecules of this type have been reported. These include Zeise's salt[187], $(PH_3)_2(CH_3\text{-}C{\equiv}C\text{-}CH_3)Pt$, $(PH_3)_2(CH_3\text{-}C{\equiv}C\text{-}H)Pt$ and $(PH_3)_2(TCNE)Pt$[199,200] and *trans*-$PtCl_2(NH_3)(C_2H_4)$[152].

Since the discovery of Zeise's and Bukhovets' salts, the bonding in olefin and acetylene complexes has been puzzling. The model for metal–olefin complexes originally proposed by Dewar[201] and later modified by Chatt and Duncanson[202] was well accepted for Zeise's type complexes. However, recent NMR studies (*vide supra*) indicated that the Dewar–Chatt-Duncanson model was too rigid and it was suggested by Bennett[203] that the platinum–olefin π-bonding involved a combination of the platinum d_{yz} and d_{xz} orbitals.

Isolation of complexes of the type $(R_3Q)_2M(un)$ then posed questions about the oxidation state of the metal and the coordination of the ligand[157,138,205–209]. The accumulation of large amounts of experimental data finally led Maitlis[36,166] to put forth some convincing arguments in favor of monodentate ligands and consequently complexes of zerovalent metals. These were based upon NMR data and molecular orbital theory (from consideration of atomic energy levels).

Semi-empirical one electron molecular orbital calculations for some model compounds subsequently strengthened this point of view[152,100,200] and led to modification of the Dewar–Chatt–Duncanson model and to its extension to include the acetylene complexes[199,200].

X-ray crystal structure analyses of olefin and acetylene complexes demonstrated that in the solid state the olefin or acetylene is either normal to the plane (divalent complexes) or in the plane (zerovalent complexes) of the other donor atoms (*vide supra*). The NMR evidence for the zerovalent species indicates that the configuration is the same in solution as in the solid state[35,36,112,166]. The same conclusion is also supported for the divalent species in solution at lower temperatures[19,210,184]. However, as the temperature of these solutions is raised rotation and/or dissociation of the olefin occurs.

In the solid state the zerovalent complexes are not rigidly planar but have dihedral angles varying from 6–14° between the planes containing the olefin or acetylene and the metal atom and that containing the metal atom and the two other donor atoms (Fig. 6). This prompted statements that rotation in these complexes has a low energy barrier[136]. Since rotation has been found by NMR techniques for several divalent complexes[19,209,184,180,181] even in the solid state[182], a calculation of this barrier for both the zerovalent and divalent complexes[152,227] was undertaken. The calculated energy profiles are illustrated in Fig. 14.

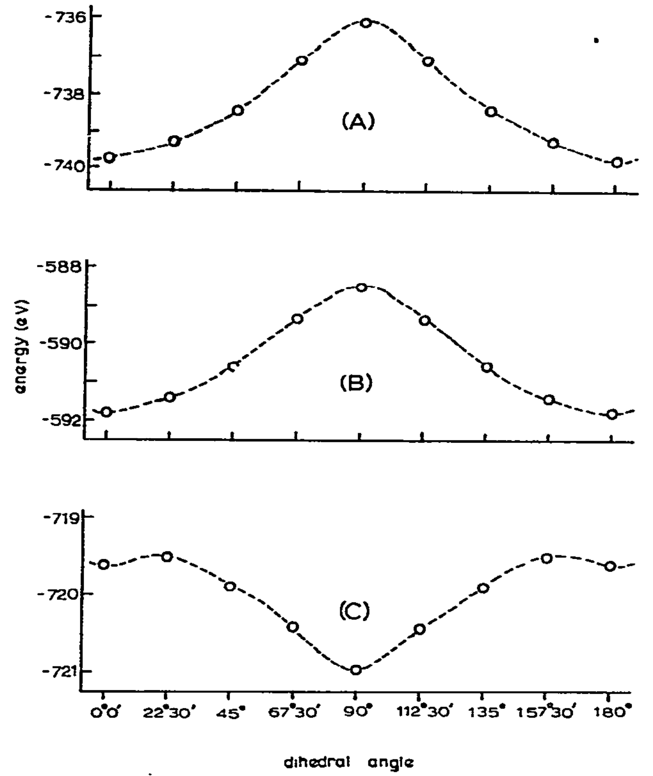


Fig. 14. Total energy (using the sum of the orbital energies as an approximation) as a function of the dihedral angle θ as defined in Fig. 7: (A) $(PH_3)_2Pt(CH_3{-}C{\equiv}C{-}CH_3)$; (B) $(PH_3)_2Pt(C_2H_4)$; (C) *trans*-$(NH_3)Pt(C_2H_4)Cl_2$.

Fig. 14 shows that the square planar configuration is calculated to be the most stable form for the zerovalent complexes. The angular dependence of the total energy is a smooth curve with no minima other than at 0 and 180° dihedral angle (square planar form). The absence of other minima (such as at 90°) seems to indicate that no barrier to rotation is interposed and that upon rotation a continuous rehybridization of the orbitals participating in π-bonding occurs rather than bond breaking[211]. This same general curve shape has been found for many calculations of zerovalent platinum olefin and acetylene complexes[227].

Calculations[152] were also performed on the divalent complex *trans*-$(NH_3)PtCl_2(C_2H_4)$ and the angular dependence of the total energy of this molecule is also depicted in Fig. 13. The calculations on this and numerous other divalent olefin and acetylene complexes[227] all predict the pseudotetrahedral configuration to be the most stable both in solution and in the solid state. However, these curves have a minimum at the square planar form, indicating that *some* bond breaking occurs upon rotation. The calculated rotational energy barrier for the divalent complex (1.1 eV for *trans*-$(NH_3)PtCl_2(C_2H_4)$) is considerably less than those for the zerovalent complexes (3.6 eV for $(PH_3)_2Pt(CH_3\text{–}C{\equiv}C\text{–}CH_3)$; 3.3 eV for $(PH_3)_2Pt(C_2H_4)$). By assuming that the energy profile is the same for other zerovalent complexes the rotational energy barriers of 3.8 eV for $(PH_3)_2Pt(CH_3\text{–}C{\equiv}C\text{–}H)$ and 2.6 eV for $(PH_3)_2Pt(TCNE)$ can be obtained from the earlier calculations[199,200]. Rotation has indeed been observed for several divalent complexes with the experimental energy barriers varying from 6–14 kcal (Table 12)[19,179,209,210,184,180–182].

