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Monomeric Metal Hydroxides, Alkoxides, and Amides of the Late Transition Metals: Synthesis, Reactions, and Thermochemistry

HENRY E. BRYNDZA* and WILSON TAM*

Central Research and Development Department, E. I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Delaware 19880-0328

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Contents

Scope

Our intention with this review is to discuss the fundamental chemistry available to hydroxides, alkoxides, and amides of the late transition metals. Our primary interest in this class of compounds comes from their interesting reactivity and potential relevance to catalysis. Since other reviews have concentrated heavily on polynuclear alkoxides of the platinum metals,[1] we have arbitrarily chosen to discuss only monomeric complexes.

In this review we will cover the synthesis, structural aspects, reaction mechanisms, and potential importance to catalysis of group VIII (groups 8–10) metal alkoxides, amides, and hydroxides. While we include anilido and phenoxo substituents within this definition, we have not attempted to cover carboxyl or carbamide complexes or other related resonance-stabilized analogues.

To structure this review we have chosen a functional-group approach. In our synthesis section we will discuss synthetic reactions subdivided by methodology rather than by each individual metal or chronological succession. Similarly, we will discuss reaction mechanisms for individual fundamental reaction steps rather than individual metals. Finally, as will be seen, since obtaining conclusive mechanistic information on catalytic systems has proven extremely difficult, we have chosen to reference catalytic reactions that *may* involve metal–oxygen or metal–nitrogen bonds but leave it to the reader to decide the veracity of mechanistic speculations.

Henry Bryndza is a native of Berkeley. He received an S.B. degree from M.I.T. in 1977 where he worked with Daniel Kemp and went on to graduate studies with Robert Bergman at the University of California at Berkeley. Since joining the Central Research and Development Department at Du Pont in 1981, his interests have included mechanistic studies of late metal-to-heteroatom bonds, organometallic thermochemistry, and homogeneous carbonylation and hydrocyanation catalysis.

Wilson Tam is a native of San Francisco. He received a B.S. degree from the University of California at Berkeley and an M.S. degree from the University of California at Riverside where he worked with Michael Rettig. Wilson received his Ph.D. in 1979 from the University of California at Los Angeles where he worked with John Gladysz. Before joining the Central Research and Development Department at Du Pont in 1980, he spent a postdoctoral year with Peter Vollhardt at Berkeley. His interests at Du Pont have included cross coupling reactions, homogeneous carbonylation catalysis, and nonlinear optical applications of organometallic complexes.

Introduction

While the synthesis and reactions of late metal to carbon bonds have been intensely studied for many years, the analogous chemistry of metal–oxygen and metal–nitrogen bonds has been left relatively unexplored. The commonly held explanation for the relative scarcity of alkoxide and amide derivatives is that such linkages are characteristically weak due to a mismatch of these hard, basic ligands with soft group VIII metal centers.[2] The difficulty in isolating alkoxide and amide complexes and the ease with which they decompose (presumably by β-hydride elimination; vide infra) to metal hydrides add credence to this hypothesis; it has been assumed that weak M–O and M–N bonds lower the intrinsic barrier to β-hydride elimination reactions by raising the ground-state free energies of alkoxides and amides relative to alkyl and aryl analogues.

The relatively recent work reviewed here contradicts some of these perceptions. Synthetic routes used to prepare metal alkyl and aryl derivatives can also be used to successfully prepare alkoxide and amide complexes. Limited structural information suggests these metal–ligand interactions are highly covalent, and mechanistically similar reaction chemistry and thermochemistry have now been noted for late-metal alkoxides and amides (vis-â-vis metal alkyl analogues). These observations, which are detailed below, suggest metal alkoxides and amides may have a rich catalytic chemistry available to them as has been elucidated for metal alkyl, aryl, and hydride derivatives.

I. Synthesis

Many standard and a few unique methods have been used to prepare late-metal alkoxides and amides. In order to make this review as useful as possible to workers in the area, we have divided this section into the different synthetic methods available to prepare M–X (X = OR, NR_2) bonds.

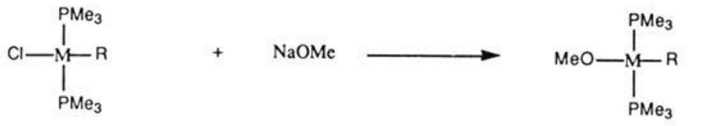
Metathesis

Platinum Alkoxides and Hydroxides

By far the most common method of preparing late-metal alkoxides, hydroxides, and amides has been through metal exchange, or metathesis, reactions (eq 1), and no class of metal alkoxides has benefited from

$$L_nM{-}X + M'{-}Y \rightarrow L_nM{-}Y + M'{-}X \qquad (1)$$

this technique more than ligated platinum(II). Otsuka and co-workers have prepared a number of *trans*-MR(OCH_3)L_2 complexes of platinum and palladium by simple metathesis on the chlorides using sodium methoxide (eq 2) and reported the stability of these complexes dramatically depends on the electron-withdrawing nature of R (decreasing in the order C_6F_5 > $C(Cl)CCl_2$ > $C(H)CCl_2$ > C_6H_5).[3] Bryndza and co-workers have prepared (DPPE)PtR(OMe) (R = Me, Et) by reaction of NaOMe with (DPPE)PtR(Cl) using mixed benzene/methanol solvents.[4] The use of methanol in these syntheses retards β-hydride elimination from taking place from the alkoxide ligands and allows isolation of even the very reactive (DPPE)Pt(OMe)$_2$ (from (DPPE)$PtCl_2$ and NaOMe). Pidcock has pointed out that problems of competitive reduction and metathesis in these systems can be minimized through the use of KOH/crown ether complexes in organic solvents.[5] Metathesis can also be carried out with thallium alkoxides.[6]



$$Cl{-}\overset{PMe_3}{\underset{PMe_3}{M}}{-}R + NaOMe \longrightarrow MeO{-}\overset{PMe_3}{\underset{PMe_3}{M}}{-}R \qquad (2)$$

M = Pd, Pt; R = alkenyl, aryl

Arresta and Nyholm have prepared chelating vinyl phenoxide derivatives shown in eq 3 by combining

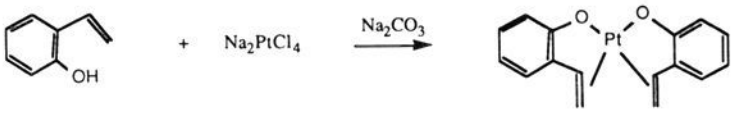


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TABLE I. Platinum Alkoxides and Hydroxides

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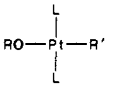
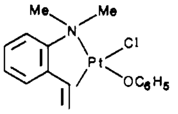
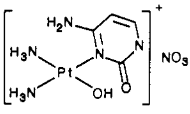
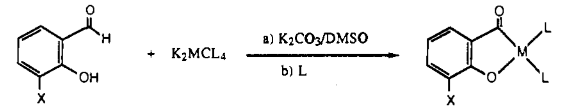
 $RO{-}\overset{L}{\underset{L}{Pt}}{-}R'$	R = H, CH_3; R′ = CH_2CN, CF_3, CH_2CF_3; L = PPh_3; L_2 = diphoe (cis analogues); R′ = CF_3; L_2 = chiraphos, prophos, diop (cis complexes)	9
	R = H; R′ = Ph, I; L = $P(Cy)_3$, $P(t\text{-}Bu)_2Me$, $P(t\text{-}Bu)Me_2$, PEt_3, L = $PPhMe_2$ gives cis analogue	10
	R = H; R′ = Me; L = $P(t\text{-}Bu)_3$, $P(i\text{-}Pr)_3$; L_2 = DPPE gives cis analogue	10
		6
		11

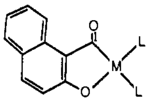
Na_2PtCl_4 with *o*-vinylphenol in buffered solutions.[7] While the mechanism was not determined, it seems likely to proceed by generating equilibrium concentrations of phenoxide, which displaces chloride from platinum; the stage at which olefin coordination ensues is not known. A similar approach, which also involves C–H bond activation, has been used by Pregosin to prepare a variety of monoacylphenoxide derivatives from K_2PtCl_4 and *o*-hydroxybenzaldehydes (eq 4).[8]



(4)

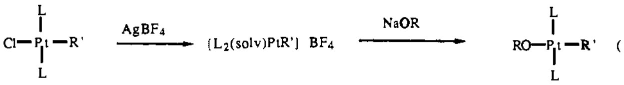
M = Pt; X = H; L = PPh_3, $P(p\text{-tolyl})_3$, $P(n\text{-}Bu)_3$, PPh_2CH_2Ph, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$, $P(O\text{-}n\text{-}Bu)_3$, $AsPh_3$, $AsPh_2Me$; L_2 = DPPE
M = Pt, Pd; X = OMe, L_2=DPPE

Also prepared:



M = Pt, L = PEt_3, L_2 = DPPE
M = Pd, L_2 = DPPE, diphoe

Many other Pt analogues with electron-withdrawing σ-ligands were prepared either by direct metathesis or by initial formation of solvato cationic intermediates (eq 5).[9] The use of solvato cationic intermediates, while generally more involved, can be carried out completely at low temperature to allow isolation of even very reactive derivatives. Bennett has prepared interesting phenyl- and methylplatinum hydroxides by reacting KOH with acetone-solvated platinum cations; for example, (DPPE)PtMe(OH) was prepared from $[(DPPE)PtMe(acetone)]BF_4$.[10] Table I lists other Pt and Pd hydroxides and alkoxides prepared by metathesis.



$$Cl{-}\overset{L}{\underset{L}{Pt}}{-}R' \xrightarrow{AgBF_4} [L_2(solv)PtR']\ BF_4 \xrightarrow{NaOR} RO{-}\overset{L}{\underset{L}{Pt}}{-}R' \quad (5)$$

Platinum Amides

Chelating bis(phosphine)platinum amides can be prepared by treating the corresponding platinum chlorides with substituted lithium amides in THF (eq 6).[12] The parent platinum amide ($-NH_2$) complexes

$$(L_2)Pt(R)(Cl) + LiN(R')(R'') \rightarrow (L)_2Pt(R)[N(R')(R'')] \quad (6)$$

L_2	R	R′	R″
DPPE	Me	Me	Ph
DPPE	Me	H	CH_2Ph
DPPE	Ph	Me	Ph
DPPE	CH_2Ph	Me	Ph
DMPE	Me	Me	Ph

with both hydride and alkyl substituents[13] have been prepared by deprotonation of the corresponding amine complexes (eq 7), and *trans*-$(PEt_3)_2PtH(NHPh)$ have been prepared by adding NaNHPh to *trans*-$(PEt_3)_2PtH(NO_3)$.[14]

$$trans\text{-}[Pt(L)_2(R)NH_3]\ ClO_4 + \text{base} \rightarrow trans\text{-}Pt(L)_2(R)(NH_2) \quad (7)$$

base: NH_2^-, 2,3-di-*tert*-butyl-5-methylphenoxide

R = H; L = PPh_3, PEt_3, PCy_3

R = Me; L = PPh_3, PEt_3, $PMePh_2$, PCy_3

Palladium Hydroxides

A few (2,2′-bipyridyl)palladium hydroxides have been reportedly generated through metathesis reactions (eq 8).[15] Basic anion exchange resin has been used in these syntheses to replace chloride with hydroxide; these species can be further derivatized by ligand exchange and σ-ligand metathesis (vide infra).

$$(bpy)PdCl_2 + \text{excess anion-exchange resin} \xrightarrow[75\ °C]{H_2O} (bpy)Pd(OH)_2(H_2O)$$

$$(bpy)PdCl_2 + 1\ \text{eq of anion-exchange resin} \xrightarrow[75\ °C]{H_2O} (bpy)Pd(OH)(Cl)(H_2O) \quad (8)$$

Also reported

$$(L_2)Pd(OH)X(H_2O)$$

L_2 = phen, TMEDA, DPPE; X = Cl

L_2 = bpy; X = Br, OAc

Nickel Alkoxides

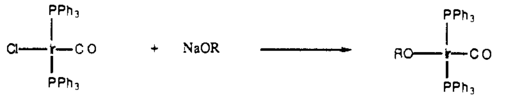
A few monomeric nickel alkoxides have been prepared by metathesis reactions. Preformed nickel cations can react directly with methoxide or phenoxides to generate nickel alkoxides. Alternately, metathesis of simple nickel chlorides can generate alkoxides (eq 9[16] and 10[17]), though generally not monomeric species.[18]

$$[(PPh_3)_3Ni(NO)]PF_6 + NaOMe \rightarrow (PPh_3)_3Ni(NO)(OMe) \quad (9)$$

$$[(py)_3NiC_6Cl_5]ClO_4 + KOC_6Cl_5 \rightarrow (py)_2NiC_6Cl_5(OC_6Cl_5) \quad (10)$$

Rhodium and Iridium Alkoxides

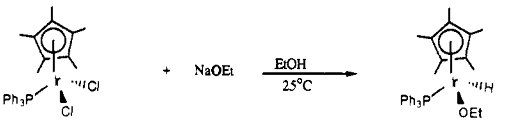
As was the case for platinum(II) systems, many L_nRhOR and L_nIrOR derivatives have been prepared by metathesis reactions. As early as 1969 Ugo and co-workers reported the synthesis of the first of many *trans*-$R'OM(PR_3)_2L$ (M = Rh, Ir; L = CO, PR_3; R′ = H, alkyl, aryl) derivatives when they combined sodium alkoxides and *trans*-$ClRh(PR_3)(CO)$ in water to generate the hydroxide, $(HO)Rh(PR_3)_2(CO)$.[19] Roper prepared the iridium analogue by adding NaOH to *trans*-$[(CH_3CN)Ir(PPh_3)_2(CO)]ClO_4$,[20] and Vaska reported the synthesis of both rhodium and iridium hydroxides and phenoxides by metathesis of *trans*-$FM(PPh_3)_2(CO)$ fluorides (M = Rh, Ir).[21] Yoshida and Otsuka have prepared analogous rhodium alkoxides, *trans*-$MeORh(P(i\text{-}Pr)_3)_2(CO)$, by metathesis on pyridine cationic complexes $[(pyr)Rh(P(i\text{-}Pr_3)_2(CO)]^+$,[22] and Atwood has described the synthesis of several iridium alkoxides by metathesis of chlorides (eq 11).[23] Examples of other metathesis syntheses of rhodium and iridium alkoxides include the addition of hydroxide to $(NH_3)_5RhH^+$ (eq 12)[24] and the reaction of NaOEt with $(C_5Me_5)Ir(PPh_3)Cl_2$ (eq 13).[25]



(11)

R = Me, *i*-Pr, *t*-Bu, Ph, C_6F_5

$$(NH_3)_5RhH^{2+} + O_2 + OH^- \rightarrow (NH_3)_5Rh(OH)(OOH)^+ \quad (12)$$



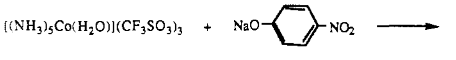
(13)

As for platinum amide syntheses, rhodium chlorides also undergo metathesis reactions with sources of amide anions (eq 14)[26] to generate thermally metastable rhodium amides.

$$ClRh(PPh_3)_3 + LiN(SiMe_3)_2 \rightarrow [(Me_3Si)_2N]Rh(PPh_3)_3 \quad (14)$$

Cobalt and Iron Alkoxides and Amides

While many simple cobalt alkoxides and amides tend to dimerize, a few monomeric species have been synthesized by metathesis. For example, Jordan has prepared substituted cobalt phenoxides (eq 15),[27] and Power has prepared interesting sterically congested cobalt alkoxides, amides, and mixed alkoxy amides (eq 16).[28] This approach has also been applied to the synthesis of iron and nickel analogues. Koch and Millar have reported the synthesis of anionic iron tetraphenoxides from $FeCl_3$ (eq 17).[29]



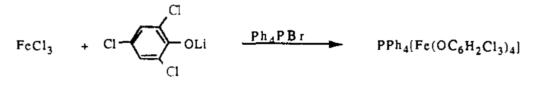
(15)

$$CoCl_2 + 2LiNPh_2 \xrightarrow[-78\ ^\circ C]{THF/hexane} [Co(NPh_2)_2]_2$$

$$CoCl_2 + 2LiO\text{-}t\text{-}Bu \rightarrow [(t\text{-}BuO)_2CoCl]Li(THF)_3$$

$$Co(N(SiMe_3)_2)_2 + t\text{-}BuOH \rightarrow [(t\text{-}BuO)_2CoN(SiMe_3)_2]\cdot Li(THF)_{4.5}$$

$$Co(N(SiMe_3)_2)_2 \xrightarrow[(2)\ LiN(SiMe_3)_2]{(1)\ t\text{-}BuOH} [(t\text{-}BuO)_2CoN(SiMe_3)_2]Li \quad (16)$$



(17)

