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Complexes of the Platinum Metals Containing Weak Donor Ligands

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I. Introduction

Many complexes of the platinum metals (Ru, Os, Rh, Ir, Pd, and Pt) have been shown to act as active homogeneous catalysts in reactions of industrial importance, including the hydrogenation,[1,2] hydrosilation,[3,4] hydroformylation,[5,6] and oxidative hydrolysis[7,8] of olefins and the carbonylation of methanol.[9,10] Some success in the activation of alkanes has also been achieved by complexes of these metals.[11] The ease with which an organic substrate can enter the coordination sphere of a metal ion is thought to be a key factor in determining the ability of such an ion to catalyze the reactions of the substrate. The importance of platinum metal complexes containing weak donor ligands in the homogeneous activation of organic substrates, which are themselves only modest ligands,[12] is thus apparent.

This present review describes the weak bonding in these complexes by use of a simple molecular orbital model essentially derived from the Lewis acid–base definitions. The chemistry of platinum metal complexes containing weak donor ligands is outlined, divisions being made according to the nature of the weak donor and the applicability of the bonding model examined. Comments on preparative techniques and the relevance of such complexes in homogeneous catalysis are included.

II. Metal–Ligand Interactions: An Approach to the Phenomenon of Weak Bonding

The original acid–base definition as stated by Lewis[13] (". . . the basic substance furnishes a pair of electrons for a chemical bond; the acid substance accepts such a pair") may be applied to a wide range of chemical interactions. In inorganic chemistry, all metal ions may

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TABLE I. Stability Series for Class a and Class b Acids

for class a acids	for class b acids
N >> P > As > Sb > Bi	N << P > As > Sb > Bi
O >> S > Se > Te	O << S ~ Se ~ Te
F >> Cl > Br > I	F < Cl < Br << I

act as Lewis acids, and hence ligands become a subset of the more general term Lewis base. One of the major points to arise from the Lewis definitions is the relative nature of acidity and basicity;[14] for example, ethyl acetate can act as both Lewis acid (during hydroxide addition to the carbonyl group) and Lewis base (complexing with a proton via an oxygen donor site). Indeed, as the donor orbital on the base is usually the highest occupied molecular orbital (HOMO) and the acceptor orbital on the acid is usually the lowest unoccupied molecular orbital (LUMO) [this is not always true, as exceptions occur among the transition metals for steric and symmetry reasons[15] (exemplified below); for the case of monoatomic donors and acceptors, atomic rather than molecular orbitals should be applied], the HOMO–LUMO separation of each reactant and the difference in orbital energies between the reactants will effectively define the course of the reaction. The wide variety of acid–base phenomena observed in the reactions of many compounds makes it desirable to have a classification whereby the relative reactivities of such compounds may be predicted. In 1950[16] it was observed that in the reaction between aquated metal ions and halide ions, the metal ions tended to group in two categories, those which favored large polarizable bases (such as iodide) and those which favored small unpolarizable bases (such as fluoride). Further work[17] led to the labels class A acceptor (those metal ions which favored small unpolarizable bases) and class B acceptor (those metal ions which favored large polarizable bases). The first major development in this field, in 1958,[18] was the addition of data concerning the relative affinities of bases having group 5B and 6B donor atoms to that for bases of group 7B. This led to the terminology class a and class b acceptor, paralleling the earlier class A and class B approach. The stability series for class a acids (acceptors which tend to have inert gas configurations) and class b acids (acceptors which tend to have a large number of d electrons in their valence shells) are shown in Table I. This classification recognized that some acceptors did not show typical class a or class b behavior, and these were termed borderline acids. Classification of acids in their normal valence states as class a, borderline, or class b is shown in Table II. The class a–class b nomenclature is limiting as it is derived from free-energy data for metal–ligand interactions. This major limitation was partially overcome in 1963 when the classification system was extended to cover a wide range of acids and bases (including many examples from organic chemistry) based on both thermodynamic and kinetic data.[19] The extended ranges of acids and bases were named hard (roughly equivalent to class a) and soft (roughly equivalent to class b). The new nomenclature arose from considering the general properties of those acids and bases under discussion; these properties are detailed in Table III. The properties show that ions exhibiting hard behavior (class a type) tend to be small in size with closely held orbitals (emphasized by the name hard) and ions exhibiting soft behavior (class b type) tend to be large with less closely held orbitals (again emphasized by the name soft). A borderline category was also recognized.

The acids and bases originally grouped in these categories are shown in Table IV.[20] The principle of hard and soft acids and bases (HSAB) relates the relative reactivity of these species to one another by stating that hard acids prefer to associate with, and react readily with, hard bases and that the same is true for soft acids and soft bases. This implies that the thermodynamics and kinetics of a series of reactions follow the same correlation. Although the use of the adjectives "hard" and "soft" may imply that polarizability is the most important factor in controlling the interaction of acids and bases, this is not so, and it has been repeatedly emphasized that it is necessary to consider all the properties listed in Table III to obtain a correlation.[19-23]

A four-parameter equation (eq 1) has been put forward for predicting the enthalpies of acid–base reactions (ΔH_{AB}) in either the gas phase or in poorly solvating solvents.[24-31]

$$-\Delta H_{AB} = E_A E_B + C_A C_B \qquad (1)$$

In this the acid and base are characterized by two independent parameters, E and C. E measures their ability to participate in electrostatic bonding and C their ability to participate in covalent bonding. The correlation is fairly successful for weak interactions in the gas phase and in nonpolar solvents where the enthalpy of interaction is 50 kcal·mol^{-1} or less but fails for strong interactions, interactions in polar solvents, and interactions between sterically demanding acids and bases. Since the latter two points are particularly important in the complexes of platinum metals with weak donor ligands, we shall not consider equation 1 further.

A molecular orbital approach to acid–base interactions starts by approximating the wave function for a given complex, ψ_{AB}, as

$$\psi_{AB} = a\psi_A + b\psi_B \qquad (2)$$

where ψ_A and ψ_B are the wave functions of the acid and base, respectively, and a and b reflect their relative importance. The actual degree of electron donation is indicated by the ratio a^2:b^2. When general perturbational molecular orbital theory is applied to such a system, the initial change in the energy (ΔE) of the

TABLE II: Classification of Acids in Their Normal Valence States as Class a, Borderline, or Class b

H																
Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	*Rh*	*Pd*	*Ag*	Cd	In	Sn	Sb	Te	I
Cs	Ba	La[a]	Hf	Ta	W	Re	Os	*Ir*	*Pt*	*Au*	*Hg*	Tl	Pb	Bi	Po	At
Fr	Ra	Ac[b]														

[a] All lanthanides. [b] All actinides. Class a acids: script; borderline acids: underlined; class b acids: italics.

TABLE III: Properties of Hard and Soft Species

soft species	hard species
1, high polarizability	low polarizability
2, large size	small size
3, easy to oxidize (bases)	hard to oxidize (bases)
4, easy to reduce (acids)	hard to reduce (acids)
5, low pK_a (bases)	high pK_a (bases)
6, low electronegativity difference between donor and acceptor atoms[a]	high electronegativity difference between donor and acceptor atoms[a]

[a] This refers to the electronegativities of the donor and acceptor sites as atoms (ref 15).

system upon incipient complex formation may be approximated by eq 3, where q_B = total net charge density

$$\Delta E = \frac{-q_B q_A}{r_{AB}\epsilon} + 2\sum_{m_B}\sum_{n_A}\frac{(C_B{}^m C_A{}^n \beta_{AB})^2}{(E_m{}^* - E_n{}^*)} \qquad (3)$$

at the donor atom, q_A = total net charge density at the acceptor atom, r_{AB} = distance between the donor and acceptor atoms, ϵ = dielectric constant of the solvent, $C_B{}^m$ = coefficient of the donor orbital m at the donor atom, $C_A{}^n$ = coefficient of the acceptor orbital n at the acceptor atom, β_{AB} = resonance integral between the donor and acceptor atoms at distance r_{AB}, $E_m{}^*$ = energy of the donor orbital m in the field of acid A corrected for any solvation or desolvation accompanying the removal of an electron from the orbital, $E_n{}^*$ = energy of the acceptor orbital n in the field of base B corrected for any solvation or desolvation accompanying the addition of an electron to the orbital and $\sum_{m_B}$ and $\sum_{n_A}$ represent summations over all the occupied orbitals m of species B and n of species A, respectively.[32-35] The first term in eq 3 is electrostatic and depends on the net charge densities and distance apart of the donor and acceptor atoms as well as the dielectric constant of the intervening medium. The second term represents the covalent interaction which depends on the overlap, symmetry, and energies of the donor and acceptor orbitals (m and n) as modified by the solvent in which the reaction is occurring.

Analysis of eq 3 shows that strong interactions should occur between acids that have large net positive charge densities at their acceptor sites and bases that have large net negative charge densities at their donor sites since these will maximize the first term in eq 3. Similarly the donor and acceptor orbitals should have the appropriate symmetries to ensure that the resonance integral in the second term is not zero and good overlap to maximize the value of β_{AB}. In addition the energies of the donor and acceptor orbitals should be similar in order to minimize the denominator in the second term. Since the properties that maximize the first term in eq 3 are mutually exclusive of those which maximize the second term, Klopman has suggested that donor–acceptor interactions can be divided into "charge controlled", which are dominated by the first term, and "orbital controlled", which are dominated by the second term.