TABLE 12

THERMODYNAMIC DATA FOR OLEFIN ROTATION IN COMPLEXES OF THE TYPE Pt(acac)Cl(olefin)*

Olefin	*Coalescence temp (°K)*	$\Delta G_T^{\neq}$ *(kcal/mole)*	*E (kcal/mole)*	$\Delta S^{\neq}$
Ethylene	245 ± 3	12.5 ± 0.6	—	—
Propylene	260 ± 3	13.5 ± 0.2	—	—
cis-But-2-ene	253 ± 5	13.3 ± 0.2	—	—
trans-But-2-ene	309.0	15.8	13.5 ± 1.4	−8.5 ± 5
Tetramethylethylene	219	10.9	8.7 ± 0.7	−12.0 ± 4

* Data taken from Ref. 184.

The calculated energy barrier of 1.1 eV = 25.3 kcal is an overestimate but is certainly of the right order of magnitude. Thus it might be possible to observe rotation for the zerovalent species (as yet unobserved).

The $d\pi\text{–}p\pi$ bonding between the metal d-orbitals and the olefin or acetylene π^*orbitals seems to be the most important factor in stabilizing metal olefin and acetylene complexes. This is supported by stability constant data for both the zerovalent and divalent complexes by infrared studies and by NMR studies. A recent review[26] gives a detailed discussion of the relative strengths of σ- and π-components. Since the σ-bonding should not restrict rotation, the energy barrier should be a measure of the relative π-acceptor ability of the various ligands in analogous complexes †.

X-ray studies of these complexes have shown that in every case the substituents on both the olefins and acetylenes are bent back from the metal atom. Blizzard and Santry[212] using CNDO calculations have shown that addition of electron density to the π^* orbital of the coordinating acetylene could lead to either a *cis*-bent or a *trans*-bent structure, with the *cis*-structure being slightly lower in energy. The experimentally found presence of *cis*-bent acetylenes in these complexes then seems to be strong evidence for π-bonding. This bending is then primarily an electronic effect with little, if any, contribution from steric interactions.

(ii) Group theoretical results

The molecular orbital calculations indicated that the metal in $(QR_3)_2M(un)$ type complexes is best regarded as being zerovalent[199,200] and that the strength of the metal olefin or acetylene interaction was governed by the amount of π-bonding. Since these same calculations indicated that the platinum 6s orbital does not participate in bonding, group theory was employed to develop a new bonding model consistent with the more general molecular orbital results. The metal atom was then considered to be zerovalent and three coordinate with dp^2 hybridization (Fig. 15).

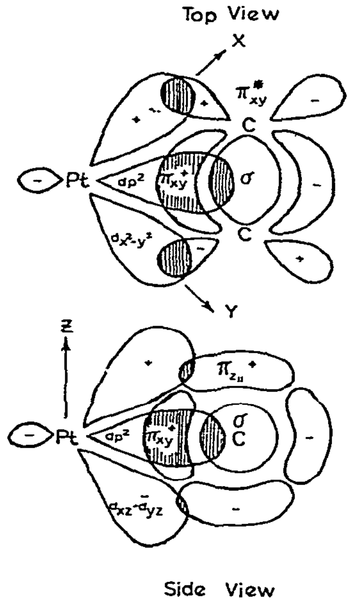
This scheme gives rise to a dp^2 hybrid orbital $(d_{xy}+p_x+p_y)$ overlapping with the acetylene π_{xy} orbital and a d^2 hybrid orbital $(d_{xz}+d_{yz})$ overlapping with the acetylene $\pi_{z\parallel}$. These two bonds are synergically opposed by $d_{x^2-y^2}$ overlap with the π_{xy} antibonding orbital and a d^2 hybrid orbital $(d_{xz}-d_{yz})$ overlapping with the $\pi_{z\parallel}$ antibonding orbital on the acetylene.

For the divalent complexes the description of the bonding is essentially that of the Dewar–Chatt–Duncanson model. The only difference is a change in the hybridization of the metal from dsp^2 to d^2p^2 since the molecular orbital calculations indicate that the platinum 6s orbital does not participate in bonding. Fig. 16 shows the orbitals involved in bonding.

Use of the d_{xy}, $d_{x^2-y^2}$, p_x and p_y orbitals to construct the d^2p^2 hybrids necessitates the staggered "pseudotetrahedral" form to allow any π "back bonding". This hybridization scheme predicts that the divalent complexes of acetylenes and olefins would have similar stabilities because only one π-bond can be formed. Very few acetylene complexes of divalent metals have been isolated[213-218]. Stable complexes are formed only when the acetylenes possess bulky substituents or

---

† σ-bonding can restrict rotation indirectly by shortening the metal– un bond and increasing steric interaction; this has been demonstrated by calculations on divalent complexes[227]. However, it does not seem to occur with the zerovalent complexes.