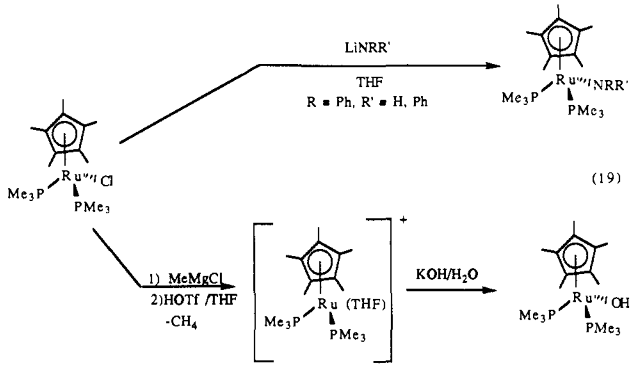
Ruthenium Alkoxides and Amides

Wilkinson and co-workers have prepared a monomeric ruthenium hydrido hydroxide (eq 18) by metathesis.[30]

$$(PPh_3)_3Ru(H)(Cl) + MOH \rightarrow (PPh_3)_2RuH(OH)(solv) \quad (18)$$

$$M = Na, K;\ solv = THF, H_2O$$

Bryndza, Bercaw, and co-workers have reported a metathetical route to substituted ruthenium amides, which, unfortunately, could not be used to prepare the analogous hydroxide derivative. Instead, addition of aqueous KOH to a solvated ruthenium cation allowed synthesis of this material (eq 19).[31]



(19)

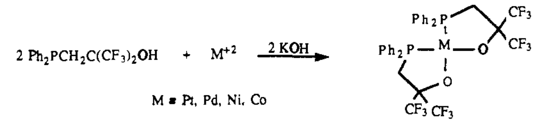
Weak Alkoxide Complexes by Metathesis

The interaction of fluoro-substituted alkoxides with group VIII metal halides and cations has proven to be a fairly general method for the preparation of bisalkoxide derivatives of unusual stability (with regard to their hydrocarbon analogues). For example, as early as 1970 Stone prepared metastable platinum and nickel fluoroalkoxides containing β-hydrogen atoms by metathesis on bis(phosphine)metal chlorides (eq 20).[32]

$$cis\text{-}(PPh_3)_2PtCl_2 + 2NaOCH(CF_3)_2 \rightarrow cis\text{-}(PPh_3)_2Pt(OCH(CF_3)_2)_2$$

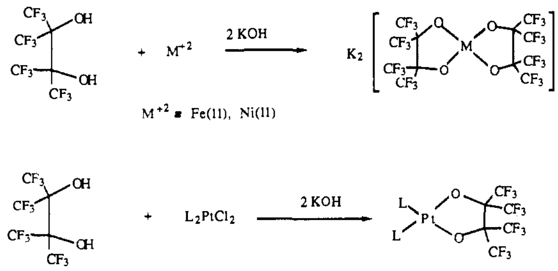
$$cis\text{-}(PEt_3)_2NiCl_2 + 2NaOCH(CF_3)_2 \rightarrow cis\text{-}(PEt_3)_2Ni(OCH(CF_3)_2)_2 \quad (20)$$

Willis and co-workers have reported the synthesis of a number of quite stable chelating bis(fluoroalkoxide) complexes (eq 21 and 22) that do not contain any hydrogen atoms β to the metal centers.[33]



(21)

M = Pt, Pd, Ni, Co



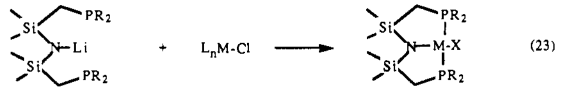
(22)

M^{+2} = Fe(II), Ni(II)

L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, SMe_2, SEt_2, DMSO, 2,5-dithiahexane

Chelating Amide Complexes

In addition to the above general methods of preparing metal alkoxides and amides, Fryzuk and co-workers have made extensive use of metathesis reactions to prepare chelating bis(phosphine)amido complexes of nickel, palladium, platinum, rhodium, and iridium (eq 23).[34] The route employed is apparently general for this type of ligand, and the complexes have interesting chemistry different from that of other amide derivatives (vide infra). Additionally, these amide linkages are inhibited from undergoing homolytic or heterolytic dissociation by the chelating ligand structure. The lack of β-hydrogen atoms precludes β-hydride elimination.



(23)

R	L_nMCl	X
Ph	L_2NiCl_2 L = PPh_3, PMe_3, DME	Cl
Ph, *i*-Pr	$[(COE)_2MCl]_2$	COE
Ph	$[L_4M]Cl$ L = PMe_3, PPh_3 M = Rh, Ir	L
Ph	$[L_2MCl]_2$ L = CO, C_2H_4 M = Rh, Ir	L
Ph	$(PhCN)_2PdCl_2$	Cl
Ph	$K[PtCl_3(C_2H_4)]$	Cl

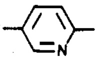
Azide Reactions

A few nongeneral amide syntheses proceed through reactions of organic azides. The mechanisms are not fully understood, and the methods have not been widely employed. However, Beck and Bauder have prepared a number of unique amides through this procedure (eq 24).[35]

$$trans\text{-}(R_3P)_2PtH(X) + R'N_3 \rightarrow trans\text{-}(R_3P)_2Pt(NHR')(X) \quad (24)$$

R = Et, Ph; X = Cl, NCO, N_3, CN

R'= Ph, PhCO, $PhSO_2$, *p*-$NO_2C_6H_4$, CO_2Et, O_2N–



Oxidative Syntheses

The second major method of preparing late-metal alkoxide, amide, and hydroxide complexes is through oxidative addition reactions. Under this broad category we include examples of H–OR and H–NR_2 oxidative additions to metal centers as well as metal additions to C–O bonds and radical-trapping syntheses that form M–O bonds. The so-called "σ-ligand metathesis" reactions which may involve oxidative additions will be discussed below.

Additions of L_nM to H–OR Bonds

While this type of reactivity has been sought for many years, it was not reported as a synthetic route to metal hydrido alkoxo derivatives until 1977 when Stone and Green published observations on the reactions of $(P(Cy)_3)_2Pt$ with alcohols and amines (eq 25).[36] Otsuka

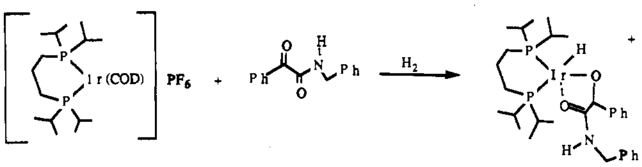
$$Pt(P(Cy)_3)_2 + H\text{–}X \rightarrow trans\text{-}Pt(P(Cy)_3)_2(X)(H) \quad (25)$$

H–X = HOPh, HOC_6H_4-*p*-R, pyrrole, aniline

has studied the reactions of bis(phosphine)platinum derivatives with water in some detail and reported isolating *trans*-$(P(i\text{-}Pr)_3)_2PtH(OH)$ (eq 26).[37] Otsuka

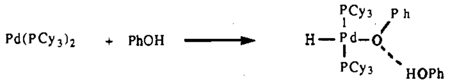
$$\underset{n = 2,\,3}{Pt(P(i\text{-}Pr)_3)_n} + H_2O \xrightarrow[(\leftarrow)]{} trans\text{-}Pt(P(i\text{-}Pr)_3)_2(OH)(H) \quad (26)$$

has also reported preparing an iridium hydrido alkoxide derivative in a reducing system (eq 27).[38] Milstein has



(27)

described the oxidative addition of water across $[(PMe_3)_4Ir]PF_6$ to generate $[(PMe_3)_4IrH(OH)]PF_6$.[39] Recently, the addition of phenol to a bulky palladium(0) bis(phosphine) complex has been reported to give a hydrido phenoxide derivative (eq 28) containing 1 mol of phenol hydrogen bonded to the phenoxide substituent in the solid state by an asymmetric Pd–O···H–O interaction (vide infra),[40] and Casalnuovo has observed oxidative addition of ammonia to an iridium(I) center (eq 29),[41] though this ultimately gives a bridging amide derivative.



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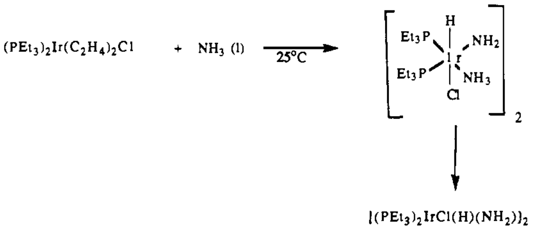
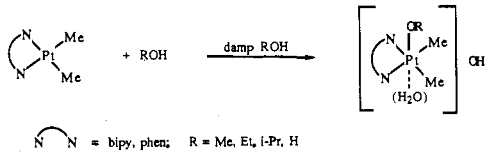


(29)

Puddephatt has prepared platinum(IV) alkoxides, which are surprisingly inert, but they have proven difficult to fully characterize in many cases (eq 30).[42]



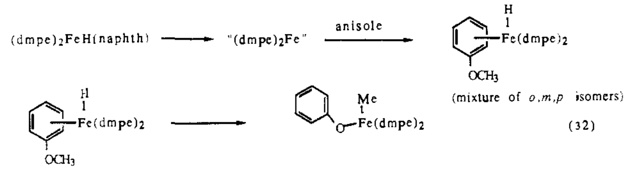
(30)

The presence of adventitious water apparently generates hydroxide counterions to these cationic platinum derivatives; ion exchange results in isolation of complexes that can be fully characterized. The pyridine analogue $[(pyr)_2PtMe_2(OR)]OH$ has also been described;[43] the formulation as an inner-sphere/outer-sphere complex comes from the substitutional stability of the alkoxide ligand vis-à-vis the "counterion". Finally, Akl and Tayim have recently shown that addition of both Sn–Cl and H–O bonds to platinum can take place (eq 31).[44]

$$Pt(PPh_3)_4 + SnCl_4{\cdot}2H_2O \xrightarrow{EtOH} (PPh_3)_2Pt(SnCl_3)(H)(Cl)(OEt) \quad (31)$$

Additions of L_nM to C–O Bonds

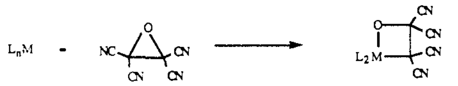
The oxidative addition of late transition metals to C–O bonds has been observed for epoxides, organic esters, and anisole. This latter case is an example of an especially reactive iron center that first kinetically inserts into an aromatic C–H bond (probably by precoordination of the arene ring) and then inserts into the O–CH_3 linkage of that molecule to give the thermodynamic product of the reaction (in which a C–O bond has been preferentially activated over the C–H and other C–O bonds in the molecule (eq 32)). Studies on other



(32)

arene C–H bond activations with this system suggest the electron-donating methoxy substituent destabilizes the intermediate addition product.[45]

The activation of C–O bonds in epoxides to generate oxymetallacycles may be a general reaction. However, due to the instability of these species with respect to rearrangements, only a few derivatives not containing β-hydrogen substituents have been isolated (eq 33). Even blocking the β positions with cyanide groups does not always prevent rearrangements; some new metal cyano enolate derivatives have been prepared in these cases.[46]

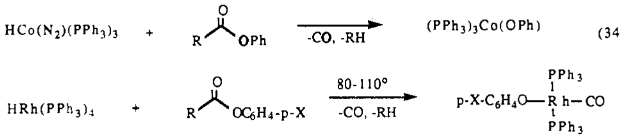


(33)

L_nM : M = Pt ; L = PPh_3, $P(p\text{-tolyl})_3$, $AsPh_3$; n = 4

trans-$(PPh_3)_2(CO)MX$: M = Rh, Ir; X = Cl, Br

Oxidative addition of low-valent late metals to C–O bonds in organic esters has been studied for potential relevance to ester synthesis (the microscopic reverse of that process). Yamamoto has isolated both cobalt and rhodium alkoxide complexes from the interactions of esters with low-valent metal centers (eq 34),[47] while



(34)

R = Me, Et; X = H, OMe

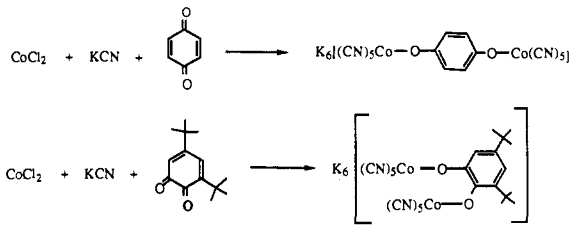
Otsuka has observed the decarbonylation of nickel and palladium carbophenoxide derivatives to give phenoxide complexes (eq 35).[48]

$$(t\text{-BuNC})_2M(X)CO_2Ph \xrightarrow{-CO} (t\text{-BuNC})_2M(X)(OPh) \quad (35)$$

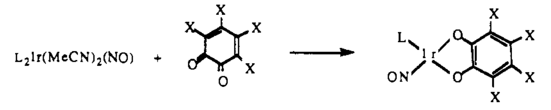
X = Cl, Br; M = Ni, Pd

Oxidative Reactions with Quinones and Dioxygen

A number of metal–oxygen bonds have been prepared through interactions of metal complexes with quinones and molecular oxygen. While these reactions are not common enough to have developed familiar patterns of reactivity, they have resulted in the preparation of novel alkoxide and phenoxide complexes that would be difficult to prepare by other methods. For example, Vleck and co-workers have prepared a number of alkoxide derivatives of pentacyanocobaltate (eq 36),[49] and Ghedini has prepared a chelating iridium bisalkoxide through the same type of interaction (eq 37).[50]



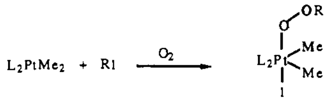
(36)



(37)

L = PPh_3, $AsPPh_3$; X = Cl, Br

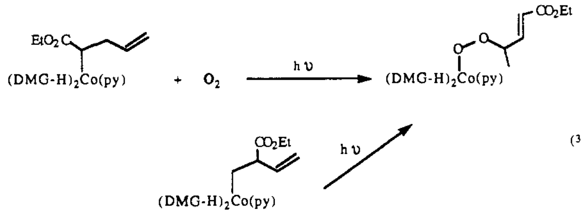
Formal oxidative addition reactions of alkyl iodides and low-valent metal centers often involve organic radical fragments. Puddephatt has noted that a platinum peroxide is formed during the addition of isopropyl iodide to (phen)$PtMe_2$ if the reaction is carried out in air (eq 38). Under nitrogen only the isopropyl



(38)

R = *i*-Pr, *t*-Bu; L_2 = phen
R = *i*-Pr, L_2 = bipy

iodide complex is isolated.[51] Cobalt–carbon bond homolysis is thought to be responsible for the incorporation of oxygen into the Co–C bond shown in eq 39.[52]



(39)

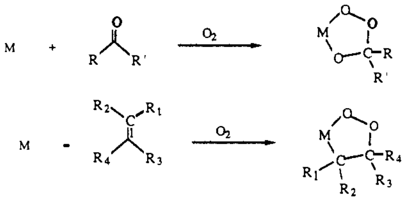
The mechanism of the reaction shown in eq 40 is not known but may involve an iridium dioxygen complex as an intermediate in the formation of the hydroxide.[53]

$$[HIr(NO)(PPh_3)_3]BF_4 + O_2 \rightarrow [Ir(OH)(NO)(PPh_3)_3]BF_4 + OPPh_3 \quad (40)$$

Finally, the formation of *n*-$BuOCo(CO)_4$ has been reported upon addition of *n*-BuOCl to $NaCo(CO)_4$ in a reaction that results, formally, in an oxidation state change for cobalt (eq 41).[54]

$$NaCo(CO)_4 + n\text{-}BuOCl \rightarrow n\text{-}BuOCo(CO)_4 \quad (41)$$

Before leaving formal oxidative syntheses, we should at least mention the peroxymetallacycles, which are thought to be important intermediates in ketone, aldehyde, and olefin oxidations by group VIII metals. These species, shown schematically in eq 42, can



(42)

sometimes be isolated or observed spectroscopically; given the limited scope of this review we cannot hope to discuss these compounds or their relevant chemistry.

We can only cite a few leading references for the interested reader to pursue independently.[55]

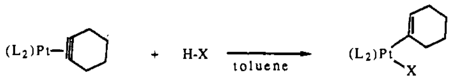
Protonations and σ-Ligand Metatheses

σ-Ligand metathesis, represented by eq 43, differs from the synthetic routes outlined in the previous sections in that no second metal is involved in the reaction; only hydrogen atoms transfer between σ ligands. The process, as written *and* practiced, is extremely general and has important thermochemical consequences. These considerations, as well as the many possible mechanisms for these reactions, will be discussed in detail in the Reactivity section of this review. For synthetic purposes, these reactions can be broken into two types: irreversible and reversible.[56] Because we will concentrate on the latter in the Reactivity section of this review, it will be given only cursory treatment at the end of this section. Conversely, the "irreversible" reactions will be discussed in slightly more detail here.

$$L_nM{-}X + H{-}Y \underset{(\leftarrow)}{\longrightarrow} L_nM{-}Y + H{-}X \qquad (43)$$

Irreversible σ-Ligand Metatheses

Bennett and co-workers have developed the reaction of alcohols and water with late-transition-metal complexes as a fairly general route to platinum cyclohexenyl alkoxides and hydroxides (eq 44).[57] These reactions are certainly thermodynamically very favorable. When *trans*-cyclohexenyl methoxo complexes are produced, hydrides generally result, though some are stable enough to isolate. The cis derivatives appear to be much more robust toward β-hydride elimination (vide infra).



(44)

X = OH, OMe; L_2 = DPPE, DPPP, DPPB, diphoe, 2 $PMePh_2$, 2 PPh_3
X = p-MeC_6H_4O; L_2 = DPPE

Another type of "irreversible" σ-ligand metathesis reaction to form alkoxide complexes is somewhat general and involves reaction of relatively acidic alcohols with transition-metal alkyl complexes. It is unclear precisely what role protonation plays in any of this chemistry, but, with only a few exceptions, this route has only been used to prepare phenoxide derivatives. The reaction appears to be either kinetically or thermodynamically irreversible since alkane activation has rarely been seen with alkoxide complexes. Recent thermochemical data[31] suggest kinetics may be more significant here than thermodynamics.