The relative reactivities of acids can be compared by considering two acids A^1 and A^2 such that A^1 has a high net positive charge density at its acceptor atom and high-lying LUMO energy while A^2 has the opposite properties. If a series of bases B^1, B^2, and B^3 are considered such that the net negative electron density at their donor atoms is $B^1 > B^2 > B^3$ while the HOMO energy increases $B^1 < B^2 < B^3$, then because of its high-lying LUMO and high positive charge density the interaction of A^1 with these bases will be "charge controlled". Accordingly A^1 will give an apparent base strength order of $B^1 > B^2 > B^3$. However the interaction of A^2 which has a low positive charge density and a low-lying LUMO will be "orbital-controlled" depending particularly on the magnitude of the HOMO ($E_m{}^*$)–LUMO ($E_n{}^*$) gap. Thus the higher the energy of the base HOMO, the closer will it approach the energy of the acid LUMO and the greater will be the magnitude of the second term in eq 3. Hence A^2 will indicate a base strength order of $B^3 > B^2 > B^1$. A^1 and B^1 correspond to class a or hard acids and bases whereas A^2 and B^3 correspond to class b or soft acids and bases. These two situations are shown schematically in Figure 1. Thus eq 3 provides molecular orbital theory support for the qualitative HSAB theory.

So far we have considered only the situation in which an acid reacts with a single base. However in the case of metal complexes the acid reacts with several bases, and each acid–base interaction modifies the energies of

TABLE IV: Classification of Hard, Borderline, and Soft Acids and Bases[a]

hard	soft	borderline
	Acids	
H^+, Li^+, Na^+, K^+	Ag^+, Cu^+, Au^+, Ti^+, Hg^+	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+	Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}
Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}	$Co(CN)_5{}^{2-}$, Pt^{4+}, Te^{4+}, Tl^{3+}	Rh^{3+}, Ir^{3+}, $B(CH_3)_3$, SO_2, NO
N^{3+}, Cl^{3+}, Gd^{3+}, Lu^{3+}	$Tl(CH_3)_3$, BH_3, $Ga(CH_3)_3$, $GaCl_3$	Ru^{2+}, Os^{2+}, R_3C^+
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, CH_3Sn^{3+}	GaI_3, $LnCl_3$, RS^+, RSe^+, RTe^+	$C_6H_5{}^+$, GaH_3
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, U^{4+}, Pu^{4+}	I^+, Br^+, HO^+, RO^+	
Ce^{3+}, Hf^{4+}, WO^{4+}, Sn^{4+}	I_2, Br_2, ICN, etc.	
UO_2^{2+}, $(CH_3)_2Sn^{2+}$, VO^{2+}, MoO^{3+}	trinitrobenzene, etc.	
$BeMe_2$, BF_3, $B(OR)_3$, $Al(CH_3)_3$	chloranil, quinones, etc.	
$AlCl_3$, AlH_3, $RPO_2{}^+$, $ROPO_2{}^+$	tetracyanoethylene, etc.	
$RSO_2{}^+$, $ROSO_2{}^+$, SO_3	O, Cl, Br, I, N, $RO\cdot$, $RO_2\cdot$	
I^{7+}, I^{5+}, Cl^{7+}, Cr^{6+}, RCO^+, CO_2, NC^+	metal atoms, bulk metals	
HX (hydrogen bonding molecules)	CH_2, carbenes	
	Bases	
H_2O, OH^-, F^-	R_2S, RSH, RS^-	$C_6H_5NH_2$, C_5H_5N
$CH_3CO_2{}^-$, $PO_4{}^{3-}$, $SO_4{}^{2-}$	I^-, $\underline{S}CN^-$, $\underline{S}_2O_3{}^{2-}$	$N_3{}^-$, Br^-, $NO_2{}^-$, $SO_3{}^{2-}$
Cl^-, $CO_3{}^{2-}$, $ClO_4{}^-$, $NO_3{}^-$	R_3P, R_3As, $(RO)_3P$, CN^-	N_2
ROH, RO^-, R_2O, $S_2\underline{O}_3^{2-}$	RNC, CO, C_2H_4, C_6H_6	
NH_3, RNH_2, N_2H_4, $\underline{N}CS^-$	H^-, R^-	

[a] The underlined atom is the donor in cases where ambidentate coordination is possible.

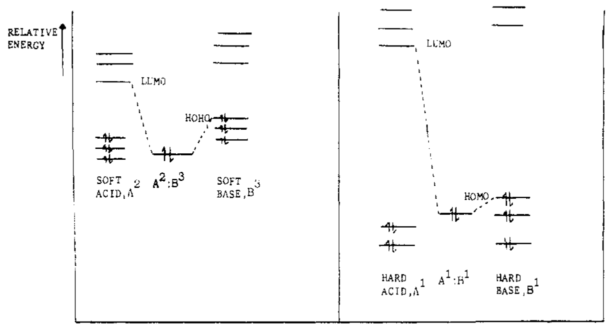


Figure 1. Initial orbital interactions of soft–soft and hard–hard systems.

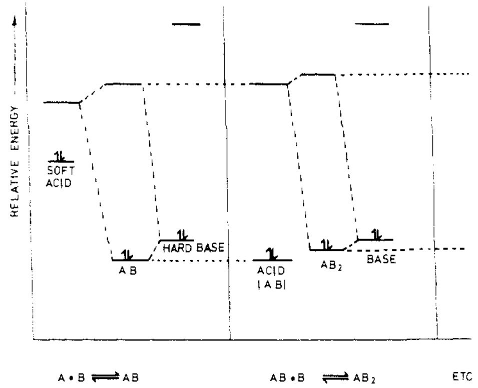


Figure 2. Interaction between the frontier oribtals of a hypothetical soft acid and a series of hypothetical hard bases.

the acid orbitals. Two extreme effects have been documented, symbiosis and antisymbiosis. In symbiosis[36] hard bases tend to retain their valence electrons when they coordinate to a given acid, thereby doing little to reduce the positive charge density on the acid and so keeping it hard. Soft bases, on the other hand, tend to give up their valence electrons to the acid, so reducing its positive charge density and so making it a softer Lewis acid. Thus in the stepwise formation of a soft metal–hard base complex, [A·B$_n$], the initial interaction of B and A results in an A·B complex whose frontier orbitals bear more resemblance to a hard species than a soft species. The addition of a second hard base unit to yield A·B$_2$ is thus more favored as the reaction is tending toward a hard–hard interaction. This situation is described diagramatically in Figure 2. The process whereby the presence of a base alters an acid's acceptor characteristics to facilitate addition of further similar base units has been termed symbiosis.[36] The occurrence of, for example, [PdL$_4$]$^{n+}$ (L = hard ligand) would be expected to be more common than [PdL$_3$L′]$^{n+}$ (L′ = soft ligand, L = hard ligand), and this is borne out in practice (vide infra).

While many metal ions show symbiotic behavior, many soft metal ions behave in an antisymbiotic manner[37] in which the coordination of a soft base to an already soft Lewis acid lowers the affinity of the site trans to that soft base for another soft base. This is particularly true of the soft platinum group metals. The principle of antisymbiosis may be summarized by the statement that "two soft ligands in mutually trans positions will have a destabilizing effect on each other when attached to a soft metal atom". Antisymbiosis arises because two mutually trans soft ligands compete with each other for the same metal orbitals; it therefore does not matter whether they are purely σ donors or σ donors as well as π acceptors. Since the phenomenon of antisymbiosis operates through the metal orbitals, it applies to "orbital-controlled" interactions. It is thus particularly important in the case of soft acids such as the platinum metal ions and unknown in "charge-controlled" complexes.

TABLE V: Properties of Palladium(II) and Platinum(II) as Soft Acids

	palladium(II)[a]	platinum(II)[b]
covalent radius,[c] Å	1.31	1.31
optical electronegativity[c]	2.2	2.3
oxidation potential,[c] V ($M \rightleftharpoons M^{2+} + 2e^-$)	−0.92	−1.2
ionization potentials,[c] eV		
$M^0 \to M^+$	8.33	9.0
$M^+ \to M^{2+}$	19.42	18.65
$M^{2+} \to M^{3+}$	39.92	28.5
$M^{3+} \to M^{4+}$	48.8	41.1

[a] Oxidation states up to +4 are known. [b] Oxidation states up to +6 are known. [c] Data from ref 43a.

Since the order of decreasing softness of ligands is R$^-$, H$^-$ > *S*CN$^-$ > PR$_3$ > *N*CS$^-$ > X$^-$, it is readily seen that antisymbiosis can explain the observations that virtually all platinum(II) dialkyl complexes have cis structures,[38] platinum(IV) trialkyl complexes have *fac* structures,[38] and the hard N-bonded thiocyanate in [Pd(Ph$_2$PCH$_2$CH$_2$CH$_2$NMe$_2$)(NCS)(SCN)] is trans to the softer phosphorus while the soft S-bonded thiocyanate is trans to the harder nitrogen of the bidentate ligand.[39] The importance of the trans effect in promoting antisymbiotic behavior is well illustrated by the fact that *trans*-[Pt(pyr)$_2$(CH$_3$)Cl] shows strong antisymbiotic behavior whereas *trans*-[Pt(PPh$_3$)$_2$Cl$_2$] reacts very slowly with hard bases and very rapidly with soft bases compared to *trans*-[Pt(pyr)$_2$Cl$_2$].[40] Fuller discussions of complexes stabilized by antisymbiosis are available elsewhere.[41,42]

In conclusion, the bonding scheme outlined above, with its simple molecular orbital rationale, provides a useful model for understanding weak metal–ligand interactions in the context of their chemical reactivity.

III. Complexes of the Platinum Metals Containing Weak Donor Ligands

In order to generate complexes of the platinum metals containing weak donor ligands, it is necessary to consider the properties of the metal ions in their desired oxidation state and compare them with the properties listed in Table III. A direct comparison of these properties for palladium(II) and platinum(II), shown in Table V, illustrates that both may be considered as typical soft acids. A similar situation exists for the other platinum metals in their low oxidation states. It would therefore be envisaged that interactions between a low-valent platinum metal ion and a hard base would be unfavorable and result in a weak bonding situation unless that interaction were to take place trans to a high trans-effect ligand, in which case the antisymbiotic effect would promote interaction. Examination of the series of hard bases (Table IV) shows that those bases which are uncharged (and hence relatively weak) are generally compounds which are used as solvents in coordination chemistry (e.g., H$_2$O, ROH, R$_2$O). (Such weak solvent–solute interactions are desirable if the system is to be used as a reaction medium. The

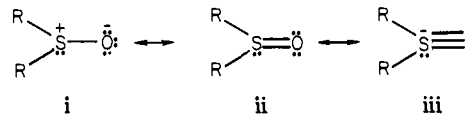


Figure 3. Canonical forms of simple sulfoxides of type R_2SO.

coordination chemistry of, for example, platinum(II), using a liquid phosphine solvent, would obviously be extremely limited.) It would thus be expected that any interaction between a low-valent platinum metal ion and a solvent molecule (resulting in a so-called "solvento complex")[44,45] would be weak. In this section we consider the chemistry of platinum metal complexes containing either coordinated solvent molecules or coordinated "noncoordinating" anions. Emphasis is placed on the chemistry resulting from the weak metal–ligand interaction; this section is not intended to be an exhaustive review in other respects.