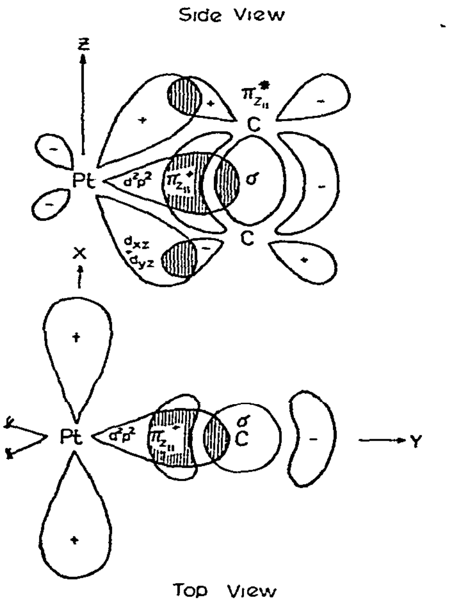


Fig. 15. Orbitals participating in bonding for zerovalent platinum acetylene complexes.

Fig. 16. Orbitals participating in bonding for divalent platinum olefin complexes.

functional groups which can interact with the metal atom or other ligands. With "ordinary" acetylenes polymerization products are isolated instead of complexes. This argues strongly that both the inplane, xy and out of plane π-bonding are necessary to stabilize these complexes.

Acetylenes should be both better σ-donors and π-acceptors than olefins since their π-orbitals are at lower energy. When both π-orbitals can be involved in bonding (as in zerovalent complexes), the acetylene complexes have stronger metal–ligand interactions than the olefin complexes. When only one π-orbital and its antibonding counterpart can be involved, the synergic bonding destabilizes the other π-orbital raising it to an essentially non-bonding energy causing the complex to behave as a Lewis base. Consequently, unless polymerization is chemically or sterically opposed it will occur rather than the formation of stable acetylene complexes.

The bonding schemes for olefin, molecular oxygen, molecular nitrogen and acetylene complexes have been discussed[35,36,138,157,207,209,217] by several authors and it now seems apparent that all of these molecules coordinate to transition metals in a similar manner. They should therefore be considered as neutral monodentate ligands occupying one coordination site. However, oxygen and nitrogen can coordinate in an end on fashion or by bridging two metal atoms[219–221].

When acetylene coordinates as the anionic acetylide it is isoelectronic with carbon monoxide and the bonding in these complexes has been amply described[168].

F. CATALYSIS

Since Hartley[26] has discussed the olefin reactions in an recent excellent review article, this paper will discuss only catalytic oligomerization and polymerization of acetylenes by complexes of the nickel triad which bear a direct relationship to the complexes discussed in this review.

The catalyst $(PPh_3)_2Ni(CO)_2$ has been extensively investigated[12,74,75] since it catalyses the polymerization of a variety of acetylenes to both benzene derivatives and linear oligomers. However, it does not polymerize several disubstituted acetylenes, conjugated diacetylenes or monoacetylenes containing *t*-butyl, carboxyl, amide or nitrile groups[74,75]). The mechanisms proposed for these reactions are illustrated in Figs. 17 and 18.

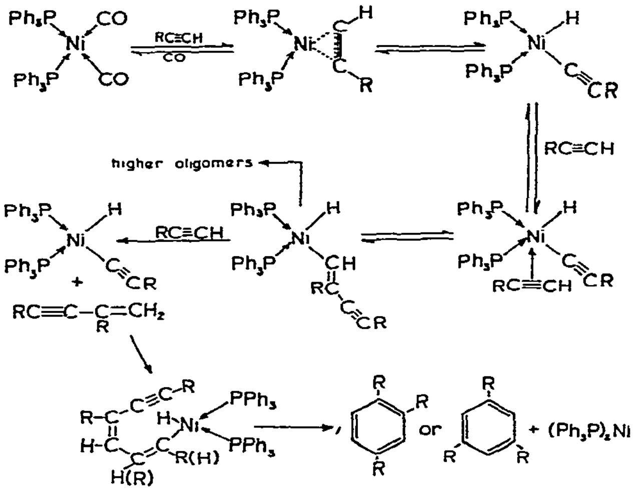


Fig. 17. Proposed reaction mechanism for the oligomerization of monosubstituted acetylenes by $Ni(CO)_2(PPh_3)_2$.

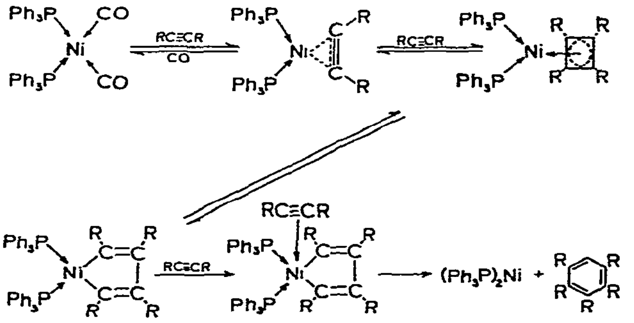


Fig. 18. Proposed reaction mechanism for the oligomerization of disubstituted acetylenes by $Ni(CO)_2(PPh_3)_2$.

The mechanism proposed for the monosubstituted acetylenes explains the production of polymeric material and $(PPh_3)_2Pt$(acetylene) and $(PPh_3)_2Pt$(acetylene$-H)_2(H)_2$ type complexes obtained from the reaction of $(PPh_3)_4Pt$ with monosubstituted hydroxyacetylenes[35] as well as the multistage equilibria of Fig. 5. The mechanism (Fig. 17) is thus very plausible. It seems unlikely, however, that the disubstituted acetylenes and monosubstituted acetylenes are polymerized by different reaction pathways[12]. Attempts to demonstrate the existence of cyclobutadiene intermediates in these reactions have not yet been successful.

The complexes *cis-* and *trans-*$(PPh_3)_2PtCl_2$, *trans-*$(PPh_3)_2PtHCl$, $(PPh_3)_2Pt$, $(PPh_3)_2Pt(H{-}C{\equiv}C{-}Ph)$ and *cis-* and *trans-*$(PPh_3)_2Pt(C{\equiv}C{-}Ph)_2$ have been investigated as catalysts for the polymerization of phenylacetylene[226]. The active species in the catalytic process were found to be $(PPh_3)_2Pt(C{\equiv}C{-}Ph)Cl$ and *cis-* and *trans-*$(PPh_3)_2Pt(C{\equiv}C{-}Ph)_2$ which formed only linear polymers. The mechanism these authors proposed is shown in Fig. 19.