Unlike the platinum(II) cyclohexyne derivatives mentioned above, reaction of palladium or nickel methyl derivatives with aryl alcohols generates metal aryl oxides and releases methane gas (eq 45).[58] Similar reactions of phenol with nickel[59] and cobalt[60] methyl complexes also generate metal phenoxides (eq 46).

$$L_2(Me)_2 + p\text{-}X\text{-}C_6H_4OH \rightarrow L_2M(Me)(OC_6H_4\text{-}p\text{-}X) + CH_4 \qquad (45)$$

$$M = Ni;\ L_2 = bpy,\ 2PEt_3;\ X = H,\ CN,\ Ph$$

$$M = Pd;\ L_2 = bpy,\ 2PEt_3;\ X = CN,\ OMe,\ H$$

$$M = Pd;\ L_2 = 2PMePh_2,\ 2PEtPh_2;\ X = CN$$

$$(PMe_2Ph)_3NiMe_2 + PhOH \rightarrow (PMe_2Ph)_3NiMe(OPh) + CH_4$$

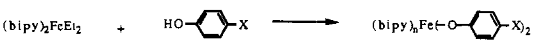
$$(PMe_3)_4CoMe + PhOH \rightarrow (PMe_3)_4Co(OPh) + CH_4 \qquad (46)$$

As early as 1968 Keim reported a similar result on heating phenol with rhodium methyl and phenyl derivatives (eq 47).[61]

$$(PMe_3)_3RhR + PhOH \rightarrow (PMe_3)_3Rh(OPh) + RH$$
$$R = Me,\ Ph \qquad (47)$$

Also reported: $[(PMe_3)_2Rh(OPh)]_2$

Labeling studies confirmed the hydrocarbon included hydrogen originating from the H–O bond of phenol. Bergman has prepared some alkylphosphine analogues of this phenoxide; solution and crystallographic studies confirm that, in the presence of excess phenol, these complexes bind to another molecule of aryl alcohol through fairly robust asymmetric hydrogen bonds.[62] Wilkinson has also reported preparing an iridium phenoxide through this type of reaction. Under vacuum, dihydrogen can be removed from $HIr(PMe_3)_3(CO)$ and p-nitrophenol to give $(p\text{-}NO_2C_6H_4O)Ir(PMe_3)_2(CO)$.[63] Yamamoto has demonstrated similar results in an iron system; substituted phenols add to $(bpy)FeEt_2$ to give bis(phenoxides) as shown in eq 48.[64] Finally, Wilkinson has also shown $(PMe_3)_4RuH_2$ reacts with water to give $(PMe_3)_4Ru(OH)_2$.[65]



(48)

n = 1; X = H, Me, Cl, CN
n = 2; X = NO_2, CN

Reversible σ-Ligand Metatheses

The most prevalent type of σ-ligand metathesis reaction used to prepare alkoxides complexes comes from the addition of alcohols, peroxides, amines, and water to *other* metal alkoxides, amides, and hydroxides. These reactions are often reversible and are "driven" to "completion" by the addition of excess reagent to the metal complex. σ-Ligand metatheses have been reported to generate platinum(II) alkoxides,[4a,c,12] hydroxides,[3,4a,9a,b,10b,57d] amides,[9b,10b,12] and peroxides[66] by adding alcohols, water, amines, and peroxides to Pt–O and Pt–N bonds. Iridium alkoxides,[25,39,53] hydroxides,[23b,39] and peroxides[67] have been prepared by this technique, and cobalt alkoxides have been prepared from corresponding amides[68] as well. Finally, examples of σ-ligand metathesis have been extensively studied in the $(C_5Me_5)(PMe_3)_2RuX$ system[31] and have been used to prepare osmium alkoxides as well.[69] These examples, and others, will be discussed in detail in the Reactivity section of this review.

II. Structures of Late-Transition-Metal Alkoxide and Amide Complexes

There are a small number of structures determined for monomeric late-transition-metal (group VIII) alkoxide complexes and even fewer for monomeric metal amido derivatives. The majority of structures determined are for platinum(II) alkoxides and hydroxides; these are summarized in Table II. The Pt–O distances range from 1.99 to 2.07 Å, indicating primarily covalent

TABLE II. Bond Lengths (Å) in Platinum Alkoxides and Hydroxides

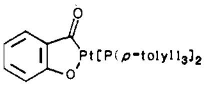
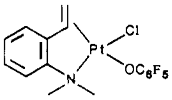
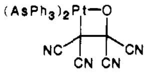
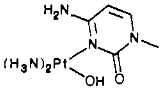
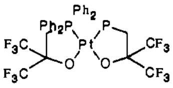
entry (ref)	complex	Pt–O	Pt–L trans to O	other remarks
1 (8a)	(DPPE)PtMe(OMe)	1.990 (10)	2.211 (3)	Pt–P: 2.281 (3) O–C: 1.258 (19) Pt–C: 2.145 (17)
2 (8c)	(DPPE)Pt(OMe)$_2$	2.037 (7) 2.041 (7)	2.222 (3) 2.228 (3)	O–C: 1.369 (14) O–C: 1.370 (13)
3 (73)	(DPPE)PtMe(OH)	2.025 (8)	2.200 (4)	Pt–P: 2.298 (3) Pt–C: 2.087 (10)
4 (46)		2.07 (1)	2.271 (4)	Pt–P: 2.348 (5) O–C: 1.37 (2) Pt–C: 1.96 (2)
5 (10)		2.017 (5)	Pt (olefin): 2.123 (8) 2.117 (8) mean Pt–C: 2.120 (6)	O–C: 1.341 (9) Pt–N: 2.083 (5)
6 (46a)		2.050 (5)	2.341 (1)	Pt–As: 2.402 (1) C–O: 1.361 (9)
7 (11)		2.027 (9)	2.036 (8)	Pt–NH: 2.02 (1) Pt–N: 2.035 (8)
8 (74)		2.030 (6) 2.034 (6)	2.210 (3) 2.220 (3)	C–O: 1.36 (1) 1.38 (1)

TABLE III. Bond Lengths (Å) in Iridium Alkoxides and Hydroxides

entry (ref)	complex	Ir–O	Ir–P	other remarks
1 (23a)	*trans*-Ir(PPh$_3$)$_2$(CO)(OPh)	2.049 (4)	2.328 (1) 2.344 (1)	O–C: 1.324 (6)
2 (23c)	*trans*-Ir(PPh$_3$)$_2$(CO)(OC$_6$F$_5$)	2.058 (3)	2.321 (1) 2.320 (1)	O–C: 1.302 (6)
3 (39)	*cis*-[(PMe$_3$)$_4$IrH(OH)]PF$_6$	2.119 (5)	2.259 (2) (trans to Ir–O)	Ir–P: 2.369 (2) (trans to Ir–H)
4 (39)	*cis*-[(PMe$_3$)$_4$IrH(OMe)]PF$_6$	2.118 (8)	2.274 (3) (trans to Ir–O)	O–C: 1.334 (16) Ir–P: 2.374 (3) (trans to Ir–H) other Ir–P: 2.345 (3) 2.336 (3)

bonding is involved. Interestingly, the O–C bonds in the alkoxo ligands are *shorter* than expected; this is especially true for oxygen bonded to sp^3 carbon, where O–C distances range from 1.26 to 1.38 Å (entries 1, 2, 6, and 8). For comparison, O–C bond distances of 1.43 Å were found for diethyl ether and ethanol, and 1.39 Å was noted for cobalt-complexed methanol.[70] This also seems to be the case for iridium (Table III); the O–C distance for *cis*-[(PMe$_3$)$_4$Ir(OCH$_3$)]PF$_6$ is 1.334 Å. For platinum alkoxides with sp^2 carbons attached to the oxygen, the O–C distances in the two cases reported are as expected (1.37 and 1.34 Å for entries 4 and 5 vs 1.34 Å found for formic acid and 1.369 Å for phenol).[40] However, with *trans*-Pd(PCy$_3$)$_2$(H)(OPh), the O–C distance is again shorter than expected (1.326 vs 1.369 Å for phenol). Also, for iridium alkoxides with sp^2 carbon bonded to oxygen, the O–C distances are 1.32 and 1.30 Å for entries 1 and 2 of Table III. As further structural determinations become available, it will be interesting to determine if short O–C bonds are a general feature of palladium, platinum, and iridium alkoxides.

The O–C distances are as expected in peroxo complexes. The O–C distances for (PPh$_3$)$_2$Pt(Ph)(O–O-*t*-Bu)[66c] and (phen)Pt(Me)$_2$(I)(O–O-*i*-Pr)[51a] are 1.47 (2) and 1.455 (13) Å, respectively. The Pt–O distances are within the range described above (1.99 (1) and 2.032 (6) Å).

The trans effect of the alkoxo and hydroxo ligands is smaller than for alkyl, acyl, and hydride substituents. For *cis*-L$_2$Pt(R)(OR′) (L$_2$ = DPPE, L = AsPh$_3$ and P(*p*-tolyl)$_3$; R = alkyl or acyl; see entries 1–4 and 6 of Table II), the Pt–P distance trans to the alkoxo or hydroxo ligand is shorter than the Pt–P distance trans to the R group. For iridium (entries 3 and 4 of Table III), the Ir–P distances trans to the alkoxo and hydroxo ligands (2.274 and 2.259 Å) are shorter than the Ir–P distances trans to the hydride (2.374 and 2.369 Å).

The Ir–O distances are shorter for iridium(III) than for iridium(I) (see Table III).

Structures of two tetrabis(phenolato)iron(III) complexes have been determined. Koch and Millar reported the structures of tetraethylammonium tetrakis(2,3,4,6-tetramethylphenolato)iron(III) and tetraphenylphosphonium tetrakis(2,4,6-trichlorophenolato)iron(III).[29] The Fe–O distances are 1.847 and 1.866 Å, respectively. In these cases, the O–C distances range from 1.32 to 1.35 Å, which are again shorter than expected. There are several reports on alkoxy–metalloporphyrin complexes;[71] O–C bond lengths in these porphyrin complexes average approximately 1.38 Å, though values range from 1.358[71e] to 1.45 Å.[70]

Several structures of cobalt alkoxides have been determined and they are summarized in Table IV. It appears that the O–C distances in these compounds are as expected.

TABLE IV. Bond Lengths (Å) in Cobalt Alkoxides and Amides

entry (ref)	complex	Co–O	Co–N	O–C
1 (28b)	$[(t\text{-BuO})_2CoCl]Li(THF)_3$	1.840 (5) 1.838 (3)		1.393 (7)
2 (28b)	$[(t\text{-BuO})_2CoN(SiMe_3)_2][(Li(THF)_{4.5}]$	1.849 (7) 1.851 (7)	1.985 (9)	1.38 (2) 1.40 (1)
3 (28b)	$[(t\text{-BuO})_2CoN(SiMe_3)_2]Li$	1.939 (6) 1.925 (6)	1.906 (2)	1.446 (9) 1.417 (10)
4 (68)	$[Co(OC(Ph)_3)]_2(THF)_2$	1.872 (2)		1.407 (3)
5 (70)	MeOCo(salen)(py)(MeOH)	1.89 (1)		1.45 (2) 1.39 (1) (for MeOH)

The coordinated alkoxo group is capable of forming hydrogen bonds. For example, the last entry of Table IV shows hydrogen bonding to methanol in solution, and the crystal structure of *trans*-(PhO)(H)Pd-$(PCy_3)_2$·HOPh has been reported, which shows the σ-bound phenoxide oxygen forms an unsymmetrical hydrogen bridge with the uncoordinated phenol molecule (eq 28).[40] Similarly, the structure of $(PMe_3)_3Rh(OC_6H_4\text{-}p\text{-}Me)$·*p*-cresol also shows asymmetric hydrogen bonding of the alkoxo ligand with the uncoordinated cresol with an O–O bond distance of 2.62 Å.[62]

There are only a few structures of late-transition-metal amide complexes reported, and only one structure has been determined that contains β-hydrogen atoms. The structure of (DMPE)PtMe[NMe(Ph)] has been reported. The Pt–N distance is 2.080 Å and the Pt–P distance trans to the amide group is shorter than the Pt–P distance trans to the methyl group (2.210 vs 2.275 Å). In this structure the trigonal plane of nitrogen is 68° out of the coordination plane of platinum. The N–C distances are as expected (1.455 Å for sp^3 C–N and 1.361 Å for sp^2 C–N).[12]

The paucity of monomeric late-transition-metal amide complexes may be due to the propensity for nitrogen to form stable intermetallic bridges. The use of large amido ligands has allowed the synthesis of several complexes containing terminal amido ligands. Structures with bulky ligands, $N(SiMePh_2)_2$,[28c] $N[Si(Me)_2CH_2PPh_2]_2$,[34b,d,e] $N(SiMe_3)_2$,[72] and NPh_2,[28a] have been reported. With $N(SiMe_3)_2$ and NPh_2, complexes containing both bridging and terminal ligands have been reported; $[\{M(NR_2)_2\}_2]$ (M = Ni, Co; R = Ph; M = Co; R = $SiMe_3$) contains both a bridging and terminal ligand[28a,72] where the bridging M–N distances are longer than the terminal M–N distances (e.g., Ni–N(bridging) = 1.91 Å vs Ni–N(terminal) = 1.83 Å).[73,74]

III. Fundamental Reactivity and Mechanisms

General

Late-metal alkoxide and amide complexes have generally been thought of as highly nucleophilic strong bases, with their high reactivity attributed to very weak M–O and M–N bonds. As noted in the previous sections of this review, in fact, structurally these linkages are predominantly covalent in nature and can be prepared and isolated for a wide variety of metals, ligand environments, and oxidation states by many different synthetic techniques, all of which indicate at least moderate thermodynamic stability.

Moreover, Bennett has examined $^1J_{PPt}$ for a wide variety of (DPPE)PtMe(X) systems and confirmed alkoxide and hydroxide ligands are moderate to weak trans-labilizing ligands (compared with alkyl or aryl substituents) and are best described as covalent linkages in the organic solutions studied.[10a] This characterization has been confirmed by Michelin and Strukul, who showed platinum(II) hydroxides are nonconductive in polar organic solutions.[66c,75] Only in very weakly basic alkoxide ligands, such as the perfluoropinacolates, where the trans influence drops to that of halogens or acetate, is there any suggestion of ionic character to these Pt–O bonds.[33b]

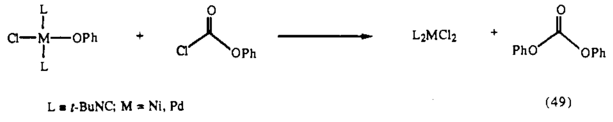
Rhodium and iridium complexes show similar characteristics. Vaska has studied the π-acidity of "X" ligands by measuring CO stretches in *trans*-X–M-$(PPh_3)_2(CO)$ (M = Rh, Ir) complexes and showed π-acidity decreases in the order X = I > SePh > Br > SPh > CN > Cl > NO_2 > NCS ~ N_3 > ONO_2 > NCO > OCOMe > OCOPh > OPh > OH ~ F.[21] He concluded the π-acceptor character of hydroxide is negligible and that of phenoxide is detectable, but insignificant.

In this section on the chemical reactivity of metal alkoxides and amides it will become clear that transformations involving these M–O and M–N bonds show many of the same mechanistic features as have been noted in the reactions of metal alkyl and hydride derivatives. To be sure, significant differences make these ligands unique. However, this unique reactivity of late-metal alkoxides and amides does not necessarily arise from weak M–X bonds.

Electrophilic and Nucleophilic Substitutions: σ-Ligand Metathesis Reactions

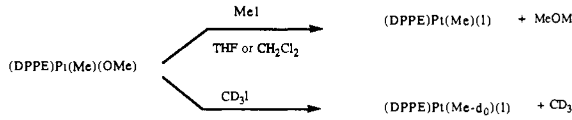
Reactions with Strong, Aprotic Nucleophiles and Electrophiles

Otsuka showed that palladium and nickel phenoxides react with acyl chlorides to generate diaryl carbonates as shown in eq 49.[48] Along the same lines, Bryndza has



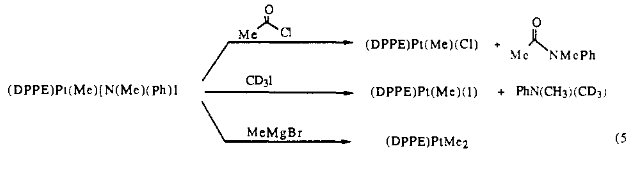
L = *t*-BuNC; M = Ni, Pd (49)

shown that (DPPE)PtMe(OMe) reacts with methyl iodide to quantitatively give the corresponding platinum iodide and dimethyl ether (eq 50).[4a] Estimates



(50)

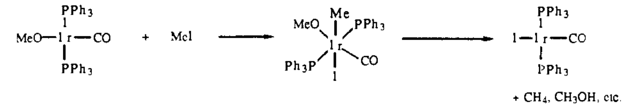
show methoxide dissociation from this complex (under reaction conditions) is at least a factor of 10^6 slower than this reaction, indicating that predissociation of methoxide is not involved in ether formation. Labeling studies (eq 50) show only the methoxide ligand and methyl iodide participate in dimethyl ether formation, suggesting a nucleophilic pathway rather than one involving oxidative addition of the electrophile to generate (DPPE)PtMe$_2$(I)(OMe) as an intermediate.[76] Similar nucleophilic chemistry has been reported for (DPPE)PtMe(NMePh) with acetyl chloride and CD$_3$I (eq 51).[12]



(51)

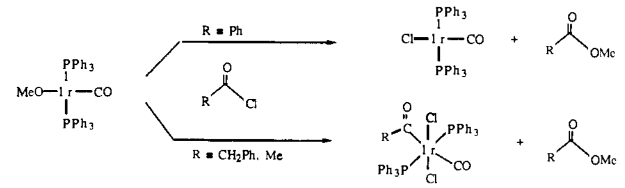
Additionally, these amide and alkoxide complexes react with MeMgBr to generate (DPPE)PtMe$_2$, indicating these ligands can be leaving groups under some circumstances.