A. Sulfoxide Complexes (Particularly Dimethyl Sulfoxide)

The coordination chemistry of sulfoxides is a much studied topic.[46,47] Sulfoxides are known to exhibit ambidentate donor ability, coordinating to specific metal ions via either oxygen or sulfur. Interest in sulfoxide complexes is far from academic, as dimethyl sulfoxide is among the most effective aprotic solvents known,[48,49] while the higher sulfoxides have found application in the extraction of metals during refining processes; indeed, some potential in the separation of platinum metals has been noted.[50]

In terms of explaining the ambidentate donor ability of sulfoxides, it is particularly unfortunate that the simple sulfoxides, R_2SO, may be represented as a resonance hybrid of three canonical forms as in Figure 3. The corollary of this is that it has been implied[47] that O-bonding is a result of a dominant contribution of form i and S-bonding a result of a dominant contribution of form iii. A compilation of the available physical data of Me_2SO and its transition-metal complexes[46] shows that this is not so and that form i makes a dominant contribution to the resonance hybrid in both the free molecule and its O-bonded complexes while form ii makes a dominant contribution in S-bonding. It seems likely that O-bonding results from electron donation from an sp^2 hybrid orbital on oxygen and that S-bonding involves donation from an sp^3 orbital on sulfur.[46] It is generally observed that sulfoxides coordinate to hard metals via oxygen and to soft metals via sulfur,[46,47] exactly as expected in terms of the HSAB principle. The simple resonance-hybrid explanation of ambidentate coordination is really the only model available, as attempts to account for this by semiempirical electronic structure calculations[51] have been shown to be unsatisfactory.[46]

The effects of O- and S-bonding on the x-ray absorption,[52] infrared,[46,47] and nuclear magnetic resonance spectra[47] of sulfoxide complexes have been well documented and often permit differentiation between the two modes of bonding. Recently, electron spectroscopy for chemical analysis (ESCA) has been applied to the study of ambidentate coordination in sulfoxide complexes[53] and, although comparative data are scarce, appears to be able to determine whether coordination is through O or S. Application of this variety of techniques to the complexes $[Pd(Me_2SO)_2Cl_2]$, $[Pd(Me_2SO)_4][BF_4]_2$, and [Pd(diisoamyl sulfoxide)$_4$][BF_4]$_2$[53-56] shows that the bis(sulfoxide) complex contains S-bonded sulfoxides, the tetrakis(dimethyl sulfoxide) complex contains both O- and S-bonded sulfoxides, and the tetrakis(diisoamyl sulfoxide) complex contains all O-bonded sulfoxide ligands. As S-bonding is expected in sulfoxide complexes of the soft-metal palladium(II), the observation of O-bonding in the tetrakis(diisoamyl sulfoxide) complex is ascribed to the high degree of steric overcrowding present. However, steric effects are not the sole cause of palladium–oxygen bonding in sulfoxide complexes. If they were, then $[Pd(Me_2SO)_4]^{2+}$ would be *trans*-$[Pd(OSMe_2)_2\{S(O)Me_2\}_2]^{2+}$ whereas in fact it exists in the cis configuration, *cis*-$[Pd(OSMe_2)_2\{S(O)Me_2\}_2]^{2+}$.[55,56] This configuration is exactly that predicted by antisymbiosis as a consequence of the electronic factors responsible for the trans influence. Each soft sulfur donor which has a modest trans influence comparable to that of ethylene[57] is trans to a hard oxygen donor. The observation of oxygen-bonded dimethyl sulfoxide in both $[Pd(Ph_2PCH_2CH_2PPh_2)(Me_2SO)Cl][ClO_4]$ and $[Pd(Ph_2PCH_2CH_2PPh_2)(Me_2SO)_2][ClO_4]_2$ is expected on both steric and electronic (antisymbiosis) grounds.[58] The contribution of the high trans influence of the diphosphine ligand to the stability of these complexes is difficult to estimate unambiguously as the bis(*O*-Me_2SO) complex is very stable while the mono(*O*-Me_2SO) complex is exceedingly reactive, undergoing deoxygenation of the sulfoxide to the corresponding thioether and dimerization to a binuclear dication.[58] $[Pd(Ph_2PCH_2CH_2PPh_2)(Me_2SO)_2[ClO_4]_2$ is of particular interest as similar complexes of the type [Pd(diphosphine)(solvent)$_2$]$^{2+}$ are known to be active catalysts for a variety of reactions[59] (vide infra). Other platinum metal complexes containing O-bonded sulfoxide ligands have been reported, including $[Ru(Me_2SO)_4Cl_2]$ (S,S,S,O),[61] $[Rh(Me_2SO)_5Cl]^{2+}$ (S,S,O,O,O),[61] $[Rh(Me_2SO)_3Cl_3]$ (S,S,O),[62] $[Rh(\eta^5\text{-}C_5Me_5)(Me_2SO)_3]^{2+}$ (O,O,O), and $[Ir(\eta^5\text{-}C_5Me_5)(Me_2SO)_3]^{2+}$ (O and S).[63] Sulfoxide complexes of the transition metals are currently being developed as homogeneous catalysts for a variety of organic transformations, including the hydrogenation, hydroformylation, and oligomerization of olefins.[46] Attempts to exploit the weak bonding in *O*-R_2SO complexes of the platinum metals are as yet in their infancy and will no doubt prove fruitful areas for future research.

B. Amide Complexes (Particularly Dimethylformamide)

Dimethylformamide (DMF) is a much used organic solvent[64] whose interaction with metal ions has been little studied. Examination of the orbital energy diagram of DMF (Figure 4) shows two possible donor orbitals available for coordination to a metal ion: the nonbonding σ orbital associated largely with nitrogen and either the nonbonding σ orbital associated largely with oxygen or the π(C=O) orbital, depending upon their relative energies. Bonding through nitrogen is virtually unknown in transition-metal–DMF complexes, and it has been postulated that coordination via oxygen is more favored due to steric hindrance at the substituted nitrogen atom.[65] Infrared studies[66] on the com-

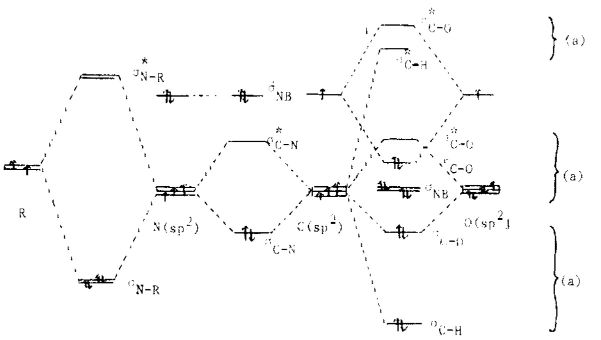


Figure 4. Oribtal diagram for amides of type R_2NCHO. Relative energies of orbitals marked (a) are uncertain.

plexes $[M(CO)_5L]$ and *cis*-$[M(CO)_4L_2]$ (M = Cr, Mo, W; L = P(III) or N(III) donor, alcohol, amide, or ether donor) have shown that ν(CO) of the carbonyl ligands occurs at lower frequency for L = DMF than for L = amine, alcohol, or ether. As amine, alcohol, and ether ligands have no π-acceptor capabilities, the lowering in ν(CO) for L = DMF suggests that DMF is acting as a π donor. The effect of coordination on the stretching frequency of the carbonyl group in DMF (the "amide 1" band) also suggests π donation is occurring. Shifts to lower frequency for the amide 1 band of 40–70 cm^{-1} have been reported for the complexes $[Cr(RCONR'R'')_3Cl_3]$ (R = H, alkyl; R′, R″ = Me, Ph)[65] and of 85 cm^{-1} for the complex $[Pd(DMF)_2Cl_2]$.[67] The evidence that DMF utilizes the π(C=O) orbital in coordination to metal ions implies that π(C=O) is the HOMO and its energy, relative to the nonbonding σ orbital associated with oxygen, is as shown in Figure 4.

Coordination of DMF to low-valent platinum metal ions would thus be expected to result in a weak bonding situation, and this has been exploited in the preparation of π-allylpalladium(II) complexes from the interaction of olefins and $[Pd(DMF)_2Cl_2]$.[68] The proton basicity of DMF (whereby the $[(DMF)_2H]^+$ cation is formed) coupled with its lability in these complexe makes it a most suitable ligand for such reactions. The lability of DMF coordinated to palladium(II) is demonstrated by the facile conversion of $[Pd(Ph_2PCH_2CH_2PPh_2)(DMF)Cl]^+$ to the dimeric complex $[Pd_2(Ph_2PCH_2CH_2PPh_2)_2Cl_2]^{2+}$, with concomitant elimination of DMF.[69] The lability of DMF when coordinated to a soft metal center may well be one reason for the catalytic activity of certain DMF complexes, such as the isolable $[Ru(PPh_3)_2(CO)(DMF)Cl_2]$ complex which catalyzes the hydrogenation of 1-alkenes under ambient conditions.[1a] Similarly, solutions of $[RuCl_3]$ and $[PdCl_2]$ in DMF are active hydrogenation catalysts.[70] The complex $[Pd(Ph_2PCH_2CH_2PPh_2)(DMF)Cl]^+$ shows limited ability as a hydrogenation catalyst under ambient conditions,[59] but as palladium(II) complexes are generally ineffective in this respect,[1b] even the limited ability of this complex is worthy of note.