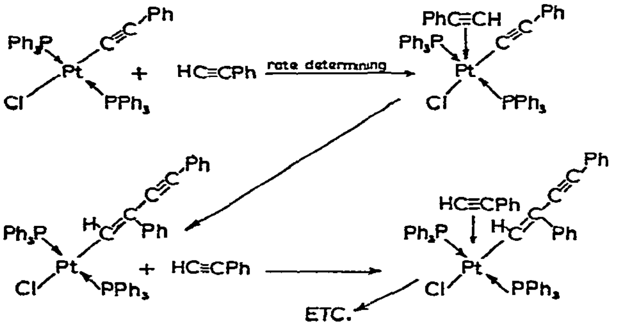


Fig. 19. Proposed reaction mechanism for the linear polymerization of acetylenes by platinum acetylide complexes.

Even though several of these complexes have catalytic properties and some are very plausible intermediates, the mechanisms of these reactions are not very well understood. Proof of the mechanistic pathway is very important as the chemistry of zerovalent complexes should be very similar to that of solvated metal atoms[3]. An understanding of the mechanism should help in the clarification of the relationship between the homogeneous and heterogeneous catalytic action of these metals.

ACKNOWLEDGEMENTS

We thank Dr. P. M. Maitlis, Dr. W. H. Baddley, Dr. D. M. Roundhill and Dr. M. Orchin for communicating results prior to publication. The financial support of the Esso Research Laboratories, Humble Oil and Refining Co., Baton Rouge, Louisiana, is gratefully acknowledged.

REFERENCES

1 J. P. Collman, *Transition Metal Chem.*, 2 (1966) 1.
2 L. Malatesta, R. Ugo and S. Cenini, *Advan. Chem. Ser.*, 62 (1967) 318.
3 R. Ugo, *Coord. Chem. Rev.*, 3 (1968) 319.
4 G. R. Dobson, I. W. Stolz and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, 8 (1966) 1.
5 C. Hoogzland and W. Hübel, in I. Wender and P. Pino (Eds.), *Organic Synthesis via Metal Carbonyls*, Vol. 1, Interscience, New York, N.Y., 1968, pp. 343–372.
6 W. Hübel, *ibid.*, pp. 273–343.
7 J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7 (1968) 54.
8 M. F. Lappert and B. Prokai, *Advan. Organometal. Chem.*, 5 (1967) 225.
9 J. P. Collman, *Accounts Chem. Res.*, 1 (1968) 136.
10 N. R. Davies, *Rev. Pure Appl. Chem.*, 17 (1967) 83.
11 A. Aguilo, *Advan. Organometal. Chem.*, 5 (1967) 321.
12 V. O. Reikhsfeld and K. L. Makovetskii, *Russ. Chem. Rev.*, 35 (1966) 510.
13 E. Ochiai, *Coord. Chem. Rev.*, 3 (1968) 49.
14 M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, 2 (1964) 325.
15 R. G. Guy and B. L. Shaw, *Advan. Inorg. Chem. Radiochem.*, 4 (1962) 77.
16 R. Jones, *Chem. Rev.*, 68 (1968) 785.
17 W. H. Baddley, *Inorg. Chim. Acta Rev.*, 2 (1968) 7.
18 M. Orchin and P. J. Schmidt, *Coord. Chem. Rev.*, 3 (1968) 345.
19 M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta Rev.*, 2 (1968) 123.
20 M. I. Bruce and F. G. A. Stone, *Prep. Inorg. Reactions*, 4 (1968) 177.
21 P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, 1 (1964) 143.
22 L. Malatesta, *Prog. Inorg. Chem.*, 1 (1959) 283.
23 G. N. Schrauzer, *Advan. Organometal. Chem.*, 2 (1964) 1.
24 M. A. Bennett, *Chem. Rev.*, 62 (1962) 611.
25 F. A. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, 3 (1968) 227.
26 F. R. Hartley, *Chem. Rev.*, 69 (1969) 799.
27 G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds*, Vol. II, Methuen, London, 1968.
28 J. P. Candlin, K. A. Taylor and D. T. Thompson, *Reactions of Transition Metal Complexes*, Elsevier, New York, N.Y., 1968.
29 M. Dub, *Organometallic Compounds*, Vol. I, 2nd ed., Springer, New York, N.Y., 1966.
30 R. W. Weiss, *ibid.*, Vol. 2, 1967.
31 M. Dub, *ibid.*, Vol. 3, 1968.
32 E. O. Fischer and H. Werner, *Metal π-complexes*, Vol. I, Elsevier, Amsterdam, 1966.
33 Preprints, *Symposium on Homogeneous Catalytic Reactions Involving Palladium, American Chemical Society, Minneapolis, Minn., April* 1969.
34 J. Chatt, G. A. Rowe and A. A. Williams, *Proc. Chem. Soc.*, (1957) 208.
35 J. H. Nelson, H. B. Jonassen and D. M. Roundhill, *Inorg. Chem.*, 8 (1969) 2591.
36 E. O. Greaves, C. J. Lock and P. M. Maitlis, *Can. J. Chem.*, 46 (1968) 3879.
37 G. C. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, D. Morelli, S. Cenini and F. Bonati, *Chem. Commun.*, (1967) 739.
38 R. Ugo, F. Cariati and G. LaMonica, *Chem. Commun.*, (1966) 868.
39 P. Uguagliati and W. H. Baddley, *J. Amer. Chem. Soc.*, 90 (1968) 5446.
40 H. C. Clark and W. S. Tsang, *Chem. Commun*, (1966) 123.
41 D. A. Harbourne and F. G. A. Stone, *J. Chem. Soc. (A)*, (1968) 1765.
42 H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforsch.*, 15B (1960) 763.
43 H. C. Clark, K. R. Dixon and W. J. Jacobs, *J. Amer. Chem. Soc.*, 90 (1968) 2259.
44 H. C. Clark, W. S. Tsang, *J. Amer. Chem. Soc.*, 89 (1967) 529.
45 F. D. Rochon and T. Theophanides, *Can. J. Chem.*, 46 (1968) 2973.
46 J. P. Birk, J. Halpern and A. L. Pickard, *Inorg. Chem.*, 7 (1968) 2672.
47 V. Albano, P. L. Bellon and V. Scatturin, *Chem. Commun.*, (1966) 507.
48 R. Cramer and G. W. Parshall, *J. Amer. Chem. Soc.*, 87 (1965) 1392.