Atwood has examined the reaction of *trans*-MeOIr(PPh$_3$)$_2$(CO) with methyl iodide to form *trans*-Ir(PPh$_3$)$_2$(I)(CO). An iridium(III) oxidative addition product, presumed to be an intermediate, can be isolated from reaction solutions (eq 52).[77] Electrophilic



(52)

reactions of the iridium methoxide with acid chlorides all yielded methyl esters (eq 53). No intermediate acyl methoxides were isolated; however, the mechanism is presumed to be the same as postulated for methyl iodide.

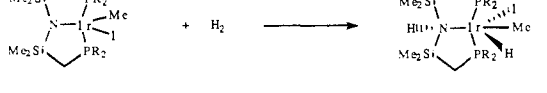


(53)

The chelating amides prepared by Fryzuk (eq 23) show interesting reactivity with nucleophiles and electrophiles. Rhodium and iridium(I) chelating amides react with methyl iodide to form M(III) (M = Rh, Ir) methyl iodido derivatives but there is no evidence of reductive coupling in these cases (eq 54).[34d,78] The

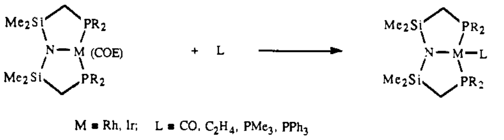
(54)

iridium(I) amides even react with activated C–H bonds, like those in toluene, to give amido hydrido alkyl derivatives.[79] Reaction of high-valent M(III) (M = Rh, Ir) species with electrophiles results in the *heterolytic* functionalization of the amide linkages; for example, when an iridium(III) methyl iodido complex is treated with hydrogen, the hydrogen atoms of the resulting hydrido amine complex are located on *opposite* sides of the N–Ir–P$_2$ coordination plane (eq 55).[78,80]



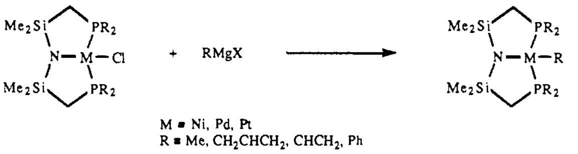
(55)

These amides also react quite cleanly with nucleophiles. When these rhodium or iridium(I) amides containing dative *cis*-cyclooctene ligands are treated with other dative ligands, the cyclooctene is displaced by the new donor ligand, leaving the amide linkages unaffected (eq 56).[34c,d] Nickel, palladium, and platinum



(56)

chelating amido chlorides can be treated with strong nucleophiles such as alkyl, alkenyl, and aryl Grignard reagents to generate new alkyl, alkenyl, and aryl amides (eq 57).[34b,e] Chelation of amide ligands may prevent

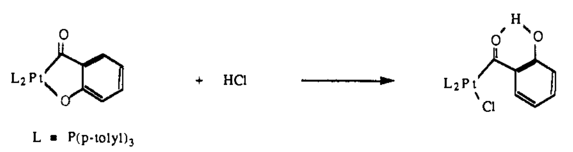


(57)

their displacement as a leaving group in the manner noted for the nonchelating platinum(II) analogues discussed above (eq 51).

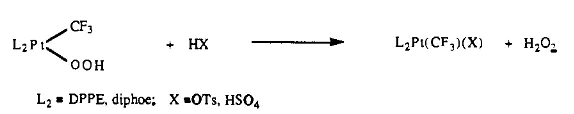
Reactions with Strong, Protic Electrophiles

With strong acids clean protonation of platinum(II) hydroxides, alkoxides, and peroxides with HX has been noted by Pregosin[8b] (eq 58) and by Ros, Michelin, and



(58)

Strukul[66a] (eq 59). As early as 1971 buffered solutions



(59)

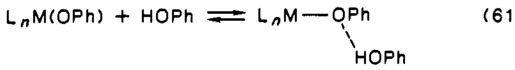
were used to generate (PEt$_3$)$_3$MH$^+$ cations from (PEt$_3$)$_3$Pt[81] and (PEt$_3$)$_3$Pd.[82] Kalck has observed similar protonation chemistry for (bpy)Pd(OH)$_2$(H$_2$O) with HCl to give (bpy)Pd(OH)(Cl)(H$_2$O).[15a]

An interesting contrast to this chemistry comes from the platinum(IV) alkoxides synthesized by Puddephatt and co-workers. In these compounds, ion exchange takes place with the outer-sphere ligand (believed to be hydroxide in most cases) but even strong acids leave the inner-sphere alkoxide ligand intact (eq 60).[42a,b]

$$[(bpy)Pt(OR)(Me)_2(H_2O)]OH + HX \rightarrow (bpy)Pt(OR)(Me)_2(X) + 2H_2O \quad (60)$$

trans-ROIr(PPh$_3$)$_2$(CO) and (C$_5$Me$_5$)Ir(PPh$_3$)H(OEt) also react with HCl to give *trans*-ClIr(PPh$_3$)$_2$(CO)[63] and (C$_5$Me$_5$)Ir(PPh$_3$)H(Cl),[25] respectively, and Lappert has reported a rhodium amide which is so reactive that it releases amine at 25 °C in benzene.[26,83]

Although there is little mechanistic information concerning the reactions of late-metal alkoxides, hydroxides, and amides with strong acids, some clue to the mechanism of these protonation reactions may be found in the recent work of Bergman[62] and Pasquali,[40] who have isolated and structurally characterized rhodium and palladium phenoxides, respectively, which are hydrogen bonded to phenol both in solution and in the solid state (eq 61). Bergman has shown that in solution



$$L_nM(OPh) + HOPh \rightleftharpoons L_nM{-}\underset{\textstyle \backslash HOPh}{O}Ph \qquad (61)$$

$(PMe_3)_3RhOAr(HOAr)$ complexes exchange the hydrogen-bonded aryl alcohols with free phenols very rapidly at room temperature. However, exchange of free aryl alcohols with σ-bound phenoxides requires significantly higher temperatures (70 °C). These results suggest hydrogen bonding of the entering acid to lone electron pairs on a σ ligand may assist the overall σ-ligand metathesis process discussed below. Thermochemical measurements in a variety of hydrocarbon solvents have shown the hydrogen bonds in these complexes are robust (10–14 kcal/mol), indicating there is considerable electron density at oxygen in the ground state of these inner-sphere phenoxides.

Reactions with Weak, Protic Electrophiles

While σ-ligand metathesis reactions were briefly discussed as a synthetic strategy to convert alkoxide derivatives to hydroxides and amides, the real generality of this reactivity (and its important thermochemical consequences) has not yet been discussed. The literature on this subject is heavily weighted with examples from the platinum(II) chemistry of Bennett.[10a,84] Dissolution of (DPPE)PtMe(OH) in "weak acids" (H–X) results in the formation of new Pt–X bonds with the concomitant release of water (eq 62).[10b] Similar reactions were reported by Ros and Michelin[9a,b] and Otsuka[3,85] for other palladium and platinum systems (eq 63).

$$L_2Pt(R)(OH) + H\text{-}X \rightarrow L_2Pt(R)(X) + H_2O \qquad (62)$$

$X = CH_2COMe, CH(COMe)_2, CH_2CN, CH_2NO_2,$
$OC_6H_4OMe, SH, SPh, NHCOMe,$
$CH(CN)_2, C(COMe)_3, CCPh, C_5H_5$

$R = Me, L_2 = DPPE$

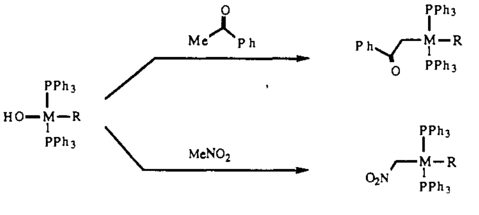
$L_2 = diphoe, 2PPh_3; R = CH_2CF_3, CH_2CN, CF_3$

$X =$
$CCPh, NHCOMe, NMePh, CH_2NO_2, CH_2C(O)Ph$

$X = CH_2NO_2, CH_2COMe, OC_6H_4Me, CCPh,$
$NHCOMe, NMePh$

$R = Me; L = P(t\text{-}Bu)_2Me, P(i\text{-}Pr)_3$

$R = Ph; L = PCy_3, P(t\text{-}Bu)_2Me, P(t\text{-}Bu)Me_2, PEt_3,$
$PMePh_2, PMe_2Ph$



(63)

R = C_6F_5, $CCl{=}CCl_2$, $CH{=}CCl_2$, Ph; M = Pt, Pd

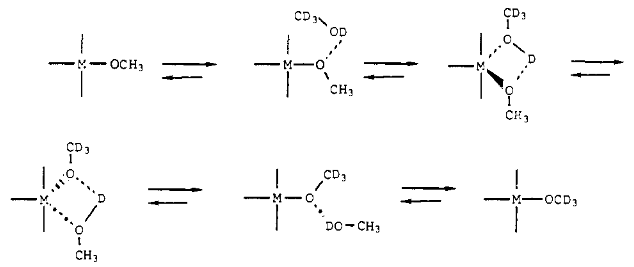
The mechanisms of these reactions have recently been explored.[4b] The reaction of (DPPE)PtMe(OMe) with water (to generate the hydroxide complex) is *reversible* (eq 64) and nearly thermoneutral. Similarly, the equilibrium constant for addition of amines to (DPPE)PtMe(OMe) is 0.8 and is invariant over a wide range of concentrations, temperatures, solvents, and changes in reaction vessels (eq 65).[12] Other quantitative measurements for exchange reactions of (DPPE)-Pt(Me)(OMe) and $(DPPE)Pt(OMe)_2$ with $DOCD_3$ (eq 66) have also been reported.[4c] A mechanistic study of these thermoneutral, degenerate exchange reactions showed bimolecular kinetics over a wide range of conditions. This result demonstrates the reaction does not proceed by methoxide dissociation, even in 50/50 $CD_3OD/THF\text{-}d_8$.[4c] These experiments place an *upper* limit (but *not* an absolute value) on the rate of methoxide dissociation of 10^{-7} s^{-1} ($\Delta G > 27$ kcal/mol) for both (DPPE)Pt(Me)(OMe) and $(DPPE)Pt(OMe)_2$ based on the limits of detectability of dissociative pathways.[86]

$$(DPPE)Pt(Me)(OMe) + H\text{-}OH \rightleftharpoons (DPPE)Pt(Me)(OH) + H\text{-}OMe \qquad (64)$$

$$(DPPE)Pt(Me)(OMe) + H\text{-}NMePh \underset{\text{THF or toluene}}{\overset{K = 0.8}{\rightleftharpoons}} (DPPE)Pt(Me)(NMePh) + H\text{-}OMe \qquad (65)$$

$(DPPE)Pt(R)(OMe) + D\text{-}OCD_3 \rightleftharpoons$
$R = Me$
$(DPPE)Pt(R)(OCD_3) + D\text{-}OCH_3 \rightleftharpoons$
$(DPPE)Pt(R)(OCD_3) + D\text{-}OCH_3 \rightleftharpoons$
$R = OMe$
$(DPPE)Pt(OCD_3)_2 \quad (66)$

SCHEME I



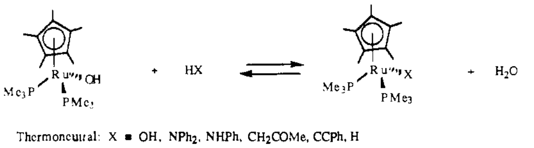
Interestingly, at very low methanol concentrations, good donor solvents can apparently compete with methanol for the necessary coordination site on platinum and, thereby, retard the degenerate exchange reaction. Thus while the possibility of initial methanol coordination to platinum through hydrogen bonds to the methoxide ligands (as in the Bergman and Pasquali phenoxides) may be critical to this reactivity, it appears that access to the metal is also helpful for productive exchanges to take place.

Methanol exchange can be catalyzed by traces of acids or bases in these solutions. Thus while the mechanism for "weak acid" exchange in these systems might proceed as depicted in Scheme I, the involvement of autocatalytic mechanisms cannot be ruled out under conditions where no added acid or base is present. Routes involving protonation of methoxide ligands and displacement by methanol or simple degenerate displacement of methoxide by OCD_3^- are kinetically indistinguishable from the mechanism in Scheme I, although the heterolysis constants for methanol might be expected to vary significantly with solvent.

Bryndza and Bercaw quantified σ-ligand exchange reactions for a number of platinum and ruthenium derivatives as shown in eq 67 and 68 in order to obtain

$$(DPPE)PtMe(OMe) + H\text{-}X \rightleftharpoons (DPPE)PtMe(X) + H\text{-}OMe \quad (67)$$

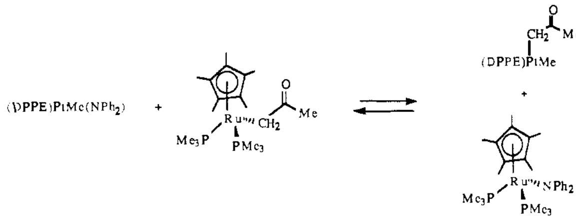
Thermoneutral: X = OMe, OH, NMePh, NPh_2, NHPh, CH_2COMe
"Irreversible": X = Cl, SH, CN, $CpM(CO)_3$ (M = Cr, Mo, W), $Si(OEt)_3$



(68)

Thermoneutral: X = OH, NPh_2, NHPh, CH_2COMe, CCPh, H
"Irreversible" : X = SH, CN, $CpM(CO)_3$ (M = Cr, Mo, W), $Si(OEt)_3$, Cl

relative M–X bond strengths for these derivatives (vide infra).[31] In cases where the H–X compounds studied contained other first-row, main-group elements, the reactions were essentially thermoneutral.[87] The equilibrium constants were invariant despite changes in concentrations, temperature, solvents, and reaction vessel walls. However, for derivatives of second-row, main-group elements (or transition metals), reactions 67 and 68 are essentially irreversible.[88] The reactions of ruthenium were generally faster than those of platinum; rapid exchange of σ ligands between the platinum diphenyl amide and the ruthenium acetone enolate (eq 69) demonstrates that protic materials (i.e., hydrogen-bonding interactions) need not be involved for these reactions to take place. While coordination of substrates to platinum apparently assists exchange reactions, it is not always required. The reaction shown in eq 69 would be expected to be very slow if it depends on a bimolecular interaction of such large complexes.



(69)

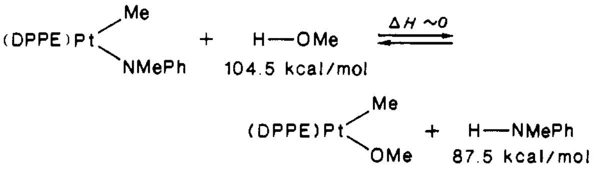
The ruthenium exchange reactions take place much faster than coordination sites are opened by phosphine ligand dissociations in those systems,[89] indicating that either(1) four-centered transition states are formed when H–Y substrates interact with Ru–X bonds or 2) the η^5-C_5Me_5 ring changes hapticity to accommodate a coordinative reaction. The results of Bergman (for rhodium) suggest the former, with the lone electron pairs on oxygen or nitrogen able to act as "anchors" directing a four-centered transition state.

In a related reaction with $[(PMe_3)_4IrH(OH)]^+$, Milstein showed σ-ligand exchange of that material with D_2O results in the rapid formation of $[(PMe_3)_4IrH(OD)]^+$, indicating that four-centered transition states (rather than reductive elimination–oxidative addition sequences) are viable mechanisms for these exchange reactions (eq 70).[39]

$$[L_4IrH(OH)]^+ + \text{excess } D_2O \rightarrow [L_4IrH(OD)]^+ + HOD \quad (70)$$

Homolytic L_nM–X (X = OR, OH, NR_2) Bond Strengths

The most significant aspect of near-unity equilibrium constants for reactions 65, 67, and 68 is that relative L_nM–X (X = H, CR_3, NR_2, and OR) bond strengths may be estimated from these data. As outlined for eq 65,[12] the near-unity value of this equilibrium constant shows the free energy of equilibrium is essentially zero. Since the equilibrium is independent of temperature, both entropy and enthalpy contributions to ΔG are also necessarily near zero. Because the equilibrium is independent of solvent and concentration, gas-phase bond strengths for the H–O and H–N bonds in methanol and methylaniline may be used in a conventional functional group additivity analysis of this equilibrium (eq 71).[90]



(71)

Pt-O > Pt-N by 17 kcal/mol

Such an evaluation suggests that the M–O bond in (DPPE)Pt(Me)(OMe) must be 17 kcal/mol stronger than the M–N bond in (DPPE)Pt(Me)(NMePh) (eq 71). Put another way, this suggests (DPPE)PtMe$^\bullet$ radical fragments behave like large hydrogen atoms in terms of binding organic radical fragments.