C. Pyridine Complexes

Many reactions in which platinum metal complexes act as catalysts proceed via an oxidative addition of a small molecule to the metal center (e.g., Pt(II) $d^8 \rightarrow$ Pt(IV) d^6) followed by a reductive elimination step.[71,72] Pyridine is one of few coordinating solvents which allows isolation of such metal complexes in their elevated oxidation states. The very fact that such complexes are isolable suggests that any oxidative-addition/reductive-elimination cycle will be precluded and that pyridine complexes of the platinum metals will be of limited use catalytically. Thus, although the complex $[Rh(pyr)_2(DMF)Cl_2(BH_4)]$ is an active hydrogenation catalyst,[1c] a direct comparison of the ability of $[Pd(Ph_2PCH_2CH_2PPh_2)(solvent)Cl]^+$ species to hydrogenate styrene shows limited ability for solvent = DMF and no ability for solvent = pyridine.[59] Nevertheless, as models for complexes which do not allow isolation of the Pt(IV)–solvent species, or equivalent, pyridine complexes are of interest. Due to the availability of the π system of the aromatic ring, metal–pyridine bonding is believed to consist of both σ and π components.[43b] In consequence, pyridine exhibits some properties more typical of P(III) donors in its complexes, such as the stabilization of metal–carbon σ bonds[73] and Pt(IV) species. Pyridine has been classified as a borderline base, and this is in agreement with its observed reactions with platinum(II) olefin complexes[74] of the type $[Pt(olefin)_2R_2]$ where the olefin is displaced to yield $[Pt(pyr)_2R_2]$. The displacement of weakly bound organic substrates from the metal center and the stabilization of elevated oxidation states, such as Pt(IV), make pyridine too strong a ligand to promote catalytic activity but a useful model for ligands with lesser coordinating ability.

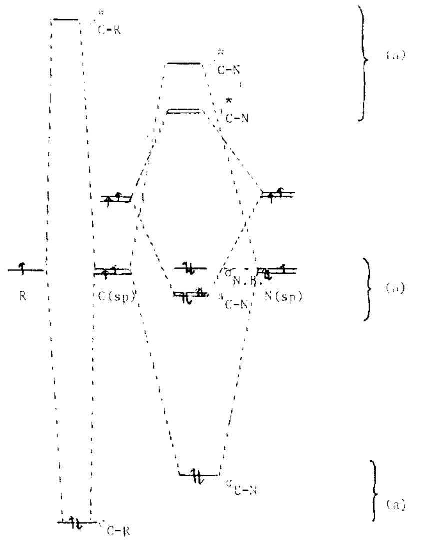


Figure 5. Oribtal diagram for organonitriles of type RC≡N. Relative energies of orbitals marked (a) are uncertain.

D. Organonitrile Complexes

Organonitrile complexes have received considerable attention[75,76] as the RC≡N ligand is isoelectronic with molecular nitrogen. Additionally such complexes have shown utility as precursors in the preparation of a wide range of coordination compounds.[76] Organonitriles have two potential coordination sites (see Figure 5), namely the nonbonding σ orbital associated largely with nitrogen (σ-bonded nitriles) and the π orbitals of the C≡N bond (π-bonded nitriles). The vast majority of fully characterized nitrile complexes are of the former type, and the latter mode of coordination has rarely been definitely established.[76] X-ray crystallography has shown that the M–N–C angle is approximately 180°, demonstrating linear coordination, in most cases.[76] Preliminary studies on the complex $[Pt(PPh_3)_2$-

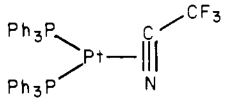


Figure 6. Geometry of the π-bonded organonitrile complex $[Pt(PPh_3)_3(NCCF_3)]$.

$(NCCF_3)]$[77] show this to be the first π-bonded nitrile complex. The geometry is shown in Figure 6. Errors in assigning the infrared spectra of organonitrile complexes have arisen[78] due to the value of $\Delta\nu(C{\equiv}N)$ ($\Delta\nu(C{\equiv}N) = \nu$(coordinated nitrile) − ν(free nitrile)) being positive or negative, essentially because of varying degrees of π-back-bonding from different metal centers, and this has led to claims of π-bonded nitrile complexes which have not been confirmed by Raman and other studies.[79-81] In reality, crystallographic data are necessary to unambiguously characterize organonitrile complexes, but the assumption made here, that the base HOMO is the donor orbital, suggests that unless symmetry and steric constraints are dominant, then σ bonding will occur, and this is indeed observed. The most prominent feature of the chemistry of organonitrile complexes of the platinum metals is the ease of replacement of the nitrile ligand. This is even observed for complexes of the softer "borderline" metals, such as Mo(0). Thus, olefin complexes of palladium(II) and molybdenum(0) can be prepared by substitution reactions using $[Pd(NCCH_3)_2Cl_2]$[82] and $[Mo(NCCH_3)_3(CO)_3]$.[83,84] The utility of such complexes as precursors is demonstrated by the displacement of acetonitrile from *trans*-$[Pd(PPh_3)_2(CNCH_3)(NCCH_3)]^{2+}$ by Me_3N, pyridine, PPh_3, PEt_3, $P(OMe)_3$, SMe_2, MeNC, I^-, Cl^-, CN^-, N_3^-, NO_2^- and OH^-.[85] The use of nitrile complexes in homogeneous catalysis has met with mixed results and is discussed further below.

E. Complexes of Oxygen-Donor Ligands

Those complexes of the platinum metals which have been isolated containing neutral oxygen donors either have several hard donors coordinated to the metal center which through the symbiotic effect[36] have altered the metal center's acceptor characteristics to enable hard base coordination or alternatively have the oxygen donor trans to a ligand of high trans effect such as hydride, alkyl, or aryl ligands where the antisymbiotic effect[37] promotes coordination. The high reactivity of mixed hard ligand–soft ligand complexes of soft metals, especially those which are *not* stabilized by high trans-influence donors, makes them potential intermediates with application in many areas of inorganic chemistry. Details of such complexes are given below.

1. Aquo Complexes

Multiple hard base complexes of the platinum metals are relatively common; for example, $[M(H_2O)_4]^{2+}$ (M = Pd, Pt),[86] $[M(dien)(H_2O)]^{2+}$ (M = Pd, Pt),[44,87,88] and other similar complexes are well-known. In addition, aquo complexes in which the aquo ligand is bound trans to a soft ligand such as ethylene are also well-known.[89] However, hydroxy complexes are often formed in situations where aquo complexes might have been the expected product. For example, reaction of $[M(PR_3)_2Cl_2]$ (M = Pd, Pt, R = Et, Ph) with 2 equivs of silver(I) tetrafluoroborate in "moist" acetone (ca. 0.5% water) yields not the aquo complex $[M(PR_3)_2(H_2O)_2][BF_4]_2$ but the dimeric hydroxy-bridged product $[M_2(PR_3)_4(OH)_2][BF_4]_2$.[90] This product also results from halide abstraction from $[M(PEt_3)_2(PPh_3)(Cl)][BF_4]$ with concomitant elimination of triphenylphosphine.[90] Investigations into the activation of water by platinum(0) complexes have shown that hydroxy complexes may be formed by oxidative addition of water[91,92] (reaction 4).

$$[Pt(P\text{-}i\text{-}Pr_3)_2] + H_2O \rightleftharpoons$$

$$[Pt(P\text{-}i\text{-}Pr_3)_2(H)(OH)] \xrightleftharpoons{pyr}$$

$$[Pt(P\text{-}i\text{-}Pr_3)_2(H)(pyr)][OH] \xrightleftharpoons{BF_4^-}$$

$$[Pt(P\text{-}i\text{-}Pr_3)_2(H)(pyr)][BF_4] \quad (4)$$

Such reactions may have some bearing on the formation of platinum(II) hydroxy complexes via an oxidative-addition/reductive-elimination mechanism (Pt(II) → Pt(IV) → Pt(II)).

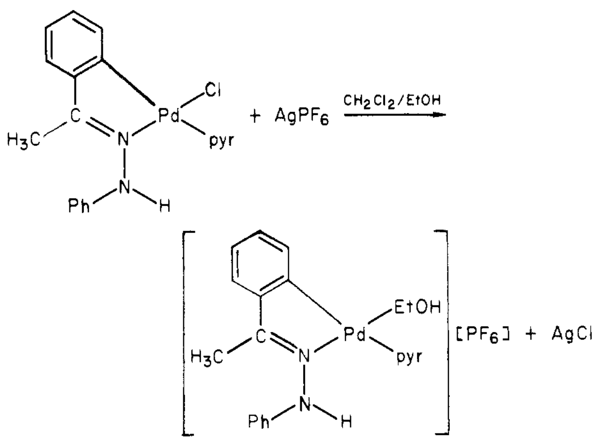
2. Alcohol Complexes

Alcohol and alkoxy complexes of soft metals are of interest as likely intermediates in the oxidation of alcohols to carbonyl compounds. For example, in the reaction with palladium chloride[93,94] (reaction 5), either

$$2RCH_2OH + PdCl_2 \rightarrow 2RCHO + Pd_M + 2HCl \quad (5)$$

alcohol or alkoxy complexes may be intermediates. Kinetic studies[95] show straight-chain alcohols (MeOH, EtOH) form significant amounts of platinum(II)–alcohol complexes in solution whereas branched alcohols such as *t*-BuOH do not.[43c] Alternatively, experiments have been performed to trap reactive alkoxy species, with some success. Reaction of sulfur dioxide with a solution of palladium(II) chloride in MeOH or EtOH allows isolation of the corresponding sulfinato complex as the tetraphenylarsonium salt.[93] Analogues can be prepared from palladium(II) phosphine complexes by similar reactions.[94] Interestingly, unstable alkoxy complexes have been proposed as intermediates in the reaction of alcohols with $[Pt(PR_3)_2]$ complexes,[95] via an oxidative addition reaction, similar to eq 2. Alkoxy complexes are also believed to be intermediates in the reduction of $[PtCl_2(PR_3)_2]$ complexes with alcoholic potassium hydroxide to yield the corresponding hydridochlorides.[96] Dinuclear platinum(II) complexes containing bridging methoxy groups have been reported, although their chemistry is yet to be explored[97] The recent interest in complexes of soft metals containing very weak ligands has led to attempts to isolate complexes of type $[M(\eta^5\text{-arene})(solvent)_3]^{2+}$ (M = Rh, Ir; η^5-arene = C_5H_5, C_5Me_5); isolable complexes have been obtained for solvent = Me_2SO, pyridine, and acetonitrile, but could only be generated in situ for solvent = methanol.[98-101] Similarly the complex *trans*-$[Pt(PPhMe_2)_2(Me)(MeOH)][PF_6]$ could be generated in situ, but decomposed when isolated as a solid.[102] *trans*-$[Pt(PEt_3)_2H(MeOH)]^+$, an olefin hydrogenation catalyst, has been identified in solution but not isolated.[103,104] A palladium(II)–ethanol complex has been isolated via a halide abstraction reaction[45] (reaction 6).