49 G. W. PARSHALL AND F. N. JONES, *J. Amer. Chem. Soc.*, 87 (1965) 5356.
50 V. G. ALBANO, P. L. BELLON AND M. SANSONI, *Chem. Commun.*, (1969) 899.
51 V. G. ALBANO, G. M. BASSO RICCI AND P. L. BELLON, *Inorg. Chem.*, 8 (1969) 2109.
52 T. P. CHEESEMAN, A. L. ODELL AND H. A. RAETHEL, *Chem. Commun.*, (1968) 1496.
53 J. CHATT, R. S. COFFEY, A. GOUGH AND D. T. THOMPSON, *J. Chem. Soc. (A)*, (1968) 190
54 H. C. CLARK, P. W. R. CORFIELD, K. R. DIXON AND J. A. IBERS, *J. Amer. Chem. Soc.* 89 (1967) 3360.
55 W. H. BADDLEY AND J. M. SINGER, unpublished results.
56 J. P. COLLMAN, J. N. CAWSE AND J. W. KANG, *Inorg. Chem.*, 8 (1969) 2574.
57 J. A. OSBORN, *Chem. Commun.*, (1968) 1231.
58 S. OTSUKA, A. NAKAMURA AND K. TANI, *J. Organometal. Chem.*, 14 (1968) P 30.
59 W. C. ZEISE, *Pogg. Ann.*, 21 (1931) 497.
60 J. CHATT, N. P. JOHNSON AND B. L. SHAW, *J. Chem. Soc.*, (1964) 1662.
61 P. FITTON AND J. E. MCKEON, *Chem. Commun.*, (1968) 4.
62 D. M. ROUNDHILL AND G. WILKINSON, *J. Chem. Soc. (A)*, (1968) 506.
63 D. T. ROSEVEAR AND F. G. A. STONE, *J. Chem. Soc. (A)*, (1968) 164.
64 E. O. GREAVES AND P. M. MAITLIS, *J. Organometal. Chem.*, 6 (1966) 104.
65 S. OTSUKA, A. NAKAMURA AND Y. TATSUNO, *J. Amer. Chem. Soc.*, 91 (1969) 6994.
66 R. W. WEISS, *Organometallic Compounds*, Vol. 2, 2nd ed., Springer, New York, N.Y., 1967, p. B29.
67 H. REINHEIMER, H. DIETL, J. MOFFAT, D. WOLFF AND P. M. MAITLIS, *J. Amer. Chem. Soc.*, 90 (1968) 5321.
68 P. M. HENRY, *J. Amer. Chem. Soc.*, 86 (1964) 3246.
69 I. I. MOISEEV, M. N. VARGAFTIK AND YA. K. SYRKIN, *Dokl. Akad. Nauk S.S.S.R.*, 152 (1963) 147; *Chem. Abstr.*, 60 (1964) 184d.
70 S. V. PESTRIKOV AND I. I. MOISEEV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, (1965) 349; *Chem. Abstr.*, 62 (1965) 16018d.
71 S. V. PESTRIKOV, I. I. MOISEEV AND T. N. ROMANOVA, *Zh. Neorgan. Khim.*, 10 (1965) 2203; *Chem. Abstr.*, 63 (1965) 15836b.
72 S. V. PESTRIKOV, I. I. MOISEEV AND B. A. TSĬVILIKHOVISKAYA, *Zh. Neorgan. Khim.*, 11 (1966) 1742; *Chem. Abstr.*, 65 (1966) 13757c.
73 S. V. PESTRIKOV, I. I. MOISEEV AND L. M. SVERZH, *Zh. Neorgan. Khim.*, 11 (1966) 2081; *Chem. Abstr.*, 66 (1967) 45991.
74 L. S. MERIWETHER, E. G. COLTHUP AND G. W. KENNERLY, *J. Org. Chem.*, 26 (1961) 5163.
75 L. S. MERIWETHER, M. F. LETO, E. G. COLTHUP AND G. W. KENNERLY, *J. Org. Chem.*, 27 (1962) 3930.
76 W. REPPE AND W. J. SCHWECKENDIEK, *Ann. Chem.*, 104 (1948) 560.
77 G. WILKE AND G. HERRMANN, *Angew. Chem.*, 74 (1962) 693.
78 G. WILKE AND G. HERRMANN, *Angew. Chem. Int. Ed. Engl.*, 1 (1962) 549.
79 E. W. GOWLING, S. F. KETTLE AND G. M. SHARPLES, *Chem. Commun.*, (1968) 21.
80 T. L. GILCHRIST, F. J. GRAVELING AND C. W. REES, *Chem. Commun.*, (1968) 821.
81 C. D. COOK AND G. S. JAUHAL, *J. Amer. Chem. Soc.*, 90 (1968) 1464.
82 M. DUBECK, *J. Amer. Chem. Soc.*, 82 (1960) 502.
83 J. F. TILNEY-BASSETT AND O. S. MILLS, *J. Amer. Chem. Soc.*, 81 (1959) 4757.
84 M. I. BRUCE AND M. Z. IQBAL, *J. Organometal. Chem.*, 17 (1969) 469.
85 O. S. MILLS AND B. W. SHAW, *J. Organometal. Chem.*, 11 (1968) 595.
86 O. S. MILLS AND B. W. SHAW, *Acta Cryst.*, 18 (1965) 562.
87 H. BEHRENS AND A. MÜLLER, *Z. Anorg. Allg. Chem.*, 341 (1965) 124.
88 J. R. OLECHOWSKI, C. G. MCALISTER AND R. F. CLARK, *Inorg. Chem.*, 4 (1965) 246.
89 R. S. VINAL AND L. T. REYNOLDS, *Inorg. Chem.*, 3 (1964) 1062.
90 L. MALATESTA AND C. CARIELLO, *J. Chem. Soc.*, (1958) 2323.
91 L. MALATESTA AND M. ANGOLETTA, *J. Chem. Soc.*, (1957) 1186.
92 P. HEIMBACH, *Angew. Chem. Int. Ed. Engl.*, 3 (1964) 648.
93 J. CHATT AND B. L. SHAW, *J. Chem. Soc.*, (1960) 1718.
94 J. CHATT AND B. L. SHAW, *J, Chem. Soc.*, (1959) 705.
95 J. CHATT AND B. L. SHAW, *J. Chem. Soc.*, (1959) 4020.