The observation that H–X bond strengths generally correlate in a 1:1 fashion with relative L_nM–X bond strengths for reactions 67 and 68 (as summarized in eq 72)[31] allows for the determination of *relative* L_nM–O,

$$L_nM\text{-}X + H\text{-}Y \overset{\Delta H \sim 0}{\rightleftharpoons} L_nM\text{-}Y + M\text{-}X \quad (72)$$

$$\text{if } \Delta H{\sim}0, \text{ then } D(H\text{-}Y) - D(H\text{-}X) \sim D(M\text{-}Y) - D(M\text{-}X)$$

L_nM–C, L_nM–H, and L_nM–N homolytic bond strengths. Two important ramifications of these observations were cited: (1) since H–X bond strengths correlate with relative L_nM–X bond strengths, the relative strengths of L_nM–X bonds that have not yet been measured can be estimated simply by knowing the H–X bond strength of the parent organic compound and (2) since this correlation is general for these very different $(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuX$ and (DPPE)PtMeX systems, such an approach to organometallic thermochemistry may prove general for other metal systems and ligand environments as well.

For the purposes of this review, a few other points from these papers concerning the relative stabilities of L_nM–O and L_nM–N bonds should be mentioned. While L_nM–N bond strengths are weaker than L_nM–C bond strengths (presumably for the same reasons the H–N bonds in amines are weaker than the H–C bonds in alkanes), L_nM–O bond strengths for alkoxides are comparable to M–C(sp^3) bond strengths in alkyls. Moreover, L_nM–OH bonds in hydroxide complexes are significantly stronger than either L_nM–C bonds in alkyl complexes or L_nM–O bonds in alkoxide derivatives.[91] These results show that there are no significant π interactions between alkyl, alkoxide, hydroxide, or amide ligands and late-transition-metal centers (as had been concluded earlier by other studies as mentioned above) and illustrate that carbon, nitrogen, and oxygen are *equally* "hard" ligands for these late-transition-metal systems. The implication of the "irreversible" reactions noted in eq 67 and 68 (and other results in those papers) is that second-row, main-group derivatives are also as equally "hard" *as one another* but are, as a class, "softer" than first-row, main-group analogues.

No reliable method has yet been determined for placing these relative bond strengths on an absolute

SCHEME II. Heterolytic Ligand Dissociation

$$\begin{array}{lll}
 & & K_{eq} \\
(1) & \text{(DPPE)MePt-OMe} \rightleftharpoons \text{(DPPE)MePt}^+ + \text{OCH}_3^- & K_1 \\
(2) & \text{(DPPE)MePt}^+ + \text{NMePh}^- \rightleftharpoons \text{(DPPE)MePt-NMePh} & 1/K_2 \\
\hline
(3) & \text{(DPPE)MePt-OMe} + \text{NMePh}^- \rightleftharpoons \text{(DPPE)MePt-NMePh} + \text{OMe}^- & K_1/K_2 \\
 & & \\
(4) & \text{H}^+ + \text{OMe}^- \rightleftharpoons \text{H-OMe} & 1/K_a(\text{HOMe}) \\
(5) & \text{H-NMePh} \rightleftharpoons \text{H}^+ + \text{NMePh}^- & K_a(\text{HNMePh}) \\
\hline
(6) & \text{H-NMePh} + \text{OMe}^- \rightleftharpoons \text{H-OMe} + \text{NMePb}^- & K_a(\text{HNMePh})/K_a(\text{HOMe}) \\
 & & \\
(7) & \text{(DPPE)MePt-OMe} + \text{H-NMePh} \rightleftharpoons \text{(DPPE)MePt-NMePh} + \text{H-OMe} &
\end{array}$$

$$\text{For Eq. 7} \quad K = \frac{[K_1][K_a(\text{HNMePh})]}{[K_2][K_a(\text{HOMe})]} \quad ; \quad \frac{K_1}{K_2} = \frac{K_a(\text{HOMe})}{K_a(\text{HNMePh})} \quad \text{since } K - 1$$

scale. The L_nM–N bond in $(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuNPh_2$ has a homolytic bond strength *greater* than 25 kcal/mol, but an absolute D(Ru–N) for this derivative (or any other) has yet to be determined. Vaska has estimated that the Ir–O bonds in $(PPh_3)Ir(O_2)(CO)X$ compounds have homolytic strengths of between 40 and 50 kcal/mol from dioxygen binding enthalpies.[92] However, this method does not take into account changes in the O–O bond strength of dioxygen, any rehybridization and oxidation enthalpies of iridium, or enthalpies of solvation for dioxygen and so must be regarded as a fairly crude estimate.

Heterolysis of L_nM–X (X = OR, OH, NR_2) Bonds

Intrinsic Properties of L_nM–X Bonds

Another method of evaluating the equilibria shown in eq 65–72 has been described[12,31] and is illustrated for eq 65 in Scheme II. As shown, the equilibrium constant for eq 7 (Scheme II) may be expressed as the product of the ratio of acid dissociation constants (K_a's) and the ratio of (DPPE)MePt–OMe to (DPPE)MePt-Me–NMePh heterolytic dissociation constants (K_1 and K_2, respectively):

$$K_{eq} = \frac{K_1K_a(\text{HNMePh})}{K_2K_a(\text{HOMe})}$$

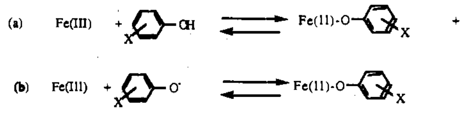
Because the measured equilibrium constant K_{eq} is approximately 1, it follows that the relative extent of (DPPE)MePt–OMe and (DPPE)MePt–NMePh bond heterolysis (K_1/K_2) is equal to the relative acid dissociation constants for H–OMe and H–NMePh [K_a(HOMe)/K_a(HNMePh)]. Using aqueous solution values of K_a for methanol and methylaniline (pK_a = 16 and 25, respectively), one finds the extent of [$NMePh^-$] dissociation from (DPPE)MePtNMePh in aqueous solution is 10^9 less than [OMe^-] dissociation from (DPPE)MePtOMe. While this ratio will vary as the ratio of K_a values varies in different solvents, the conclusion remains the same: the relative extent of (DPPE)MePt–X bond heterolysis parallels the relative K_a values of the H–X analogue.[93]

Because the thermoneutral character of eq 72 appears to be quite general, this correlation of HX and L_nMX *heterolysis* constants will also be general for these systems.[31] Put more simply, just as $L_nM^\bullet$ radicals behave like large hydrogen atoms for the binding of organic radical fragments, L_nM^+ ions will act as large protons in terms of binding anionic substrates. In concrete terms this suggests that for various L_nM–OR bonds under identical conditions, acetates will be more completely ionized than phenoxides, which, in turn, will be more ionized than hydroxides or alkoxides. The corresponding L_nM–NR_2 complexes will be even more difficult to ionize (for the same reasons that organic amines heterolyze less completely than alcohols or water). It must be stressed that under the conditions where these equilibria were studied no heterolysis was noted in any of these cases, and kinetic measurements show the rates of dissociation to be undetectable (below 10^{-7} s^{-1}). Nevertheless, as the following section will demonstrate, this appears to be precisely what has been noted for other related systems in different solvents where heterolysis can be quantified.

Role of Solvents in L_nM–X Bond Heterolysis

While it is clear from the above discussion that for a given ligated late-transition metal system, L_nM–X, the nature of X plays a major role in heterolysis, the role of environmental factors has not yet been described. As might be supposed, choices of ligand, temperature, and, especially, solvent appear to make a profound difference in the heterolysis reactions of metal hydroxides, alkoxides, and amides.

Perhaps the best illustration of the preeminent role played by solvation and ligand basicity in the heterolysis of metal alkoxides comes from some early work by Milburn, who determined ΔG, ΔH, and ΔS for eq 73a,b

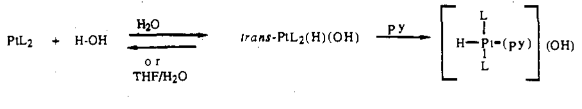


(73)

X = H, p-NO_2, m-NO_2, p-CN, m-CN, o-CN, p-Cl, m-Cl, o-Cl, p-CHO

in aqueous media of constant ionic strength at 25 °C.[94,95] Enthalpy differences in the reactions of different phenoxides with Fe^{3+} were small and entropic variations dominated the reaction free energies. Even more telling, ΔS_{eq} for the ostensibly bimolecular reactions shown in eq 73b ranged from +24 to +33 eu, indicating that *major* entropic changes in ion solvation are dominating the energetics of this aqueous reaction chemistry. The dissociation equilibrium constants ($1/K_{eq}$ for eq 73b) correlate with the K_a values of the parent phenols as indicated by eq 72.

The same profound solvation effects on dissociation equilibria have been noted in more recent work with platinum, palladium, and rhodium hydroxo complexes. For example, Otsuka first published detailed studies on the interactions of L_nPt with water in 1979[37] and reviewed this (and other) chemistry in 1980.[96] He noted that these interactions can be summarized by the dynamic and interacting equilibria shown in Scheme III, where solvation plays a major role in determining the relative importance of the various dissociation equilibria. For example, in water or water/THF systems, (P-*i*-$Pr_3)_nPt$ (n = 2, 3) forms a highly reactive *inner*-sphere hydrido–hydroxo complex by oxidative addition, as shown in eq 74. This unstable complex can be isolated



$$\text{PtL}_2 + \text{H-OH} \underset{\text{THF/H}_2\text{O}}{\overset{\text{H}_2\text{O}}{\rightleftharpoons}}_{\text{or}} \textit{trans}\text{-PtL}_2\text{(H)(OH)} \xrightarrow{\text{py}} \left[\text{H}-\overset{\text{L}}{\underset{\text{L}}{\text{Pt}}}\text{-(py)}\right]\text{(OH)}$$

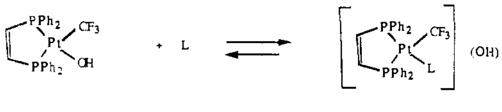
L = P(i-Pr)$_3$ (74)

SCHEME III

$$\begin{aligned}
&L_3Pt \rightleftharpoons L_2Pt + L\\
&L_2Pt + H_2O \rightleftharpoons L_2PtH(OH)\\
&L_2PtH(OH) + S \rightleftharpoons [L_2PtH(S)](OH)\\
&[L_2PtH(S)](OH) \rightleftharpoons L_2PtH(S)^{+} + OH^{-}\\
&L_3Pt + H_2O \rightleftharpoons [L_3PtH](OH)\\
&[L_3PtH](OH) \rightleftharpoons L_3PtH^{+} + OH^{-}\\
&L_3PtH^{+} + S \rightleftharpoons L_2PtH(S)^{+} + L
\end{aligned}$$

at low temperature. However, the addition of pyridine to these systems (or to the isolated hydroxo complex) results in formation of cationic platinum hydride and solvated hydroxide ions. The triethylphosphine analogues generate conducting solutions even in water alone (i.e., in the absence of pyridine). Otsuka also reports *trans*-$(PPh_3)_2PtPh(OH)$ is a nonconductor in THF but conducts in pyridine.[37]

As part of a mechanistic study on catalytic oxidation chemistry, Strukul and Michelin described details of $(L_2)PtR_x(OH)$ conductivity in different reaction media.[97] Again, profound differences in conductivity of solutions of these species are seen in different solvents. While no dissociation of hydroxide complexes was noted in nitromethane, (diphoe)$PtCF_3(OH)$ dissociates up to 20% in $H_2O/HOMe$ solution (eq 75; L = H_2O).



(75)

Moreover, more traditional donor ligands can play a significant role in M–O bond heterolysis. In dichloroethane, the normally nonconducting (diphoe)$PtCF_3$(OH) can become 15% ionized when 1 equiv of PPh_3 is added and approximately 40% ionized when 1 equiv of $P(n\text{-}Bu)_3$ is introduced (eq 75). At 4:1 $P(n\text{-}Bu)_3$:Pt the equilibrium in eq 75 is shifted essentially completely to the right in favor of ions. While no results were reported when π acids, such as olefins or CO, were added to (diphoe)$PtCF_3(OH)$, based on the trend $P(n\text{-}Bu)_3 > PPh_3 > H_2O$, it would appear that strong donor ligands favor hydroxide dissociation by stabilizing an otherwise electrophilic platinum cation.

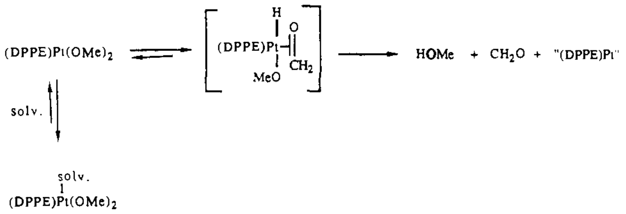
Yoshida and Otsuka report similar dissociative reaction chemistry for $(PR_3)_3RhH$ (R = alkyl) in water (eq 76).[98] They summarize the aqueous chemistry of

$$(PEt_3)_3RhH + H_2O \rightleftharpoons (PEt_3)_3RhH_2^{+} + OH^{-} \qquad (76)$$

platinum and hydridorhodium phosphine complexes by stressing that hydroxide dissociation can take place in good coordinating solvents and that electron-rich donor ligands favor ion formation.

The observations in this section may seem fairly trivial and innocuous in the overall scheme of late-metal alkoxide, hydroxide, and amide chemistry. However, metal–ligand bond heterolysis provides unique reactivity for these ligands that is not generally available to alkyl or hydride complexes of the group VIII metals. More than any other factor, the question of L_nM–X bond heterolysis has complicated mechanistic studies involving stoichiometric reactions of these compounds and has made definitive evaluation of catalytic reaction mechanisms extremely difficult, as will be seen below.

SCHEME IV



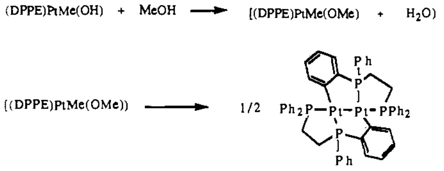
β-Hydride Elimination from Metal Alkoxides and Amides and RC(O)R′ (R = H, Alkyl, Aryl) Insertions into Metal–Hydrogen Bonds

Many late-metal hydride syntheses have been reported that are believed to involve metal alkoxide and amide intermediates.[9a,31,57e,99-104] In some cases, especially when alcohols have been added to preformed platinum hydroxide complexes, alkoxide intermediates have been spectroscopically identified. Generally, these species have not been isolated, but lead smoothly to hydrides without buildup of intermediates.

Bennett observed the first β-hydride migration from a metal alkoxide complex when he isolated and thermolyzed *trans*-$Pt(PPh_3)_2(C_6H_9)(OCH_3)$ (eq 77).[57b] The

(77)

cis analogue $(DPPE)Pt(C_6H_9)(OCH_3)$ is more resistant to β-hydride elimination. Bennett also published a crystal structure of the platinum-containing product generated in the thermolysis of (DPPE)PtMe(OH) in methanol (during which the methoxide intermediate was spectroscopically detected) (eq 78).[105] Bryndza and



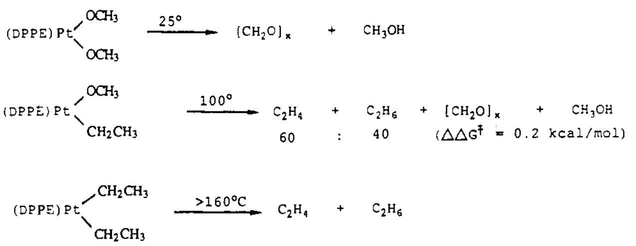
(78)

co-workers reported the preparation and thermolysis of (DPPE)PtMe(OMe) and $(DPPE)Pt(OMe)_2$. Decomposition of these alkoxide complexes gives the same platinum dimer as in eq 78 along with formaldehyde oligomers and methanol. Small amounts of CO and CO insertion products were also observed (eq 79).[4b]

$$(DPPE)Pt(OMe)_2 \xrightarrow[25\ ^\circ C]{} [CH_2O]_x + MeOH + \text{small amounts of CO} \qquad (79)$$

The thermolyses of (DPPE)PtMe(OMe), (DPPE)PtEt(OMe), $(DPPE)Pt(OCH_2CH_2O\text{–})$, and $(DPPE)Pt(OMe)_2$ have been the subject of detailed mechanistic investigations.[4c] The β-hydrogen eliminations from metal alkoxides and amides appear to be intramolecular migratory deinsertion processes that are mechanistically very similar to their hydrocarbon analogues. The thermolysis of the bis(methoxide) (Scheme IV) proceeds through preequilibrium β-hydrogen migration from a methoxide substituent to the metal followed by rate-limiting release of organic products. The facile, unimolecular decomposition ($\Delta H^{\ddagger} = 15.4 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -24 \pm 5$ eu) is more than 10^3 times faster than the *upper limit* of methoxide dissociation rates. The large negative $\Delta S^{\ddagger}$ value suggests structural rear-

SCHEME V

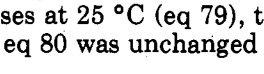


rangement of the intermediate (such as interconversion of a *trans*-hydrido methoxo intermediate into a cis geometry) may be kinetically significant. Labeling studies, which showed only the methoxide ligands are involved, suggest β elimination is a preequilibrium step (i.e., not rate limiting) and that deprotonation of one methoxide ligand by another in the same molecule is not important. Interestingly, solvent effects show donor solvents, like THF, can coordinate to the 16-electron platinum center, blocking the open coordination site, which is apparently required for β-hydrogen elimination to take place. Thus, although the bis(methoxide) decomposes at or below room temperature (at the same rates) in CD_2Cl_2, toluene-d_8, and α,α'-dimethyltetrahydrofuran, the rate of decomposition in THF-d_8 is dramatically slower, indicating that the metal is intimately involved in this transformation. This feature suggests the reason methanol cosolvent is so advantageous in the synthesis of this material is because it blocks β eliminations.