No analogous complexes containing P(III) donors are known, and it is of interest to note that the reactions of *trans*-$[Pt(PPh_3)_2(H)Cl]$ and [Pd-



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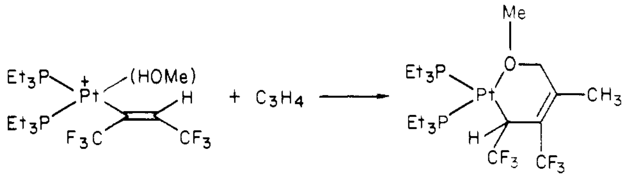
$(\mathrm{Ph_2PCH_2CH_2PPh_2})\mathrm{Cl_2}]$ with silver perchlorate in the presence of methanol allow the coordinated perchlorate complexes *trans*-$[\mathrm{Pt(PPh_3)_2(H)(OClO_3)}]$ and $[\mathrm{Pd(Ph_2PCH_2CH_2PPh_2)(OClO_3)_2}]$ rather than the methanol complexes to be isolated.[105,106] $\mathrm{Pd(Ph_2PCH_2CH_2PPh_2)(MeOH)_2}]^{2+}$ is, however, stable in solution[106] and is an active catalyst for the methanolysis of silanes.[59]

3. Ether Complexes

Ether complexes of platinum metals in their lower oxidation states are extremely scarce. The palladium(II) complex analogous to the ethanol complexes prepared in eq 6 has been isolated with coordinated diethyl ether.[45] $[\mathrm{Pd(Ph_2PCH_2CH_2PPh_2)(THF)_2}](\mathrm{ClO_4})_2$ is stable in solution, but on attempted isolation the tetrahydrofuran is displaced and $[\mathrm{Pd(Ph_2PCH_2CH_2PPh_2)(OClO_3)_2}]$ is isolated.[106] Ether complexes are typically merely generated in situ as intermediates.[107,108] One platinum(II)–ether complex has been isolated and studied by X-ray crystallography.[107] The complex is a product formed by the reaction of allene with the methanol complex $[\mathrm{Pt(PEt_3)_2(F_3CC{=}C(H)CF_3)(MeOH)}]^+$. Interestingly, the analogous acetone cation reacts quite differently[110] (eq 7 and 8). The mechanism of eq 7 is unknown; eq 8 represents the simple insertion of allene into a Pt–C σ bond, promoted by the easily displaced solvento ligand. Complexes of type 1 represent a possible route for the development of the chemistry of weakly bonded complexes. Here, the solvento group is "built in" to the molecule, enabling facile displacement by unsaturates while maintaining the coordinating group in the vicinity of the metal center. The application of such complexes in homogeneous catalysis is as yet unexplored.



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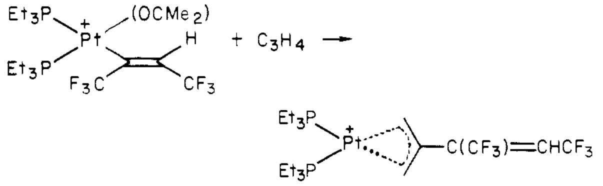

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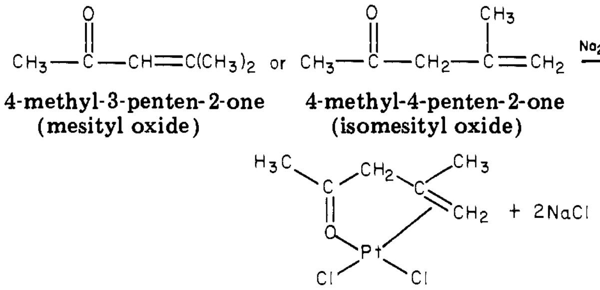
4. Ketone Complexes

Many attempts to prepare ketone complexes of low-valent platinum metals have been unsuccessful as water can compete with acetone as a ligand for these metals. As mentioned previously, hydroxy-bridged dimers have been prepared from a halide abstraction reaction of $[\mathrm{M(PR_3)_2Cl_2}]$ in moist acetone;[100] similarly the aquo complex $[\mathrm{Pd(dien)(H_2O)}]^{2+}$ resulted from halide abstraction from the corresponding iodo complex in acetone which had been dried.[48] Acetone complexes such as $[\mathrm{M}(\eta^5\text{-arene})(\mathrm{Me_2CO})_3]^{2+}$ (M = Rh, Ir; η^5-arene = $\mathrm{C_5H_5}$, $\mathrm{C_5Me_5}$),[98–101] *trans*-$[\mathrm{Pt(PR_3)_2H(Me_2CO)}]^+$ ($\mathrm{R_3}$ = $\mathrm{Et_3}$, $\mathrm{Ph_2Me}$),[111–113] $[\mathrm{Pt(diars)Me(Me_2CO)}]^+$[114] and other similar complexes have been prepared in situ but have not been obtained as analytically pure solids. Chloride abstraction from $[\mathrm{Pd(Ph_2PCH_2CH_2PPh_2)Cl_2}]$ with silver perchlorate in rigorously dried acetone has enabled the extremely moisture-sensitive bis(acetone) complex $[\mathrm{Pd(Ph_2PCH_2CH_2PPh_2)(Me_2CO)_2}](\mathrm{ClO_4})_2$ to be isolated and characterized.[115] In the infrared it shows a sharp C=O stretching vibration at 1666 $\mathrm{cm^{-1}}$. It must, however, be handled with extreme care because on heating it loses acetone readily to yield the potentially explosive $[\mathrm{Pd(Ph_2PCH_2CH_2PPh_2)(OClO_3)_2}]$. On exposure to moisture, even damp air, the acetone ligands in $[\mathrm{Pd(Ph_2PCH_2CH_2PPh_2)(Me_2CO)_2}](\mathrm{ClO_4})_2$ are replaced by water.[106] $[\mathrm{Pd(Ph_2PCH_2CH_2PPh_2)(Me_2CO)_2}]^{2+}$ is active in promoting such diverse reactions as the hydrogenation of olefins and the hydrolysis of silanes.[59]

Acetone complexes are of particular interest as certain unusual rearrangements have been observed. This stems primarily from the observation that the reaction of 4-methyl-3-penten-2-one or 4-methyl-4-penten-2-one with sodium tetrachloroplatinate yields the same complex and that this complex can also be obtained by the reaction of platinum tetrachloride with dry acetone[115] (reactions 9 and 10). The mechanism of these reactions is unclear, although an aquo complex is presumably another product of eq 9. It should be noted that some drying techniques actually enhance the quantities of mesityl oxide and isomesityl oxide present as impurities in acetone,[106] and this may have some bearing on these results. A similar rearrangement of acetone ligands has been reported[116] for the complex $[\mathrm{Ru}(\eta^6\text{-}\mathrm{C_6H_3Me_3})(\mathrm{Me_2CO})_3][\mathrm{BF_4}]_2$, which could not be isolated as an analytically pure solid, yielding the complex $[\mathrm{Ru}(\eta^6\text{-}\mathrm{C_6H_3Me_3})(\mathrm{Me_2CO})(\mathrm{MeC\{OH\}CH_2COMe})][\mathrm{BF_4}]_2$ which was characterized by single-crystal X-ray analysis.



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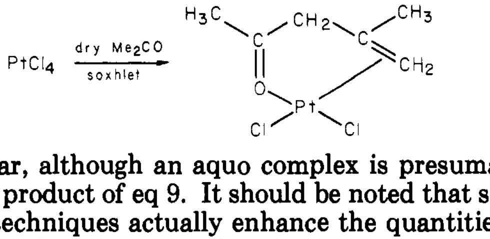

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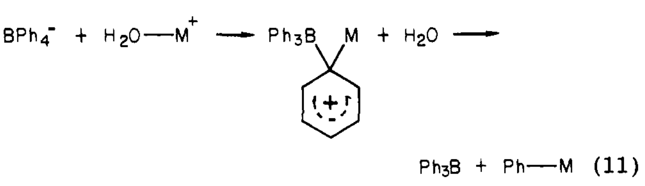
These novel template reactions could be of great synthetic value if the range of substrates can be increased.

F. Coordination of Classically "Noncoordinating" Anions

The classically noncoordinating anions (ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, BPh_4^-, etc.) are all highly symmetrical species whose ability to coordinate to soft metals is extremely limited. The high symmetry of these species is frequently lowered upon coordination to a metal center, and thus the infrared spectra of these species can often differentiate between the coordinated and uncoordinated structures. For example, the ClO_4^- anion is tetrahedral, and monodentate attachment to a metal center ($-OClO_3$) lowers the symmetry to C_{3v}.[117-120] Infrared spectroscopy easily differentiates these structures.[119,120] Coordinated perchlorate complexes of Rh(I), Ir(I), Pd(II), Pt(II), and Au(I)[121-125] have been prepared by the reaction of halo complexes with silver perchlorate in dry, noncoordinating solvents such as benzene. These preparations are notoriously hazardous as both solutions of silver perchlorate in benzene[125] and the complexes obtained[122-125] are reported to be dangerously explosive. The real utility of these complexes is in substitution reactions, a great variety of which have been reported for Rh(I),[125] Ir(I),[125] Pd(II),[121] Pt(II),[122] and Au(I)[126] perchlorate complexes.