96 I. COLLAMATI AND A. FURLANI, *J. Organometal. Chem.*, 17 (1969) 457.

97 D. M. ROUNDHILL AND H. B. JONASSEN, *Chem. Commun.*, (1968) 1233.

98 J. H. NELSON AND H. B. JONASSEN, unpublished results.

99 C. D. COOK AND G. S. JAUHAL, *Can. J. Chem.*, 45 (1967) 301.

100 W. A. SPOFFORD, III, P. D. CARFAGNA AND E. L. AMMA, *Inorg. Chem.*, 6 (1967) 1553.

101 C. N. R. RAO, *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York, N.Y., 1963, pp. 155–156.

102 K. ISSLIEB AND M. HAFTENDORN, *Z. Anorg. Chem.*, 351 (1967) 9.

103 D. C. GOODALL, *J. Chem. Soc. (A)*, (1968) 887.

104 M. A. BENNETT, J. CHATT, G. J. ERSKINE, J. LEWIS, R. F. LONG AND R. S. NYHOLM, *J. Chem. Soc. (A)*, (1967) 501.

105 M. A. BENNETT, W. R. KNEEN AND R. S. NYHOLM, *Inorg. Chem.*, 7 (1968) 556.

106 M. A. BENNETT, H. W. KOUWENHOVEN, J. LEWIS AND R. S. NYHOLM, *J. Chem. Soc.*, (1964) 4570.

107 R. E. YINGST AND B. E. DOUGLAS, *Inorg. Chem.*, 3 (1964) 1177.

108 L. V. INTERRANTE, M. A. BENNETT AND R. S. NYHOLM, *Inorg. Chem.*, 5 (1966) 2212.

109 A. J. CARTY AND A. EFRATY, *Can. J. Chem.*, 47 (1969) 2573.

110 K. S. WHEELOCK, J. H. NELSON AND H. B. JONASSEN, *Inorg. Chim. Acta*, 4 (1970) 399.

111 J. P. BIRK, J. HALPERN AND A. L. PICKARD, *J. Amer. Chem. Soc.*, 90 (1968) 4491.

112 J. H. NELSON, J. R. REED AND H. B. JONASSEN, unpublished results.

113 W. J. BLAND AND R. D. W. KEMMITT, *J. Chem. Soc. (A)*, (1968) 1278.

114 W. J. BLAND AND R. D. W. KEMMITT, *J. Chem. Soc. (A)*, (1969) 2062.

115 M. GREEN, R. B. L. OSBORN, A. J. REST AND F. G. A. STONE, *Chem. Commun.*, (1966) 502.

116 M. GREEN, R. B. L. OSBORN, A. J. REST AND F. G. A. STONE, *J. Chem. Soc. (A)*, (1968) 2525.

117 W. J. BLAND, J. BURGESS AND R. D. W. KEMMITT, *J. Organometal. Chem.*, 18 (1969) 199.

118 W. J. BLAND, J. BURGESS AND R. D. W. KEMMITT, *J. Organometal. Chem.*, 14 (1968) 201.

119 W. H. BADDLEY AND L. M. VENANZI, *Inorg. Chem.*, 5 (1966) 33.

120 P. FITTON, M. P. JOHNSON AND J. E. MCKEON, *Chem. Commun.*, (1968) 6.

121 P. D. KAPLAN, P. SCHMIDT AND M. ORCHIN, *J. Amer. Chem. Soc.*, 90 (1968) 4175.

122 A. PANUNZI, A. DERENZI, R. PALUMBO AND G. PAIARO, *J. Amer. Chem. Soc.*, 91 (1969) 3879.

123 J. CHATT, B. L. SHAW AND A. A. WILLIAMS, *J. Chem. Soc.*, (1962) 3269.

124 A. D. ALLEN AND C. D. COOK, *Can. J. Chem.*, 42 (1964) 1063.

125 J. L. BOSTON, S. O. GRIM AND G. WILKINSON, *J. Chem. Soc.*, (1963) 3468.

126 J. CHATT, G. A. ROWE AND A. A. WILLIAMS, *Proc. Chem. Soc.*, (1957) 208.

127 S. J. LOKKEN AND D. S. MARTIN JR., *Inorg. Chem.*, 2 (1963) 562.

128 D. G. MCMANE AND D. S. MARTIN JR., *Inorg. Chem.*, 7 (1968) 1169.

129 R. G. DENNING, F. R. HARTLEY AND L. M. VENANZI, *J. Chem. Soc. (A)*, (1967) 324, 328.

130 R. G. DENNING AND L. M. VENANZI, *J. Chem. Soc. (A)*, (1967) 336.

131 F. R. HARTLEY AND L. M. VENANZI, *J. Chem. Soc. (A)*, (1967) 330.

132 H. C. CLARK AND W. S. TSANG, *J. Amer. Chem. Soc.*, 89 (1967) 533.

133 J. O. GLANVILLE, J. M. STEWART AND S. O. GRIM, *J. Organometal. Chem.*, 7 (1967) p. 9.

134 C. PANATTONI, G. BOMBIERI, U. BELLUCO AND W. H. BADDLEY, *J. Amer. Chem. Soc.*, 90 (1968) 798.

135 W. DREISSIG AND H. DIETRICH, *Acta Cryst.*, B24 (1968) 108.

136 C. D. COOK, C. H. KOO, S. C. NYBURG AND M. T. SHIOMI, *Chem. Commun.*, (1967) 426.

137 K. W. MUIR AND J. A. IBERS, *J. Organometal. Chem.*, 18 (1969) 175.

138 J. A. MCGINNETY AND J. A. IBERS, *Chem. Commun.*, (1968) 235.

139 C. PANATTONI AND R. GRAZIANI, in M. CAIS (Ed.), *Progress in Coordination Chemistry*, Elsevier, Amsterdam, 1968, p. 310.

140 T. KASHIWAGI, N. YASUOKA, N. KASAI AND M. KAKUDO, *Chem. Commun.*, (1969) 743.

141 J. A. MCGINNETY, R. J. DOEDENS AND J. A. IBERS, *Inorg. Chem.*, 6 (1967) 2243.

142 S. J. LAPLACA AND J. A. IBERS, *J. Amer. Chem. Soc.*, 87 (1965) 2581.

143 T. MOELLER, *Inorganic Chemistry*, Wiley, New York, N.Y., 1952, p. 135.