Although these reactions represent a low-energy pathway for the activation of carbon–hydrogen bonds, they are not "easier" than β eliminations from metal alkyls; this is likely due to the similarity of L_nM–C and L_nM–O bond strengths. In (DPPE)PtEt(OMe) both the alkyl ligand and the alkoxide ligand bear three β-hydrogen atoms. By measuring product ratios from its thermolysis (Scheme V), β-hydride elimination from the ethyl substituent was shown to be favored by 0.2 kcal/mol ($\Delta\Delta G^{\ddagger}$) over decomposition proceeding through β elimination from the methoxide ligand. Labeling studies with (DPPE)Pt(CH_2CD_3)(OCH_3) confirm the preequilibrium nature of β elimination in the ethyl substituent.

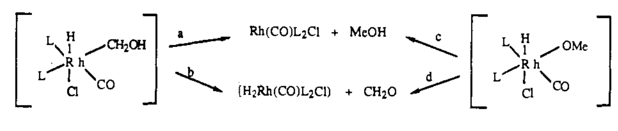
Interestingly, these results show that replacing an ethyl substituent with a methoxo ligand in either (DPPE)$PtEt_2$ or (DPPE)PtEt(OMe) results in a dramatic drop in the activation barrier for decomposition proceeding through β elimination. The origin of this acceleration is unknown, but since the alkoxide is the weaker trans-labilizing ligand, it seems unlikely that dissociation of the chelating ligand is facilitated by this change. Increasing the Lewis acidity of platinum, improving the ease of square-plane distortion, and raising the energies of the π^* orbitals on Pt have been suggested as possible explanations of this spectator ligand effect.

In addition to the basic mechanistic similarities of β-hydride eliminations from metal alkyl and alkoxide derivatives, there is a parallel in the stability of metallacycles as well. While (DPPE)$Pt(OMe)_2$ decomposes at 25 °C (eq 79), the chelating glycolate shown in eq 80 was unchanged after heating at 120 °C for 3 days. This metallacycle stability is similar to that reported for metallacyclopentanes vis-à-vis diethyl derivatives for platinum(II) bis(phosphine) systems.[106]



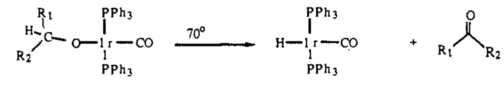
(80)

Interestingly, no hydroxymethyl species that are structural isomers of the methoxide complexes have been identified or isolated during these thermolyses, although thermochemical estimates[31] suggest they might be isoenergetic structures. Milstein has reported that the thermolysis of $(PMe_3)_2$(CO)(Cl)(H)RhOMe leads primarily to methanol instead of formaldehyde (a 95:5 preference) while the hydroxymethyl analogue gives formaldehyde in preference to methanol (an 87:13 preference for β elimination) (eq 81).[107] Thus, it may be that in the platinum system either (a) β-hydride elimination from a hydroxymethyl derivative is faster than from the methoxy isomer, (b) reductive elimination for the alkyl hydride is slower than for the methoxide, or (c) the methoxide is favored thermodynamically.[108] It is not clear for which of these reasons hydroxymethyl compounds have not been observed during methoxide thermolyses.[4b,c]



a/b = 13/87 c/d = 95/5 (81)

Atwood has obtained mechanistic information on β-hydride eliminations for some iridium alkoxides.[109] As shown in eq 82, $ROIr(PPh_3)_2(CO)$ complexes decompose at moderate temperatures to generate iridium hydrides and aldehydes or ketones. Since the hydroxide and *tert*-butoxide derivatives are stable, bond homolysis or base-catalyzed decomposition routes must be considered unlikely. No molecularity information has been reported for this transformation; the possibility that alkoxide ions serve as hydride donors cannot be dismissed at this point.



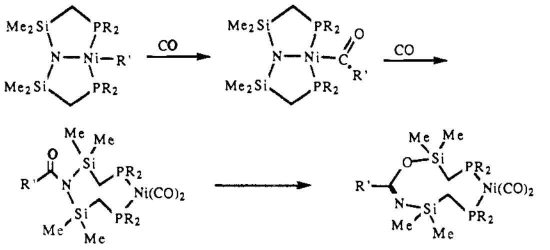
(82)

$R_1 = R_2 = H$, Me; $R_1 = Et$, $R_2 = H$

While mechanistically well-characterized examples of β-hydride elimination reactions of alkoxide and amide substituents are rare, the microscopic reverse—insertion of aldehydes and ketones into metal–hydrogen bonds to generate alkoxide ligands—has been implicated in many catalytic hydrogenation reactions (vide infra). In addition to these catalytic studies, Otsuka has shown that hydrogenation of an α-keto amide with an iridium catalyst does not proceed to completion but, rather, can be intercepted at the hydrido alkoxo stage, in which the second carbonyl group helps stabilize the complex through dative interactions with iridium (eq 27).[38]

Oxidative Addition of C–O and C–N Bonds to Late Metals and Reductive Coupling To Form C–O and C–N Bonds

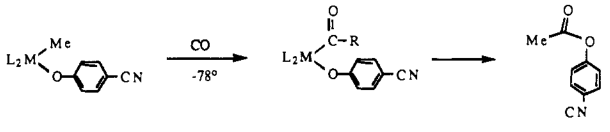
While examples of C–N or C–O bond couplings are rare, a few interesting findings have been reported. Chelating nickel and palladium amide complexes containing alkyl, alkenyl, and aryl substituents react with carbon monoxide to generate acyl derivatives. Insertion of CO into the metal–nitrogen bond of these amides has not been observed. The nickel acyl complexes react with additional CO to generate new products in which C–N reductive coupling has taken place followed by rearrangement of the disilyl amides to generate compounds having oxygen–silicon bonds (eq 83).[34e,110,111]



(83)

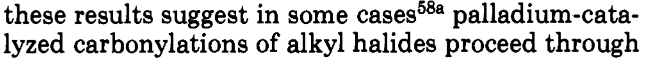
Kinetics measurements demonstrate that coordination of an additional carbon monoxide ligand to nickel to generate a five-coordinate intermediate is needed to effect the C–N coupling step.

Carbonylation of methylnickel and methylpalladium phenoxides generates acyl complexes by preferential insertion of CO into metal–carbon rather than metal–oxygen bonds (eq 84).[58] Gentle warming of these acyl phenoxide complexes yields organic esters. With nickel, this reductive coupling is assisted by π acids like CO and olefins while the palladium system is unaffected by these reagents.[112] Reaction of an acylpalladium chloride with basic methanol generates methyl phenylacetate at 80 °C (eq 85).[113] It is unclear whether C–O bond formation involves direct nucleophilic attack by methanol or methoxide on the acyl substituent bound to palladium or whether an intermediate alkoxide complex is generated. Interestingly, the palladium benzyl carbomethoxide *trans*-$(CO_2Me)Pd(PMe_3)_2(CH_2Ph)$ does not generate ester at 80 °C. Together these results suggest in some cases[58a] palladium-catalyzed carbonylations of alkyl halides proceed through CO insertions into metal–carbon, rather than metal–oxygen, bonds. Ester formation may take place through reductive coupling of acyl and alkoxo substituents. In other very similar cases the metal–oxygen bonds in (bpy)MMe(OR) [M = Ni, Pd; R = $CH(CF_3)_2$, CH_2CF_3, $CH(CF_3)C_6H_5$] complexes preferentially insert CO to form carbalkoxides which couple to form acetate esters.[58b]



M = Ni, Pd; L_2 = bipy, L = PEt_3

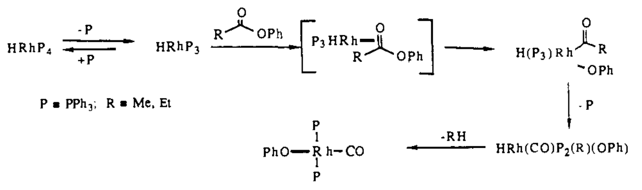
(84)

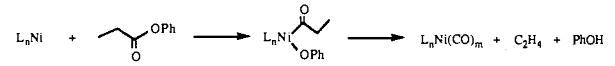


(85)

While the molecularity of these transformations has not been established, reductive coupling of metal alkoxide and amide substituents with metal acyls may be a generally useful mechanism for the production of new C–O and C–N bonds. The microscopic reverse of this process, the activation of C–O or C–N bonds to form metal alkoxides and amides, appears to be favored for many electron-rich metal phosphine complexes. Organic esters react with cobalt, rhodium, and nickel complexes to insert metals into C–O bonds. Nickel complexes can convert phenyl propionate into ethylene, CO, and phenol (eq 86).[114] Subsequent studies show P_4RhH complexes react with phenylacetates to generate rhodium carbonyl phenoxides (eq 87).[47a] Kinetics measurements suggest these reactions proceed through preequilibrium ligand dissociation followed by trapping of the coordinatively unsaturated intermediate with ester as shown in Scheme VI. The presence of electron-donating substituents (X = *p*-Et, *o*-OMe) on the phenoxide ring slows the rate of reaction while electron-withdrawing substituents (X = *m*-CF_3) accelerate it. It is unclear if electron-withdrawing substituents merely facilitate ester coordination to the electron-rich metal center or if C–O bond activation is kinetically significant in this process. There has been no indication of outer-sphere chemistry in these systems, but it is possible that the electron-rich metal center acts as a nucleophile to generate a cationic acyl complex and phenoxide anions which then collapse to form a covalent metal–oxygen bond. Since these observations of C–O bond activation have been extended to alkyl esters, the involvement of outer-sphere mechanisms must be regarded as highly unlikely. Similar chemistry has been observed in the $(PPh_3)_4RuH_2$ and $(PPh_3)_3(N_2)CoH$ catalyst systems as well.[47a,b]

SCHEME VI





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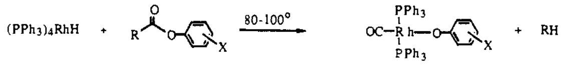


R = Me, Et; X = H, *p*-OMe, *m*-CF_3, *p*-Et, *o*-OMe

(87)

Interestingly, nickel and palladium appear to insert CO into M–C bonds in preference to M–O or M–N bonds in some cases. In other cases[58b] the reverse is true, indicating the migratory aptitudes of alkoxo and alkyl substituents may be very similar for these metals. For more information on this possibility, the reader is referred to Kubiak's work on the insertion reactivity of terminal alkoxo and hydroxo ligands in binuclear systems.[115]

Insertions into Metal–Oxygen and Metal–Nitrogen Bonds

Carbon Monoxide Insertion into Metal–Oxygen and Metal–Nitrogen Bonds

The most significant body of literature on CO insertion into metal–oxygen and metal–nitrogen bonds involves platinum(II) compounds. Clark has prepared the platinum hydroxycarbonyl complex *trans*-$ClPt(PEt_3)_2(CO_2H)$ by treating *trans*-$ClPt(PEt_3)_2(CO)$ with hydroxide.[116] A similar triphenylphosphine platinum carbomethoxide derivative was prepared by Beck when methoxide was added to a platinum carbonyl cation (eq 88).[117] This same complex was formed by reacting a

$$(PPh_3)_2Pt(CO)(CO_2Me)^+ + MeO^- \rightarrow (PPh_3)_2Pt(CO_2Me)_2 \quad (88)$$

platinum dichloride with KOH in the presence of methanol and CO (eq 89).[118] Proposed mechanisms for

$$(PPh_3)_2PtCl_2 \xrightarrow[-2KCl,\ -2H_2O]{2KOH/2MeOH/2CO} (PPh_3)_2Pt(CO_2Me)_2 + 2KCl + 2H_2O \quad (89)$$

these reactions have ranged from nucleophilic attack of RO^- on metal-bound CO to metal–oxygen bond formation followed by insertion of CO into the resulting metal–oxygen bonds.

The first well-characterized reaction of a late-metal hydroxide with CO was reported by Bennett, who found that platinum alkyl and cyclohexenyl hydroxide complexes react with CO to generate hydroxycarbonyl compounds with no indication of CO insertion into the available metal–carbon bonds (eq 90).[57b,84] Bennett has

$$(DPPE)Pt(R)(OH) + CO \rightarrow (DPPE)Pt(R)(CO_2H) \quad (90)$$

summarized his observations on these reactions and on the chemistry of $Pt(CO_2H)$ ligands,[57c,d,119] and Ros and Michelin have described general insertion reactions of a wide variety of platinum(II) complexes containing electron-withdrawing σ-ligands (eq 91).[9b]

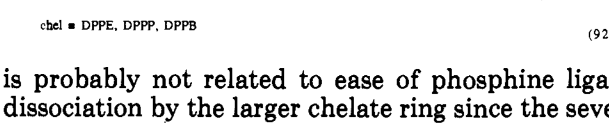
$$(L_2)Pt(R')(OR) + CO \rightarrow (L_2)Pt(R')(CO_2R) \quad (91)$$

$$R' = CH_2CN,\ CF_3,\ CH_2CF_3$$

$$R = H,\ Me$$

$$L_2 = 2PPh_3,\ \text{diphoe}$$

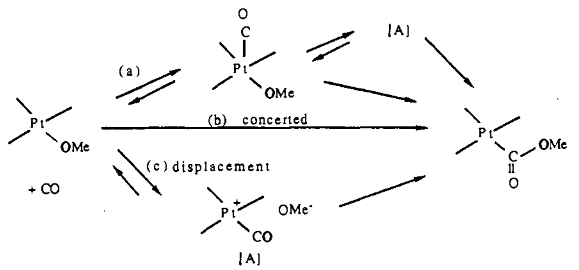
The effects of chelate ring size on insertion activity of cyclohexenyl ligands is interesting.[57e,120,121] While $(DPPE)Pt(C_6H_9)(OMe)$ inserts CO only into the metal–oxygen bond (as noted in the other platinum examples), the six-membered (DPPP) analogue inserts CO into both the metal–oxygen bond (25 °C (very fast)) and metal–carbon bond (50 °C (slow)). Moreover, with the DPPP analogue, the initial insertion reaction can be reversed to regenerate metal–oxygen bonds from the carbomethoxy ligand, although reversibility was not observed for the DPPE analogue (eq 92).[122] This effect



(92)

is probably not related to ease of phosphine ligand dissociation by the larger chelate ring since the seven-membered DPPB(Pt) ring analogue shows neither of these unique properties.

SCHEME VII



Detailed mechanistic information on the carbonylation reactions of (DPPE)PtMe(OMe), (DPPP)PtMe(OMe) (eq 93), and $(DPPE)Pt(OMe)_2$ (eq 94) has been reported.[4a,b,73,123] These reactions are best described

$$(DPPE)Pt(Me)(OMe) \xrightarrow{CO} (DPPE)Pt(Me)(CO_2Me) \quad (93)$$

$$(DPPP)Pt(Me)(OMe) \xrightarrow{CO} (DPPP)Pt(Me)(CO_2Me) \not\rightarrow (DPPP)Pt(COMe)(CO_2Me)$$

$$(DPPE)Pt(OMe)_2 \underset{CO}{\overset{-25\text{ to }+80\ ^\circ C}{\rightleftarrows}} (DPPE)Pt(CO)(OMe)_2 \rightarrow (DPPE)Pt(CO_2Me)(OMe) \xrightarrow{CO} (DPPE)Pt(CO_2Me)_2 \quad (94)$$

as inner-sphere migratory insertions involving precoordination of CO to the metal centers. The reaction of (chel)PtMe(OMe) (chel = DPPE, DPPP, DPPB) complexes with CO yields only products of CO insertion into the metal–oxygen bonds of the alkoxide complexes, indicating the migratory aptitude of a cyclohexenyl ligand is apparently greater than that of a methyl substituent. In the case of $(DPPE)Pt(OMe)_2$ the stepwise insertion of CO into both metal–oxygen bonds is realized with no indication of insertion into the available metal–(sp^2 carbon) bond.

Associative kinetics measured for the carbonylation of (DPPE)PtMe(OMe) showed overall reaction rates are more than 10^3 times faster than methoxide dissociation. This result implicates a kinetically significant bimolecular interaction of CO and platinum methoxide. Low-temperature NMR results show a rapid, reversible interaction of CO and the platinum methoxide takes place even at −80 °C. When $(DPPE)Pt(OMe)_2$ was treated with ^{13}CO, a well-behaved five-coordinate CO adduct was observed spectroscopically and its formation equilibrium was quantified from −80 to −25 °C, at which point coalescence was noted.

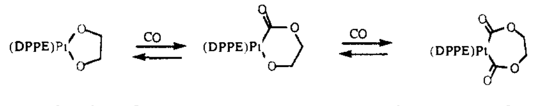
In order to determine the molecularity of this transformation, crossover studies were conducted (eq 95). To the detectability of the experiments (+0/−5%),

$$(DPPE)Pt(Me)(OCH_3) + 10CD_3OD \xrightarrow{CO} (DPPE)Pt(Me)(CO_2CH_3)\text{-}d_0 \quad (95)$$

these processes are completely inner sphere. Together these results show metal–oxygen bond carbonylations are best described by path a of Scheme VII; a good π acid binds to a platinum alkoxide to generate a discrete 5-coordinate intermediate that undergoes rate-limiting inner-sphere migratory insertion of the π acid into the polar, but covalent, metal–oxygen bonds. Apparently ionic intermediates (species A in Scheme VII) do not play a significant role in this chemistry. For the case of the bis(methoxide), a second molecule of CO inserts into the second metal–oxygen bond in preference to the Pt–C(sp^2) bond available in the molecule (eq 94).