Coordination of tetrafluoroborate has been postulated in reaction schemes for the interaction of palladium(II) and platinum(II) halo complexes and silver tetrafluoroborate in acetone solution.[127] The properties of these products are equally in accord with the formation of an acetone complex, for which analogues are known (vide supra). Anion coordination (NO_3^-, BF_4^-, PF_6^-) is well-known from spectroscopic[128] and other studies[129] of main-group organometallic compounds; indeed, it seems likely that *free* organometallic cations of main group metals exist neither in the solid state nor in solution.[129] The situation for low-valent platinum metals is, of course, very different, and apart from the few coordinated perchlorato complexes mentioned, genuine examples of coordinated complexes of "noncoordinating" anions are extremely scarce. The normally inert hexafluorophosphate anion has been shown to be subject to hydrolysis in situations where, due to the presence of weak donor ligands, there is little competition for a coordination site on a metal center. Thus, partial hydrolysis[116] of the complex $[Ru(\eta^6\text{-arene})(Me_2CO)_3][PF_6]_2$ yields the tri-μ-difluorophosphato complex $[Ru_2(\eta^6\text{-arene})_2(\mu\text{-}PO_2F_2)_3]$ (η^6-arene = C_6Me_6, $C_6H_3Me_3$). Similar reactions[98-101] have been observed for $[Rh(\eta^5\text{-}C_5Me_5)(Me_2CO)_3][PF_6]_2$, and the reaction of $[Mn(CO)_5Cl]$ with $AgPF_6$ is reported[130] to give the complex $[Mn(PO_2F_2)(CO)_5]$. The tetraphenylborate anion is also subject to decomposition when there is little competition for a vacant coordination site on a metal center and dephenylation reactions have been observed.[44,131-134] These reactions may be a parallel of the decomposition of the tetraphenylborate anion in acidic media[135] (reaction 11).



M = H,[135] $[Pd(dien)]^+$ [44]

Tetraphenylborate coordination is known for Rh(I), Ir(I), and Ru(II)[136-139] where some interaction between the metal center and the π orbitals of one phenyl ring has been proposed. Crystallographic studies[136,139] have confirmed this and shown that the geometry of the coordinated phenyl ring is perturbed by the interaction with the metal center.

It is thus evident that the correct choice of noncoordinating anion is of extreme importance in the preparation of weakly bonded complexes of the platinum metals, where competition for a coordination site on the metal center is poor, if such reactions as the hydrolysis of hexafluorophosphate anions or the dephenylation of tetraphenylborate anions are to be avoided.

IV. Preparative Techniques

A. Oxidation Methods Using Nitrosonium Salts

Certain metals can be oxidized by [NOX] (X = ClO_4, BF_4) to yield complexes containing coordinated solvent molecules of type $[M(solvent)_4][X]_2$ (reaction 12; M =

$$M + 2NOX \xrightarrow{\text{solvent}} [M(solvent)_4][X]_2 + \uparrow 2NO \quad (12)$$

Pd, solvent = MeCN, X = BF_4;[140] M = Cu, solvent = MeCN, $MeNO_2$; X = ClO_4).[141] Oxidation of metal(0) complexes has also been accomplished; for example, $[Pt(PPh_3)_2(C_2H_4)]$ reacts with $[NOBF_4]$ in acetonitrile to yield the complex $[Pt(PPh_3)_2(CH_3CN)_2][BF_4]_2$.[142] Similar oxidations of Rh(I)- to Rh(III)-acetonitrile complexes are known.[143] The inherent disadvantages of this method are the lengthy reaction time required for the two-phase oxidation of metals and the extreme sensitivity of the nitrosonium cation to water, which can lead to extensive byproduct formation.[142]

B. Halide Abstractions Reactions

Many examples of this technique have already been described, and silver(I) salts are particularly useful for this method due to the very limited solubility of silver halides in most organic solvents.[144] Additionally, thallium(I) salts as well as the complex $[Cu(MeCN)_4][BF_4]$ have been used as abstraction agents[145,146] (reaction 13). Nitrosonium salts also react

$$^1/_2[Rh_2(C_2H_4)_2Cl_2] + [Cu(MeCN)_4][BF_4] \rightarrow [Rh(C_2H_4)_3(MeCN)_2][BF_4] + CuCl + 2MeCN \quad (13)$$

with halo complexes in the presence of certain coordinating solvents to yield the corresponding solvento complex with concomitant evolution of the nitrosyl halide[147] (reaction 14).

$$[(\pi\text{-}C_5H_5)Fe(CO)_2I] + NOPF_6 \xrightarrow{MeCN} [(\pi\text{-}C_5H_5)Fe(CO)_2(MeCN)][PF_6] + NOI \quad (14)$$

C. Ligand Displacement by Hydrogenation

The unsaturated ligands of certain Rh(I) complexes are sensitive to hydrogenation, and ligand displacement may result. By use of this method, complexes containing coordinated tetraphenylborate ligands[138] and coordinated solvent molecules[148–151] have been prepared (reactions 15–17). In reaction 16, diene = 1,3-buta-

$$[\mathrm{Rh}(o\text{-}\mathrm{CH_2{=}CHC_6H_4PPh_2})_2]^+ \xrightarrow{\mathrm{H_2}} [\mathrm{Rh}(\eta^6\text{-}\mathrm{C_6H_5BPh_3})(o\text{-}\mathrm{CH_2{=}CHC_6H_4PPh_2})] + o\text{-}\mathrm{C_2H_5C_6H_4PPh_2} \quad (15)$$

$$[\mathrm{Rh(Ph_2P\{CH_2\}_3PPh_2)(diene)}]^+ + 2\mathrm{H_2} \xrightarrow[\mathrm{(S{=}Me_2CO,MeOH)}]{\mathrm{S}} [\mathrm{Rh(Ph_2P\{CH_2\}_3PPh_2)(S)_2}]^+ + \text{alkane} \quad (16)$$

$$[\mathrm{Rh(diene)L_n}]^+ + \mathrm{H_2} \xrightarrow{\mathrm{S}} [\mathrm{RhH_2L}_n\mathrm{S}_x]^+ \text{ or } [\mathrm{RhHL_nS_y}]^+ + \text{alkane} \quad (17)$$

diene, 1,5-COD, norbornadiene, etc.; S = Me_2CO, THF, 2-methoxyethanol; L = PR_3, $P(OR)_3$, AsR_3; $n = 2, 3$; $x = 2$ for $n = 2$, $y = 2$ for $n = 2, 3$.

The formation of the corresponding alkanes (reactions 16 and 17), which have, as yet, no known coordination chemistry, can lead to problems in the isolation of solid complexes from the reaction media, as many of the higher alkanes are viscous high-boiling liquids.

D. Solvolysis of Metal–Halide Bonds

The halide-bridged structures of certain metallic salts (such as $PdCl_2$, $PtCl_2$) can be broken down by coordinating solvents, and this may allow isolation of the corresponding solvento species (such as $[MS_2L_2]$, M = Pd, Pt; L = Me_2SO-*S*, pyr, RCN). Only the stronger coordinating solvents facilitate this reaction;[43d] thus, although palladium dichloride is soluble in refluxing nitromethane, the $[Pd(MeNO_2)_2Cl_2]$ complex cannot be isolated.[152] Solvolysis of metal–halide bonds in complexes is generally an equilibrium; thus the reaction between *trans*-$[Pt(PEt_3)_2(Me)Cl]$ and pyridine (a powerful coordinating solvent) is an equilibrium (reaction 18) which lies far to the left.[153] The ionic species cannot

$$trans\text{-}[\mathrm{Pt(PEt_3)_2(Me)Cl}] + \mathrm{pyr} \rightleftharpoons trans\text{-}[\mathrm{Pt(PEt_3)_2(Me)(pyr)}]^+ + \mathrm{Cl^-} \quad (18)$$

be isolated unless the free halide is removed by, for example, sodium tetraphenylborate

E. Photolysis Reactions

Certain metal carbonyls have been shown to be photochemically active with regard to ligand displacement, and solvento complexes of certain metals may be formed in this manner[154] (e.g., reaction 19). This me-

$$2[\mathrm{Mo(CO)_6}] \xrightarrow{h\nu/\mathrm{MeCN}} [\mathrm{Mo(CO)_5MeCN}] + [\mathrm{Mo(CO)_4(MeCN)_2}] + \uparrow 3\mathrm{CO} \quad (19)$$

thod has yet to be exploited in the preparation of platinum metal–solvento complexes.[155]

V. Catalytic Considerations

The vast majority of catalytic reactions involve the activation of a small molecule and its interaction with an organic substrate. A typical example of this is the homogeneous hydrogenation of olefins where the catalytic reaction involves the cleavage of the H–H bond of molecular hydrogen and interaction of the activated species with the olefin. A complex suitable for catalyzing such a reaction must therefore be able to accommodate both reagents in its coordination sphere, facilitate the activation of the small molecule, and allow subsequent interaction with the organic substrate. Complexes of the low-valent platinum metals containing weak donor ligands appear to fit these three major criteria. Highly labile ligands should provide an easy route for coordination of the organic substrate to the metal center. Activation of the small molecule is possible via a heterolytic pathway involving oxidative addition to the metal center. Thus, for comparable systems the metal showing the greatest ability to undergo oxidative addition would be expected to be the more efficient catalyst. Comparing, for example, the sums of the third and fourth ionization potentials of palladium (81.7 eV) and platinum (69.6 eV)[43a] implies that the $d^8 \rightarrow d^6$ transition is more favored for platinum(II) than for palladium(II). It is thus not surprising that the number of homogeneous hydrogenation catalysts based on platinum(II)[1d] far exceeds those based on palladium(II).[1b] Finally, interaction between the activated molecule and the organic substrate can be achieved via the so-called insertion reaction. The insertion of olefins into metal–hydrogen bonds has been well documented.[156]