144 J. N. DEMPSEY AND N. C. BAENZIGER, *J. Amer. Chem. Soc.*, 77 (1955) 4984.

145 G. R. DAVIES, W. HEWERTSON, R. H. B. MAIS AND P. G. OWSTON, *Chem. Commun.*, (1967) 423.

146 P. R. H. Alderman, P. G. Owston and J. M. Rowe, *Acta Cryst.*, 13 (1960) 149.
147 C. Panattoni, G. Bombieri, E. Forsellini, B. Crociani and U. Belluco, *Chem. Commun.*, (1969) 187.
148 T. Kashiwagi, N. Yasuoka, N. Kasai and M. Kukudo, *Chem. Commun.*, (1969) 317.
149 E. Bennedetti, P. Corradini and C. Pedone, *J. Organometal. Chem.*, 18 (1969) 203.
150 W. A. Whitla, H. M. Powell and L. M. Venanzi, *Chem. Commun.*, (1966) 310.
151 P. B. Hitchcock, M. McPartilin and R. Mason, *Chem. Commun.*, (1969) 1367.
152 K. S. Wheelock, J. H. Nelson, L. C. Cusachs and H. B. Jonassen, *J. Amer. Chem. Soc.*, 92 (1970) 5110.
153 C. E. Moore, *Atomic Energy Levels*, Vol. III, National Bureau of Standards, Circular 467, U.S. Government Printing Office, Washington, D.C., 1958.
154 M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, 90 (1968) 918.
155 M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, 88 (1966) 5454.
156 J. Pradilla-Sorzano and J. P. Fackler, *J. Mol. Spectry.*, 22 (1967) 80.
157 G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 7 (1968) 2030.
158 D. B. Powell and N. Sheppard, *J. Chem. Soc.*, (1960) 2519.
159 P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, 17 (1961) 909.
160 E. O. Greaves and P. M. Maitlis, *J. Organometal. Chem.*, 6 (1966) 104.
161 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, N.Y., 1963, p. 228.
162 D. G. Harbourne, D. T. Rosevear and F. G. A. Stone, *Inorg. Nucl. Chem. Lett.*, 2 (1966) 247.
163 V. G. Myers, F. Basolo and K. Nakamoto, *Inorg. Chem.*, 8 (1969) 1204.
164 J. Chatt, R. G. Guy, L. A. Duncanson and D. T. Thompson, *J. Chem. Soc.*, (1963) 5170.
165 M. Orchin, private communication.
166 E. O. Greaves, R. Bruce and P. M. Maitlis, *Chem. Commun.*, (1967) 860.
167 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, New York, N.Y., 1966.
168 J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, (1963) 279.
169 A. D. Beveridge, H. C. Clark and J. T. Kwon, *Can. J. Chem.*, 44 (1966) 179.
170 J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. (A)*, (1966) 770.
171 J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc. (A)*, (1966) 1711.
172 P. B. Tripathy and D. M. Roundhill, *J. Organometal. Chem.*, 24 (1970) 247.
173 J. Powell and B. L. Shaw, *J. Chem. Soc.*, (1965) 3879.
174 S. F. A. Kettle, *J. Chem. Soc.*, (1965) 6664.
175 J. A. S. Smith, *J. Chem. Soc.*, (1962) 4736.
176 L. E. Erickson, J. W. McDonald, J. K. Howie and R. P. Clow, *J. Amer. Chem. Soc.*, 90 (1968) 6381.
177 P. W. Atkins, J. C. Green and M. L. H. Green, *J. Chem. Soc. (A)*, (1968) 2275.
178 B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, 8 (1969) 379.
179 B. F. G. Johnson, C. Holloway, G. Hulley and J. Lewis, *Chem. Commun.*, (1967) 1143.
180 S. Maricic, C. R. Redpath and J. A. S. Smith, *J. Chem. Soc.*, (1963) 4905.
181 L. W. Reeves, *Can. J. Chem.*, 38 (1960) 736.
182 H. P. Fritz, K. E. Schwarzhans and D. Sellman, *J. Organometal. Chem.*, 6 (1966) 551.
183 M. A. Bennett, G. J. Erskine and R. S. Nyholm, *J. Chem. Soc. (A)*, (1967) 1260.
184 C. E. Holloway, G. Hulley, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. (A)*, (1969) 53.
185 P. D. Kaplan and M. Orchin, *Inorg. Chem.*, 4 (1965) 1393.
186 P. S. Braterman, *Inorg. Chem.*, 5 (1966) 1066.
187 J. W. Moore, *Acta Chem. Scand.*, 20 (1966) 1154.
188 S. J. Lokken and D. S. Martin, *Inorg. Chem.*, 2 (1963) 562.
189 R. G. Denning and L. M. Venanzi, *J. Chem. Soc.*, (1963) 3241.
190 S. I. Shupack and M. Orchin, *J. Amer. Chem. Soc.*, 86 (1964) 586.
191 R. G. Denning, F. R. Hartley and L. M. Venanzi, *J. Chem. Soc. (A)*, (1967) 1322.
192 G. Paiaro, P. Corradini, R. Palumbo and A. Panunzi, *Macromol. Chem.*, 71 (1964) 184.
193 G. Paiaro and A. Panunzi, *J. Amer. Chem. Soc.*, 86 (1964) 5148.