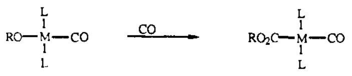
We believe it is possible that the enhanced migratory aptitude of alkoxy ligands (vis-à-vis alkyl substituents) may be due to interaction of lone electron pairs on oxygen with the π^* orbitals on CO so that substantial O–C bond formation actually ensues before M–O bond cleavage becomes significant. This can be thought of as a transition state involving inner-sphere nucleophilic attack by oxygen electron lone pairs on coordinated CO or, alternatively, as favoring a reaction intermediate with semibridging CO ligands (between platinum and oxygen). This type of interaction might also explain the enhanced migratory aptitude of cyclohexenyl substituents compared to methyl ligands.

The reactions of platinum glycolates and amides with CO have also been studied.[12,73] Reversible CO insertion into both metal–oxygen bonds of a platinum glycolate was observed at moderate temperatures (eq 96). Interestingly, the insertions are slightly faster than noted for the bis(methoxide) analogue under similar conditions. This argues for the same intramolecular inner-sphere insertion mechanism for this reaction as was established for the methyl and bis(methoxides). A related platinum amide, (DMPE)PtMe(NMePh), also reacts with CO to give (DMPE)PtMe(CONMePh).[12]



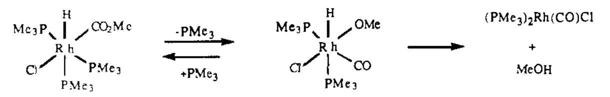
(96)

Other metal–oxygen bond carbonylations that have been studied include *trans*-ROM(PPh_3)$_2$(CO) (M = Rh, Ir) complexes (eq 97). Otsuka reported the carbonylation of the rhodium derivatives,[22] and Atwood has investigated similar reactions of iridium alkoxides with CO.[23a–c,124] During carbonylations of the iridium alkoxides, $Ir(CO)_3(PPh_3)_2^+$ has been observed spectroscopically in solution in amounts that depend on the basicity of RO^-. This cationic complex and alkoxide counterions may be intermediates in the reaction or may be the result of an unproductive side reaction in equilibrium with an inner-sphere dicarbonyliridium alkoxide intermediate. Crossover experiments reported by Milstein show deinsertion of CO from a rhodium carbomethoxide (eq 98, the microscopic reverse of CO insertion) is an inner-sphere reaction. This suggests (a) iridium may be unique in its reactivity, (b) the reaction conditions of the iridium studies may favor metal–ligand heterolysis (over those employed in the rhodium and platinum systems), or (c) the ions observed in reactions 97b may be unproductive side products in equilibrium with reaction intermediates.



$$\mathrm{RO{-}\overset{L}{\underset{L}{M}}{-}CO \xrightarrow{CO} RO_2C{-}\overset{L}{\underset{L}{M}}{-}CO} \qquad (97)$$

a) M = Rh ; L = P(i-Pr)$_3$; R = H, Me
b) M = Ir ; L = PPh_3; R = H, Me, n-Pr, Ph

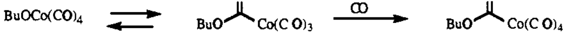


(98)

Porphyrin-based cobalt hydroxides react with CO to generate new hydroxycarbonyl linkages (eq 99).[125] Carbonylation of (n-butoxy)tetracarbonylcobaltate is illustrated in eq 100.[54] No mechanistic information is available about these transformations.

$$\mathrm{(chel)_2Co(OH)(H_2O) + CO \rightarrow (chel)_2Co(CO_2H)(H_2O)} \qquad (99)$$

chel = salen, oifen



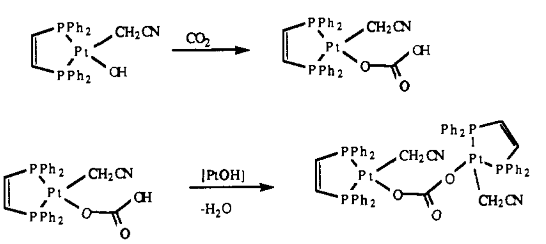
$$\mathrm{BuOCo(CO)_4 \rightleftharpoons BuO\overset{O}{\overset{\|}{C}}Co(CO)_3 \xrightarrow{CO} BuO\overset{O}{\overset{\|}{C}}Co(CO)_4} \qquad (100)$$

Insertions of CO_2, COS, CS_2, and SO_2 into Metal–Oxygen and Metal–Nitrogen Bonds

Reaction of CO_2, COS, and CS_2 with platinum hydroxides and alkoxides is shown in eq 101.[9b,126] In the case of the hydroxides, formation of dimeric platinum complexes was also noted with CO_2 (eq 102). Platinum–oxygen bonds also react with SO_2 to form insertion adducts (eq 103), and a platinum(II) anilide complex reacts with CO_2 to generate a platinum urethane product (eq 104).[14] Rhodium and iridium hydroxides react with CO_2 to form bicarbonates and carbonate-bridged metal dimers.[127,128] Interestingly, for HORh[P(Cy)$_3$]$_2$(CO), the CO_2 insertion is reversible. In all of these cases, a deficiency of CO_2 can lead to formation of the carbonate-bridged dimers, presumably through σ-ligand metathesis of the starting hydroxides with metal bicarbonates. It is not known whether the carbonate dimers can be reconverted into bicarbonate complexes by addition of water. No mechanistic information is available on these transformations.

(101)

R' = CH_2CN, CF_3, CH_2CF_3; R = H, Me
L_2 = 2 PPh_3, diphoe
X = O, S (also noted for COS)

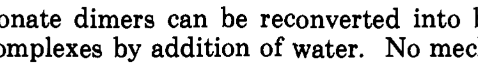


(102)

$$\mathrm{(L_2)PtR'(OR) + SO_2 \rightarrow (L_2)PtR'(SO_3R)} \qquad (103)$$

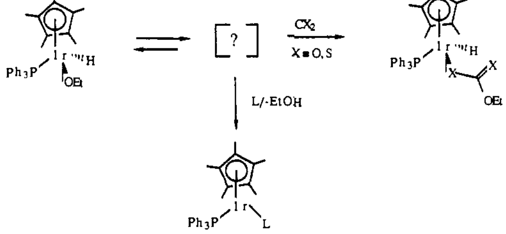
$$\mathrm{R' = CH_2CN,\ CF_3,\ CH_2CF_3;\ R = H,\ Me}$$

$$\mathrm{L_2 = 2PPh_3,\ diphoe}$$



(104)

Bergman's kinetics investigations of CX_2 insertions into iridium ethoxide ligands (eq 105) showed these reactions proceed by preequilibrium formation of an

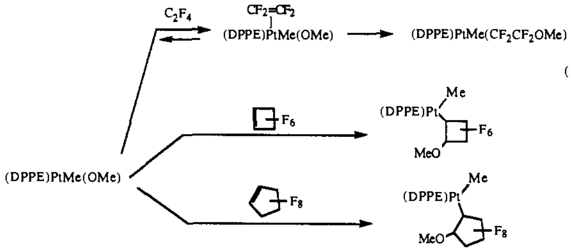


(105)

intermediate ([?] in eq 105), which undergoes rate-limiting reaction with CX_2 to give products.[25] Alternately, this intermediate can be trapped with donor ligands to generate iridium(I) products and ethanol. Reactions of the ethoxy deuteride complex show $k_H/k_D = 1.0$, and the rate of these CX_2 reactions is independent of solvent. The authors conclude the intermediate is probably an uncharged, coordinatively unsaturated species, perhaps formed by changes in hapticity of the η^5-C_5Me_5 ring or by migration of OR or H substituents to the ring.

Olefin Insertion into Metal-Oxygen and Metal-Nitrogen Bonds

(DPPE)PtMe(OMe) does not interact with ethylene to form insertion products. Addition of 1-pentene to (DPPE)PtMe(OMe) results in catalytic olefin isomerization, but no other products were noted and (DPPE)PtMe(OMe) was reisolated, unchanged. Methyl acrylate and acrylonitrile give small amounts of insertion adducts in low yields, but fluoro olefins were found to react cleanly with (DPPE)PtMe(OMe) to give the insertion adducts shown in eq 106.[4a,129] Interestingly,



(106)

the corresponding platinum hydroxide also inserts TFE into the available metal-oxygen bond but then undergoes a rearrangement to generate a tetrafluoroethoxide substituent (eq 107).

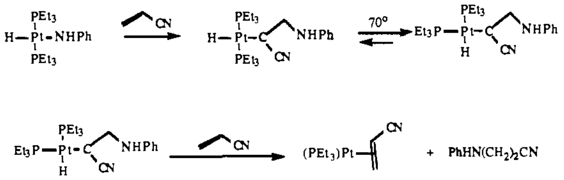
$$(DPPE)PtMe(OH) + C_2F_4 \rightarrow (DPPE)PtMe(OCF_2CF_2H) \quad (107)$$

Mechanistic studies of the tetrafluoroethylene (TFE) insertion (eq 106) show the process involves bimolecular interactions of platinum methoxide with the good π acid TFE at a rate more than 10^3 times faster than any heterolytic dissociations in this system ($\Delta H^{*} = 12.5 \pm 0.5$ kcal/mol, $\Delta S^{*} = -32 \pm 5$ eu).[129] The reactions with hexafluorocyclobutene and octafluorocyclopentene are much faster than the TFE reaction.

Crossover experiments indicate eq 106 is reversible with TFE and show that ΔG is only −5 kcal/mol for this case in which robust M–C and C–O bonds are formed at the expense of a weak C–C double bond and the M–O bond. This suggests reactions with the parent hydrocarbons are thermodynamically unfavorable, though they may be kinetically accessible.

Low-temperature ^{19}F NMR measurements on the TFE system spectroscopically detected an intermediate that could not be structurally characterized or isolated. Crossover experiments demonstrated that, to the limits of experimental detectability, these fluoro olefin insertion reactions are completely inner-sphere processes. The overall mechanism is therefore best described as written in eq 106: precoordination of the olefin to the platinum center followed by rate-limiting olefin insertion into the metal-oxygen bond.

Trogler has recently reported the clean conversion of a platinum amide to an insertion adduct (eq 108).[14]

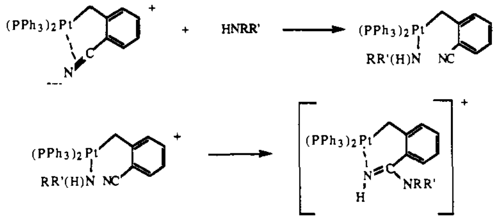


(108)

The initial trans species isomerizes to a cis analogue at 70 °C, which generates β-anilidopropionitrile and a platinum(0) olefin complex in the presence of additional acrylonitrile. In the presence of ethylene or other dative ligands, the anilide complex releases aniline and forms a platinum(0) complex. The mechanism of the insertion step has not been further elucidated.

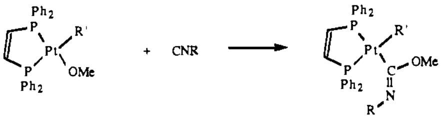
Other Insertions

A few other examples of M–O and M–N addition reactions to small molecules have been reported. Amines can be added stoichiometrically to an aryl cyanide as shown in eq 109.[130] The reaction is thought



(109)

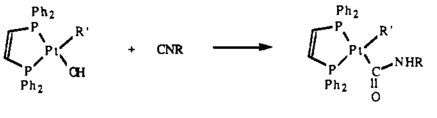
to proceed through initial coordination of amine to platinum but the role of platinum-nitrogen σ bonds has not been established. Addition of isonitriles to platinum methoxide complexes also results in the overall insertion of the organic into the metal-oxygen bonds (eq 110).[131]



(110)

R' = CF_3, CH_2CN; R = Me, p-MeO-C_6H_4, 2,6-$Me_2C_6H_3$

Reaction of platinum hydroxides is thought to proceed similarly, although the products rearrange to platinum carbamides as shown in eq 111. The mechanism of



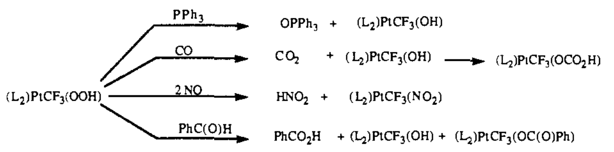
(111)

R' = CF_3, CH_2CN; R = Me, p-MeO-C_6H_4, 2,6-$Me_2C_6H_3$

these reactions have not been elucidated; both inner- and outer-sphere steps are possible even when preformed metal-oxygen bonds are present in the starting complexes. Similarly, either mechanism (nucleophilic outer-sphere attack or metal-oxygen bond formation followed by insertion) may be involved in carboamide formation by addition of hydroxide to cationic platinum isonitrile complexes.[132]

Reactions of Peroxo Complexes

Peroxide complexes of the late transition metals have unique oxygenation capabilities. Platinum hydroperoxo complexes react to oxidize triphenylphosphine, CO, and NO (eq 112).[66a] No reactions were noted with simple olefins; however, $(PPh_2Me)_2PtCF_3(OO$-t-$Bu)$ will oxi-



L_2 = dppe, diphoe, 2 PPh_3, 2 PPh_2Me (112)

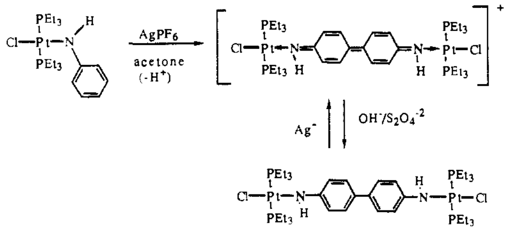
dize 1-octene to 2-octanone (eq 113).[66b] In aqueous

(113)

media these complexes catalyze the oxidation of olefins, suggesting that perhaps both inner- and outer-sphere mechanisms may be accessible depending on the reaction conditions employed.

Oxidative Coupling

One final example of rather unique reactivity of late-transition-metal arylamide complexes has been reported by Alcock.[133] Oxidation of platinum amide complexes with silver yields dimeric products coupled at the least substituted aryl carbons (eq 114). It is assumed that the metal participates in stabilizing the aminyl radical generated. Conjugation with the arene ring allows coupling at the least substituted position.

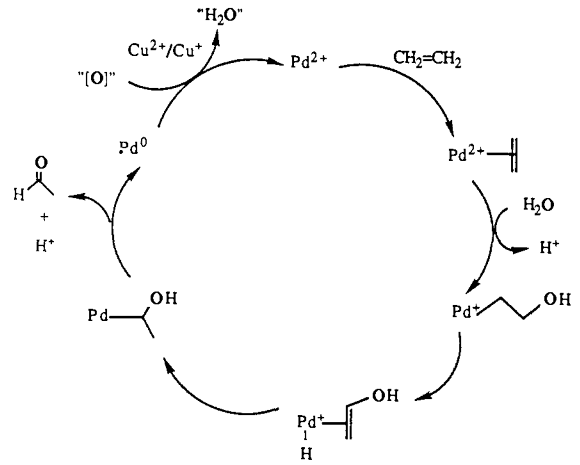


(114)

Summary

The diverse reactivity of late metal hydroxide, alkoxide, and amide complexes includes simple insertions, β-hydride eliminations, oxidative additions, and reductive coupling reactions which can take place by mechanisms similar to those previously established for metal alkyl and hydride derivatives. Moreover, these complexes, by virtue of lone electron pairs on these σ ligands, can undergo facile acid/base reactions and reversible σ-ligand metatheses which generally require higher activation energies in comparable metal alkyl and hydride derivatives. While these bonds are thermodynamically robust, they have available to them metal–ligand heterolysis reaction pathways that depend critically on free-ligand basicity, on ancillary ligand electronics and sterics, and, especially, on reaction media. These diverse modes of reactivity give M–O and M–N bonds rich and unique chemistry but make definitive mechanistic investigations difficult. In the final section of this review we look at catalytic reactions that have implicated the involvement of metal–oxygen and metal–nitrogen bonds or that utilize metal alkoxides, hydroxides, and amides as catalysts or catalyst precursors. As the reader can imagine, given the challenge of answering mechanistic questions definitively for the stoichiometric reactions mentioned in the preceding paragraphs, extending mechanistic investigations to catalytic systems of further complexity becomes extremely difficult.

SCHEME VIII



IV. Catalytic Reactions

Introduction

The roles played by metal–oxygen and metal–nitrogen bonds in catalytic reactions are far from clear. This is especially true of chemistry conducted in aqueous media with weakly basic alkoxide or hydroxide ligands—conditions that have been shown to favor metal–ligand bond heterolysis, as suggested by the work of Milburn,[94,95] Otsuka,[37,96,98] Ros,[97] and others.[31] In many of the succeeding examples the reader will note that little, if any, mechanistic information is available concerning the direct involvement of these L_nM–O and L_nM–N bonds. We have tried to list reactions where involvement is a possibility and then provide leading references to these reactions. Whenever possible, we refer the reader to the primary literature and to the pertinent stoichiometric chemistry.