Complexes of the platinum metals containing weak donor ligands have been postulated in many catalytic pathways, including those for the well-known catalysts Na_2PdCl_4,[7] $[Rh(PPh_3)_3Cl]$,[1e] and $[Ru(PPh_3)_3Cl_2]$.[1f] Isolable complexes containing coordinated solvent molecules have been examined as catalysts for a variety of reactions, with varying degrees of success. For example, although the organonitrile complex $[Pd(RCN)_2X_2]$ has shown ability in the catalytic isomerization of 1-monoenes[157] (activity: R = Ph > Me, X = Cl ≫ Br) and $[Pt(MeCN)_4]^{2+}$ catalyzes the dimerization of branched olefins,[158] catalytic systems for olefin hydrogenation based on $[Pd(Ph_2PCH_2CH_2PPh_2)(solvent)_2]^{2+}$ and $[Rh(H)_2(PR_3)_2(solvent)_2]^+$ (R = aryl, alkyl) are ineffective when the coordinated solvent is acetonitrile.[59,159] Both systems, however, are effective when the coordinated solvent is acetone, the former of these complexes being noteworthy as one of the few palladium(II) hydrogenation catalysts effective at ambient temperatures and pressures.[59] This interesting complex is also a catalyst for the hydrolysis of silanes, previously the domain of platinum(II) complexes.[59]

VI. Conclusions

A simple rationale of weak metal–ligand interactions based on a consideration of the HOMO–LUMO separation of each reactant and the difference in orbital energies between the reactants has been developed. This model is seen to fit many weak bonding situations, although care is needed where steric and symmetry constraints prevail. The chemistry of weakly bonded platinum metal complexes is outlined, and the catalytic implications of these systems are discussed. It can clearly be seen that the role of such species in catalytic cycles is unclear and a vast amount of important work is still to be done. It is particularly important that further complexes of weakly bonded ligands be isolated and characterized in order to fully understand their role as catalytic intermediates and hence extend their utility.

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VIII. References

(1) B. R. James, "Homogeneous Hydrogenation", Wiley-Interscience, New York, 1973: (a) p 94; (b) pp 319–324; (c) p 280; (d) pp 324–347; (e) pp 204–248; (f) pp 83–94.
(2) B. R. James, *Adv. Organomet. Chem.*, **17**, 319 (1979).
(3) P. N. Rylander, "Organic Syntheses with Noble Metal Catalysts", Academic Press, New York, 1973.
(4) J. L. Spencer, *Adv. Organomet. Chem.*, **17**, 407 (1979).
(5) A. J. Chalk and J. F. Harrod, *Adv. Organomet. Chem.*, **6**, 119 (1968).
(6) R. L. Pruett, *Adv. Organomet. Chem.*, **17**, 1 (1979).
(7) F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969).
(8) P. M. Henry, "Palladium Catalysed Oxidation of Hydrocarbons", D. Reidel, Dordrecht, Holland, 1979.
(9) J. F. Roth, J. H. Craddock, A. Hershman, and F. E. Paulik, *Chem. Technol.*, 600 (1971).
(10) D. Forster, *Adv. Organomet. Chem.*, **17**, 255 (1979).
(11) D. E. Webster, *Adv. Organomet. Chem.*, **15**, 147 (1977).
(12) F. R. Hartley, *Chem. Rev.*, **73**, 163 (1973).
(13) G. N. Lewis, "Valence and the Structure of Atoms and Molecules", The Chemical Catalog Co., New York, 1923, pp 141–142.
(14) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).
(15) W. B. Jensen, *Chem. Rev.*, **78**, 1 (1978).
(16) J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).
(17) G. Swarzenbach, *Experientia, Suppl. 5*, 162 (1956).
(18) S. Ahrland, J. Chatt, and N. R. Davies, *Q. Rev., Chem. Soc.*, **12**, 265 (1958).
(19) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
(20) R. G. Pearson, *J. Chem. Educ.*, **45**, 581 (1968).
(21) R. G. Pearson, *J. Chem. Educ.*, **45**, 643 (1968).
(22) R. T. Myers, *Inorg. Chem.*, **13**, 2040 (1974).
(23) C. K. Jørgensen, *Struct. Bonding (Berlin)*, **1**, 234 (1966).
(24) R. S. Drago and B. Wayland, *J. Am. Chem. soc.*, **87**, 3571 (1965).
(25) R. S. Drago, *Chem. Br.*, **3**, 516 (1967).
(26) R. S. Drago, *J. Chem. Educ.*, **51**, 300 (1974).
(27) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Am. Chem. Soc.*, **93**, 6014 (1971).
(28) R. S. Drago and D. R. McMillan, *Inorg. Chem.*, **11**, 872 (1972).
(29) R. S. Drago, *Struct. Bonding*, **15**, 73 (1973).
(30) A. P. Marks and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 3324 (1975).
(31) A. P. Marks and R. S. Drago, *Inorg. Chem.*, **15**, 1800 (1976).
(32) R. F. Hudson and G. Klopman, *Tetrahedron Lett.*, **12**, 1103 (1967).
(33) R. F. Hudson and G. Klopman, *Theor. Chim. Acta*, **8**, 165 (1967).
(34) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).
(35) G. Klopman in "Sigma Molecular Orbital Theory", O. Sinanoglu and K. B. Wiberg, Eds., Yale University Press, New Haven, CT, 1970, pp 115–120.
(36) C. K. Jørgensen, *Inorg. Chem.*, **3**, 1201 (1964).
(37) R. G. Pearson, *Inorg. Chem.*, **12**, 712 (1973).
(38) R. S. Tobias, *Inorg. Chem.*, **9**, 1296 (1970).
(39) G. R. Clark and G. J. Palenik, *Inorg. Chem.*, **9**, 2754 (1970).
(40) U. Belluco, M. Graziani, and P. Rigo, *Inorg. Chem.*, **5**, 1123 (1966).
(41) A. H. Norbury, *Adv. Inorg. Radiochem.*, **17**, 231 (1975).
(42) J. L. Burmeister in "The Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives", A. A. Newman, Ed., Academic Press, London, 1975, Chapter 2, pp 68–130.
(43) F. R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science, London, 1973: (a) Chapter 2; (b) p 117; (c) pp 171, 295, 307–308; (d) pp 126, 185, and references therein.
(44) P.-K. F. Chin and F. R. Hartley, *Inorg. Chem.*, **15**, 982 (1976).
(45) J. Dehand, M. Pfeffer, and M. Zinsius, *J. Organomet. Chem.* **118**, C62 (1976).
(46) J. A. Davies, *Adv. Inorg. Radiochem.*, **24**, 115 (1981).
(47) J. Gopalakrishnan and C. C. Patel, *J Sci. Ind. Res.*, **27**, 475 (1968).
(48) D. Martin and H. G. Hauthal, "Dimethylsulphoxide", Van Nostrand-Reinhold Co., London, 1975.
(49) S. W. Jacob, E. E. Rosenbaum, and D. C. Wood, Eds., "Dimethylsulphoxide", Marcel Dekker, New York, 1971.
(50) P. A. Lewis, D. F. Morris, E. L. Short, and D. N. Waters, *J. Less-Common Met.*, **45**, 193 (1976).
(51) V. I. Baranovskii, Yu. N. Kukushkin, N. S. Panina, and A. I. Panin, *Russ. J. Inorg. Chem.* **18**, 844 (1973).
(52) A. V. Nikolaev, V. G. Torgov, V. N. Andrievskii, E. A. Gal'tsova, E. N. Gil'bert, I. L. Kotlyarovskii, L. N. Mazalov, V. A. Mikhailov, and I. M. Cheremishva, *Russ. J. Inorg. Chem.*, **15**, 685 (1970).
(53) C. C. Su and J. W. Faller, *Inorg. Chem.*, **13**, 1734 (1974).
(54) B. B. Wayland and R. F. Schramm, *Chem. Commun.*, **1465** (1968).
(55) J. H. Price, R. F. Schramm, and B. B. Wayland, *Chem. Commun.*, 1377 (1970).
(56) J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, *Inorg. Chem.*, 11, 1280 (1972).
(57) Yu. N. Kukushkin, *Chem. Zvesti*, **25**, 380 (1971).
(58) J. A. Davies, F. R. Hartley, and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1705 (1979).
(59) J. A. Davies, F. R. Hartley, and S. G. Murray, *J. Mol. Catal.*, **10**, 171 (1980).
(60) A. Mercer and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 2480 (1975).
(61) Yu. N. Kukushkin, N. D. Rubtsova, and N. V. Ivannikova, *Russ. J. Inorg. Chem.*, **15**, 1032 (1970).
(62) Yu. N. Kukushkin and N. D. Rubtsova, *Russ. J. Inorg. Chem.*, **14**, 1115 (1969).
(63) C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1654 (1977).
(64) J. W. Vaughn, "The Chemistry of Non-Aqueous Solvents", Vol. 2, J. J. Lagowskii, Ed., Academic Press, New York, 1967, p 243.
(65) C. L. Rollinson and R. C. White, *Inorg. Chem.*, **1**, 281 (1962).
(66) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).
(67) B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, **8**, 971 (1969).
(68) F. Conti, M. Donati, G. F. Pregaglia, and R. Ugo, *J. Organomet. Chem.*, **30**, 421 (1971).
(69) J. A. Davies, F. R. Hartley, and S. G. Murray, *Inorg. Chem.*, **19**, 2299 (1980).
(70) P. N. Rylander, N. Himelstein, D. Steele, and J. Kreidl, *Englehard Ind. Tech. Bull.*, **3**, 61 (1962).
(71) B. L. Shaw and N. I. Tucker, "Comprehensive Inorganic Chemistry", Pergamon Press, *4*, 781 (1973) and references therein.
(72) J. K. Stille and K. S. Y. Lau, *Acc. Chem. Res.*, **10**, 434 (1977).
(73) G. Calvin and G. E. Coates, *J. Chem. Soc.*, 2008 (1960).
(74) C. D. Kristner, J. H. Hutchinson, J. C. Doyle, and J. C. Storlie, *Inorg. Chem.*, **2**, 1255 (1963).
(75) R. A. Walton, *Q. Rev., Chem. Soc.*, **9**, 126 (1965).
(76) B. N. Storhoff and H. C. Lewis, *Coord. Chem. Rev.*, **23**, 1 (1977).
(77) W. J. Bland, R. D. W. Kemmitt, and R. D. Moore, *J. Chem. Soc., Dalton Trans.*, 1292 (1973).
(78) M. F. Farona and K. F. Krausse, *Inorg. Chem.*, **9**, 1700 (1970).
(79) J. G. Dunn and D. A. Edwards, *J. Organomet. Chem.*, **102**, 199 (1975).
(80) B. Storhoff and A. J. Infante, *Inorg. Chem.*, **13**, 3043 (1974).
(81) J. G. Dunn and D. A. Edwards, *Chem. Commun.*, 482 (1971).
(82) J. R. Doyle, P. E. Slade, and H. B. Jonassen, *Inorg. Synth.*, **6**, 218 (1960).
(83) R. B. King, *J. Organomet. Chem.*, **8**, 139 (1967).
(84) R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).
(85) P. M. Triechel and W. J. Knebel, *Inorg. Chem.*, 11, 1289 (1972).
(86) S. E. Livingstone, *J. Chem. Soc.*, 5091 (1957).
(87) R. M. Alcock, F. R. Hartley, and D. E. Rogers, *J. Chem. Soc.; Dalton Trans.*, 1070 (1973).
(88) C. Burgess, F. R. Hartley, and G. W. Searle, *J. Organomet. Chem.*, **76**, 247 (1974).
(89) I. Leden and J. Chatt, *J Chem. Soc.*, 2936 (1955).
(90) G. W. Bushnell, K. R. Dixon, R. G. Hunter, and J. J. McFarland, *Can. J. Chem.*, **50**, 3694 (1972).
(91) T. Yoshida, T. Matsuda, T. Okano, and S. Otsuka, VIIIth International Conference on Organometallic Chemistry, Kyoto (Japan), 1977, p 153.
(92) T. Yoshida, Y. Ueda, and S. Otsaka, *J. Am. Chem. Soc.*, **100**, 141 (1978).
(93) M. Graziani, R. Ros, and G. Carturan, *J. Organomet. Chem.*, **27**, C19 (1971).
(94) K. Von Werner, W. Beck, and U. Boehmer, *Chem. Ber.*, **107**, 2434 (1974).
(95) T. Yoshida and S. Otsuka, *J. Am. Chem. Soc.*, **99**, 2134 (1977).
(96) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5073 (1962).
(97) H. C. Clark and A. B. Goel, *J. Organomet. Chem.*, **178**, C27 (1979).
(98) M. J. H. Russell, C. White, A. Yates, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 849 (1978).
(99) C. White, S. J. Thompson, and P. M. Maitlis, *J. Organomet. Chem.*, **134**, 319 (1977).
(100) C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1654 (1977).
(101) C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc. Dalton Trans.*, 1305 (1978).