194 A. Panunzi and G. Paiaro, *J. Amer. Chem. Soc.*, 88 (1966) 4843.
195 G. Paiaro and A. Panunzi, *Tetrahedron Lett.*, 8 (1965) 4411.
196 P. Corradini, S. F. Mason, G. Paiaro, A. Panunzi and G. H. Searle, *J. Amer. Chem. Soc.*, 88 (1966) 2863.
197 E. Premuzic and A. I. Scott, *Chem. Commun.*, (1967) 1078.
198 A. D. Wrixon, E. Premuzic and A. I. Scott, *Chem. Commun.*, (1968) 639.
199 J. H. Nelson, K. S. Wheelock, L. C. Cusachs and H. B. Jonassen, *Chem. Commun.*, (1969) 1019.
200 J. H. Nelson, K. S. Wheelock, L. C. Cusachs and H. B. Jonassen, *J. Amer. Chem. Soc.*, 91 (1969) 7005.
201 M. J. S. Dewar, *Bull. Soc. Chim. (France)*, 18 (1951) 79.
202 J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, (1953) 2939.
203 M. A. Bennett, *Second Conference of the Coordination and Metal Organic Chemistry Division of the Royal Australian Chemical Institute, Monash, Australia, May*, 1968.
204 M. I. Bruce, D. A. Harbourne, F. Waugh and F. G. A. Stone, *J. Chem. Soc. (A)*, (1968) 356.
205 J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, 89 (1967) 844.
206 J. Chatt, L. A. Duncanson and R. G. Guy, *Nature*, 184 (1959) 526.
207 M. Orchin, *Advan. Catal. Relat. Subj.*, 16 (1966) 1.
208 J. Chatt, in P. H. Plesch (Ed.), *Cationic Polymerization*, Heffer, Cambridge, England, 1952, pp. 40–56.
209 R. Cramer, *J. Amer. Chem. Soc.*, 86 (1964) 217.
210 T. A. Weil, P. J. Schmidt and M. Orchin, *Inorg. Chem.*, 8 (1969) 2138.
211 F. A. Cotton, private communication.
212 A. C. Blizzard and D. P. Santry, *J. Amer. Chem. Soc.*, 90 (1968) 5749.
213 J. Chatt, R. G. Guy and L. A. Duncanson, *J. Chem. Soc.*, (1961) 827.
214 A. Gel'man, S. V. Bukhovetz and E. Meilakh, *Compt. Rend. Acad. Sci., U.S.S.R.*, 46 (1945) 105.
215 S. V. Bukhovestz, *Izvest. Sekt. Platiny Drug Blagorod. Metal Inst. Obschehei Neorg. Khim.*, 29 (1955) 55.
216 S. V. Bukhovetz and K. A. Molodova, *Zhur. Neorg. Khim.*, 2 (1957) 776; *ibid.*, 3 (1958) 546.
217 J. Chatt, L. A. Duncanson and R. G. Guy, *Nature*, 184 (1959) 526.
218 S. V. Bukhovetz and K. Pukhov, *Zhur. Neorg. Khim.*, 3 (1958) 1714.
219 F. Bottomley and S. C. Nyburg, *Chem. Commun.*, 897 (1966).
220 F. Bottomley and S. C. Nyburg, *Acta Cryst.*, B24 (1968) 2189.
221 U. Thewalt and R. Marsh, *J. Amer. Chem. Soc.*, 89 (1967) 6364.
222 G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds*, Vol. II, Methuen, London, 1968, p. 273.
223 C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 31.
224 A. J. Rest, D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc. (A)*, (1967) 66.
225 W. J. Bland and R. D. W. Kemmitt, *Nature*, 211 (1966) 963.
226 A. Furlani, I. Collamati and G. Sartori, *J. Organometal. Chem.*, 17 (1969) 463.
227 J. H. Nelson, K. S. Wheelock, L. C. Cusachs and H. B. Jonassen, unpublished results.
228 J. K. Stalick and J. A. Ibers, *J. Amer. Chem. Soc.*, 92 (1970) 5333.
229 M. Black, R. H. B. Mais and P. G. Owston, *Acta Cryst.*, B25 (1969) 1753.
230 W. C. Hamilton, K. A. Klanderman and R. Spratley, *8th Intern. Congr. Crystallography, Stony Brook, N.Y., 1969*, Abstr. XIV-46.