(102) M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, 11, 1269 (1972).

(103) H. C. Clark and C. S. Wong, *J. Am. Chem. Soc.*, **96**, 7213 (1974).

(104) H. C. Clark, C. Billard, and C. S. Wong, *J. Organomet. Chem.*, **173**, 341 (1979).

(105) I. V. Gavrilova, M. Gel'fman, N. V. Ivannikova, and V. V. Razumovskii, *Russ. J. Inorg. Chem.*, **16**, 596 (1971).

(106) J. A. Davies, F. R. Hartley, and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 2246 (1980).

(107) M. C. Cornock and T. A. Stephenson, *Inorg. Nucl. Chem. Lett.*, **12**, 381 (1976).

(108) M. C. Cornock and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 501 (1977).

(109) H. C. Clark, S. S. McBride, N. C. Payne, and C. S. Wong, *J. Organomet. Chem.*, **178**, 393 (1979).

(110) H. C. Clark, C. R. C. Milne, and C. S. Wong, *J. Organomet. Chem.*, **136**, 265 (1977).

(111) H. C. Clark and H. Kurosawa, *J. Organomet. Chem.*, **36**, 399 (1972).

(112) H. C. Clark, C. R. Jablonski, and C. S. Wong, *Inorg. Chem.*, **14**, 1332 (1975).

(113) H. C. Clark and C. R. Jablonski, *Inorg. Chem.*, **13**, 2213 (1974).

(114) H. C. Clark, C. R. Jablonski, and K. Verner, *J. Organomet. Chem.*, **82**, C51 (1974).

(115) R. D. Gillard, B. T. Heaton, and M. F. Pilbrow, *J. Chem. Soc. A*, 253 (1970).

(116) M. A. Bennett, T. W. Matheson, G. B. Robertson, W. L. Steffen, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 32 (1979).

(117) R. E. Hester and R. Q. Plane, *Inorg. Chem.*, **3**, 769 (1964).

(118) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 1091 (1965).

(119) M. R. Rosenthal, *J. Chem. Educ.*, **50**, 331 (1973).

(120) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed., Wiley, New York, 1978, pp 242–243.

(121) R. Usón, J. Forniés, and F. Martinez, *J. Organomet. Chem.*, **112**, 105 (1976).

(122) R. Usón, P. Royo, and J. Gimeno, *J. Organomet. Chem.*, **72**, 299 (1974).

(123) G. Yoshida, H. Kurosawa, and R. Okawara, *J. Organomet. Chem.*, **131**, 317 (1977).

(124) I. V. Gavrilova, M. I. Gel'fman, and V. V. Razumovskii, *Russ. J. Inorg. Chem.*, **19**, 1360 (1974).

(125) J. Peone, B. R. Flynn, and L. Vaska, *Inorg. Synth.*, **15**, 68 (1974).

(126) R. Usón, P. Royo, A. Laguna, and J. Garcia, *Rev. Acad. Gienc. Exactus, Fis-Quim. Nat. Zaragoza.*, **28**, 67 (1973); *Chem. Abstr.*, **80**, 9926 (1974).

(127) G. Van Koten, K. Timmer, J. G. Noltes, and A. L. Speck, *J. Chem. Soc., Chem. Commun.*, 250 (1978).

(128) H. C. Clark and R. J. O'Brien, *Proc. Chem. Soc. London*, 113 (1963).

(129) H. C. Clark, *J. Organomet. Chem.*, **200**, 63 (1980).

(130) F. R. Wimmer and M. R. Snow, *Aust. J. Chem.*, **31**, 267 (1978).

(131) R. M. Alcock, F. R. Hartley, and D. E. Rogers, *J. Chem. Soc., Dalton Trans.*, 1070 (1973).

(132) H. C. Clark and K. R. Dixon, *J. Am. Chem. Soc.*, **91**, 596 (1969).

(133) H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, **9**, 1226 (1970).

(134) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **10**, 2699 (1971).

(135) J. N. Cooper and R. E. Powell, *J. Am. Chem. Soc.*, **85**, 1590 (1963).

(136) M. J. Nolte, G. Gafner, and L. M. Haines, *Chem. Commun.*, 1406 (1969).

(137) R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, **9**, 2339 (1970).

(138) M. A. Bennett and E. J. Hahn, *J. Organomet. Chem.*, **124**, 213 (1977).

(139) G. J. Kruger, A. L. Du Preez, and R. J. Haines, *J. Chem. Soc., Dalton Trans.*, 1302 (1974).

(140) R. F. Schramm and B. B. Wayland, *Chem. Commun.*, 898 (1968).

(141) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3705 (1960).

(142) D. A. Phillips, M. Kubota, and J. Thomas, *Inorg. Chem.*, **15**, 118 (1976).

(143) N. G. Connelly, P. T. Draggett, M. Green, and T. A. Kuc, *J. Chem. Soc., Dalton Trans.*, 70 (1977).

(144) D. C. Luehrs, R. T. Iwamoto, and J. Kleinberg, *Inorg. Chem.*, **5**, 201 (1966).

(145) D. A. White, *Synth. Inorg. Met.-Org. Chem.*, 1, 59 (1971).

(146) F. Maspero, E. Perotti, and F. Simonetti, *J. Organomet. Chem.*, **38**, 43 (1972).

(147) N. G. Connelly and J. D. Davies, *J. Organomet. Chem.*, **38**, 385 (1972).

(148) D. A. Slack and M. C. Baird, *Int. Conf. Homogeneous Catal., Corpus Christi, Texas, 1st*, 103 (1978).

(149) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **98**, 2134 (1976).

(150) J. M. Brown, P. A. Chaloner, and P. N. Nicholson, *J. Chem. Soc., Chem. Commun.*, 646, (1978).

(151) J. M. Brown, P. A. Chaloner, G. Descotes, R. Glaser, D. Lafont, and D. Sinou, *J. Chem. Soc., Chem. Commun.*, 611 (1979).

(152) S. G. Murray, personal communication.

(153) M. J. Church and M. J. Mays, *J. Chem. Soc. A* 3074 (1968).

(154) W. Strohmeier and G. Schonauer, *Chem. Ber.*, **94**, 1346 (1961).

(155) W. L. Waltz and R. G. Sutherland, *Chem. Soc. Rev.*, 1, 241 (1972).

(156) R. F. Heck, *Adv. Chem. Ser.*, **No. 49**, 181 (1964).

(157) S. Sakaki, H. Kanai, and K. Tarama, *Can. J. Chem.*, **52**, 2857 (1974).

(158) A. De Renzi, A. Panunzi, A. Vitagliano, and G. Paiaro, *J. Chem. Soc., Chem. Commun.*, 47 (1976).

(159) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **98**, 2134 (1976).