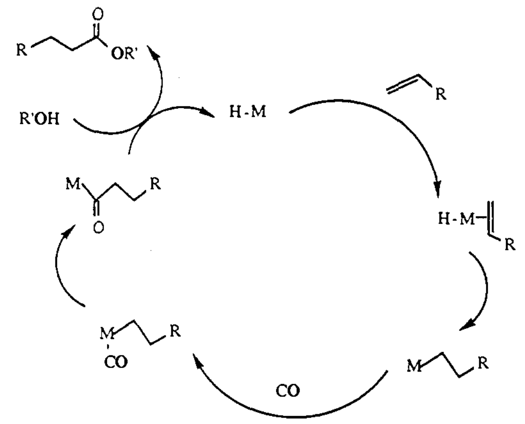
While it is often very difficult to establish the importance of a given mechanism in a catalytic reaction, it is almost impossible to prove the exclusivity of a particular mechanism. Additionally, given the obvious facility with which metal–ligand bond heterolysis reactions can take place in aqueous media, it is often exceedingly difficult to determine whether inner- or outer-sphere mechanisms operate under catalytic conditions. Moreover, in our quest for showing the veracity of a given mechanism for a catalytic reaction, we often tend to overlook the possibility that more than one mechanism may be operating even under a single set of reaction conditions or that changes in conditions may alter some delicate balance and, thereby, alter the reaction mechanism. Therefore, the use of model compounds and the study of single mechanistic steps under even slightly different reaction conditions may or may not bear on the mechanisms of these catalytic processes.

Wacker Oxidations

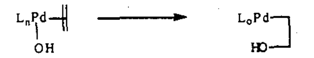
Perhaps no other reaction so fittingly illustrates the uncertainty discussed above as the palladium-catalyzed Wacker olefin oxidation process, which is depicted in its simplest form in eq 115. While the major mechanistic steps involved are probably those shown in Scheme VIII, a major debate has taken place for more

$$CH_2CH_2 + \tfrac{1}{2}O_2 \xrightarrow{Pd^{2+},Cu^{2+}} CH_3CHO \qquad (115)$$

SCHEME IX

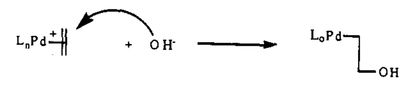


than 20 years concerning the mechanism by which the proposed β-hydroxyethyl intermediate is formed. Kinetic information suggests that inner-sphere migration of coordinated hydroxide (or water) to a coordinated olefin (eq 116) takes place under some conditions while



(116)

stereochemical model studies indicate that nucleophilic attack of free hydroxide or water (eq 117) is also a

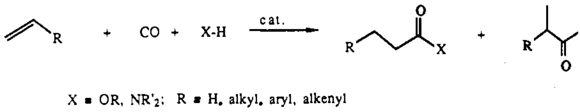


(117)

distinct possibility.[134] Given that both processes have been observed in model studies, perhaps Parshall summarizes the situation best: "It is quite possible that both mechanisms (inner- and outer-sphere addition) operate and that reaction conditions determine which predominates".[135] A similar situation appears to be involved in olefin and diene acetoxylation, though these related reactions fall outside the scope of this review.

Carbonylations

Group VIII metal catalyzed carboalkoxylation, carboxylation, and carboamidation of olefins (eq 118) and alkyl halides (eq 119) to generate organic esters, acids,



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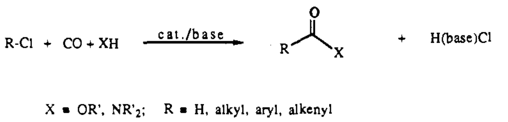
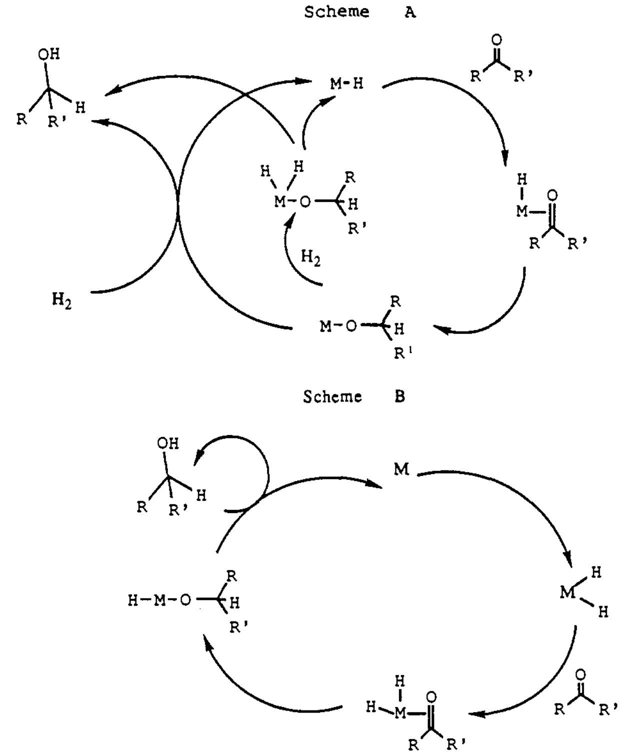


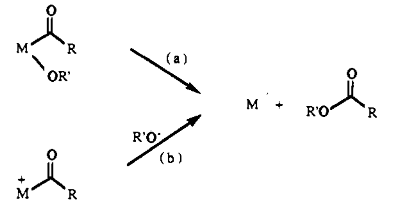
(119)

and amides and are well-known reactions. They have received considerable development as synthetic methods.[136] The mechanism shown in Scheme IX (for the representative case of olefin carboalkoxylation) has been generally accepted, although the role of metal–oxygen and metal–nitrogen bonds in this chemistry is as difficult to establish as for Wacker oxidations. Studies using rhodium[113] and palladium[58] model systems suggest that CO insertion into metal–carbon bonds is favored over carbonylation of metal–oxygen or metal–nitrogen bonds (Scheme VIII) under some conditions, although work with other metal systems[4a,b,9b,12,57b–e,58b,84,73,119–121,123] show this is not true

SCHEME X



under all conditions (eq 90–100). Inner-sphere reductive coupling of acyl and alkoxy substituents (eq 83, 84, and 120a) is a viable final step in ester synthesis.[47a,58,112,114] It seems likely that under some conditions ester formation in Scheme VIII involves carbonylation of metal–alkyl intermediates and ester release by reductive coupling of acyl and alkoxide ligands bound to the metal center.



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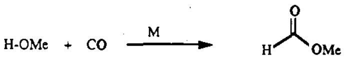
Methyl formate synthesis by methanol carbonylation (eq 121) is a special case in that no metal–carbon bond



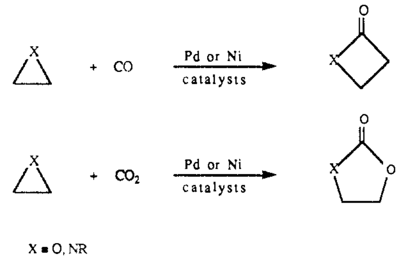
$$\mathrm{H\text{-}OMe + CO \xrightarrow{M} HC(O)OMe} \qquad (121)$$

is ever present to undergo CO insertion. Therefore, metal–oxygen bond carbonylation is thought to be involved after initial oxidative addition of the H–OMe bond to a metal center has taken place.[137] Conversely, the water–gas-shift reaction, which can be catalyzed by palladium, platinum, rhodium, and ruthenium complexes as well as many other transition-metal compounds, has been generally written as involving nucleophilic attack of water or hydroxide on coordinated CO (eq 122),[138] although inner-sphere mechanisms may

$$\mathrm{H\text{-}O\text{-}H + CO \overset{M}{\rightleftharpoons} H_2 + CO_2} \qquad (122)$$

also be important. For example, although platinum carbonyl hydrido cations can be isolated from reaction solutions containing L_3Pt complexes, water, and CO, these reactions are slower in pyridine (the solvent that promotes hydroxide complex heterolysis) than in THF or acetone. It is entirely possible that both inner- and outer-sphere processes can be involved in this reaction under different conditions and with the different metal complexes employed.

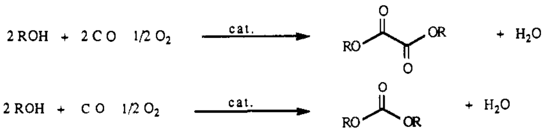
Other special cases in which metal–oxygen and metal–nitrogen bonds have been directly implicated as intermediates include the carbonylation and carboxylation of aziridines and epoxides (eq 123).^{46b,139} Other



(123)

evidence that C–N bonds in amines and, by inference, the C–O bonds in alcohols and water can be activated under these conditions comes from observation of palladium-catalyzed alkyl group interchange in alkylamines (which also must involve C–N bond cleavage).^{140}

Related reactions involving the oxidative monocarbonylation and double carbonylation of amines and alcohols using palladium and rhodium catalysts are represented in eq 124. These reactions can be em-

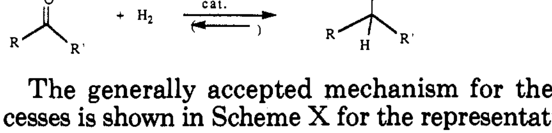


(124)

ployed to prepare dialkyl carbonates, oxazolidinones, urethanes, and oxalate esters.^{141} For the representative case of dialkyl carbonate and oxalate ester synthesis, the involvement of carbomethoxy and bis(carbomethoxy) intermediates has been implicated (vis-à-vis α,β-dicarbonyl metal complexes) although other mechanistic information is limited.^{4b,142} In simple nonoxidative carbonylations, formation of carboalkoxy and carbamoyl linkages may take place by either nucleophilic or insertion mechanisms. The selectivity obtained in diol amine carbonylations cannot be explained by a nucleophilic mechanism, suggesting inner-sphere insertions may generally be involved in these processes.^{141a}

Hydrogenations

Metal alkoxides may be involved in the homogeneously catalyzed hydrogenation of carbon monoxide, ketones, and aldehydes and in the microscopic reverse, the dehydrogenation of alcohols (eq 125).^{38,143} Similar chemistry has been noted for the homogeneous hydrogenation of nitriles to amines.^{144}



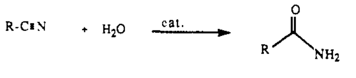
(125)

The generally accepted mechanism for these processes is shown in Scheme X for the representative case of ketone hydrogenation. The intermediacy of metal alkoxides is implied in these reactions by spectroscopic measurements and isolation of metal alkoxide complexes as shown in eq 27.^{38} While all steps of this mechanism have been studied with model compounds (an unusual circumstance in mechanistic studies of catalysis) and demonstrated to be viable under catalytic conditions (note sections above covering β-hydride migratory processes and H–OR oxidative addition reactions), the mechanistic significance of hydroxymethyl derivatives as cointermediates cannot be ruled out in most of the examples.

One final, and unique, example of hydrogenation catalysis that appears to involve metal–nitrogen bonds is the catalytic olefin hydrogenation effected by Fryzuk's rhodium and iridium chelating amides.^{34c} While the mechanism is far from clear, it appears that the amides serve to activate dihydrogen heterolytically to generate the active metal hydrides needed for hydrogenation.^{78,80,145}

Hydration and Alcoholysis Reactions

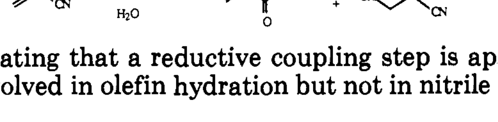
As noted briefly in the Reactivity section of this review, the catalytic hydration of nitriles to amides using platinum, palladium, and ruthenium hydroxide complexes as catalysts for catalyst precursors has been known since 1973 (eq 126).^{10b,15a,b,37,57c,132,146} Scheme



(126)

XI presents a representative, but purposely vague, mechanism for this process; platinum complexes have been utilized for demonstration purposes, since most of the work in this field has centered on their use. Platinum hydroxides undergo facile heterolysis in protic solvents when good ligands like pyridine or nitriles are present, suggesting that outer-sphere attack of hydroxide or water on nitriles bound to platinum might be involved in this chemistry.^{37} The heterolysis steps required for an outer-sphere mechanism are all favorable under nitrile hydration conditions with $(PMe_3)_2PtH(OH)$ catalyst as well.^{146c} Together, these results show outer-sphere mechanisms can explain the observed catalytic activity under at least some reaction conditions. The requisite steps for inner-sphere mechanisms have also been observed for model complexes although their importance in catalytic nitrile hydration has not been established. This catalysis has many similarities to Wacker oxidations, and it would not be surprising if both types of mechanisms are significant for the wide scope of conditions that can be employed in nitrile hydrolysis reactions.

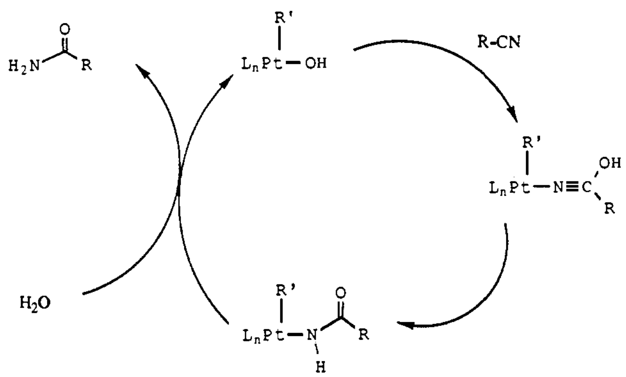
One interesting sidelight to platinum(II)-catalyzed nitrile hydration chemistry is that in cases where platinum hydrides are involved, both nitrile and olefin hydrolysis of acrylonitrile has been noted while platinum alkyl hydroxide catalysts (or catalyst precursors if outer-sphere processes are involved) show only hydration of the nitrile functional group.^{147} Otsuka first recognized this dichotomy,^{37} and Trogler demonstrated that in preformed $(PMe_3)_2DPtOH$ the D–Pt bond is not involved or even exchanged during nitrile hydrolysis.^{146c} However, olefin hydrolysis does result in specific incorporation of the deuterium label into the 1-position of the 3-hydroxypropionitrile generated (eq 127), in-



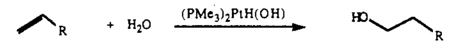
(127)

dicating that a reductive coupling step is apparently involved in olefin hydration but not in nitrile hydroly-

SCHEME XI

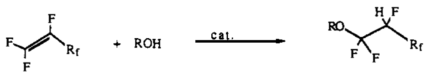


sis.[148] Trogler's catalyst also hydrates other simple unhindered linear olefins (eq 128),[149] though mechanistic details of this process are still under investigation.



(128)

Platinum(0) phosphine complexes also catalyze the methanolysis of fluoro olefins (eq 129);[4a,73] the inner-sphere mechanistic steps for these reactions have been demonstrated under catalytic reaction conditions with model compounds.

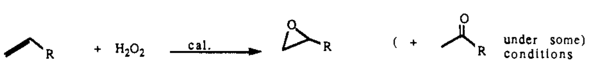


(129)

Other Olefin Oxidations

It has already been mentioned that oxidation of unsaturated organic substrates by late-metal dioxygen complex catalysts is thought to involve peroxymetallacycles,[55] but these compounds are outside the scope of this review.

An interesting class of oxidation catalysts, which have been discussed in this review, are the platinum alkyl peroxides and hydroperoxides. Olefin oxidations and epoxidations can be effected by using aqueous H_2O_2 and these complexes, or the corresponding platinum hydroxides, which probably give the peroxides through σ-ligand metathesis reactions (eq 130).[9c,66c,97,150] The stoichiometric reactivity of these $L_2PtR_x(OOR)$ complexes under anhydrous conditions is limited compared with that of the aqueous catalytic systems. This increased activity and the known ability of these metal–oxygen bonds to heterolyze under aqueous conditions suggest outer-sphere mechanisms may operate under some conditions.[151] The observation of epoxide products under some reaction conditions suggests free hydroxide is not present in those aqueous reactions. As with most of the above systems, the possibility that both inner- and outer-sphere reactions are taking place under some conditions seems likely, and the possible role of peroxymetallacycles in this chemistry is not known.



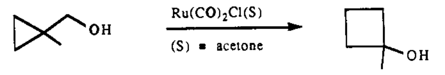
(130)

Other Reactions

Other processes in which metal hydroxides, alkoxides, and amides have been used as catalysts or catalyst precursors or have been implicated as intermediates include H–D exchange reactions between D_2O and H–C bonds,[37,98,152] the photolytic splitting of water,[58] and the rearrangement of strained hydrocarbons.[153]

In the case of isotope scrambling reactions of weak acids with D_2O, it appears (from the unique selectivity noted) that late-metal complexes are not simply serving as convenient sources of OH^-, though the role of inner- and outer-sphere mechanistic steps has not been determined unambiguously.

The rearrangement shown in eq 131 is unique in that



(131)

it appears that the metal simply acts as a Lewis acid to extract hydroxide and generate a carbocation that undergoes traditional cationic skeletal rearrangements. The involvement of metal insertion into carbon–carbon bonds has been ruled out in this process.

V. Conclusions

It has been our intention to summarize the techniques by which late-metal alkoxides, hydroxides, and amides may be prepared and to illustrate the interesting chemistry available to this class of compounds. As isolated complexes these materials have reactivity similar to that previously established for metal–carbon and metal–hydrogen bonds. The presence of lone electron pairs on these substituents gives them additional capabilities in terms of interacting with small molecules and weak acids. These interactions can result in lowering activation barriers for bimolecular reactions.

Despite general perceptions, late metal–oxygen and metal–nitrogen bonds are *not* particularly weak but are thermodynamically, in fact, quite robust. Metal–oxygen and metal–nitrogen bonds can form easily yet they are reactive enough to demonstrate interesting reactivity. In binding to late-metal centers oxygen and nitrogen σ ligands are not hard ligands relative to carbon and hydrogen; however, because of increased electron affinity of the heteroatoms involved, these bonds can heterolyze more easily than metal–hydrogen or metal–carbon linkages (for the same reason amines and alcohols heterolyze more easily than carbon–hydrogen or dihydrogen bonds). This increased ability to heterolyze gives these compounds another mode of reactivity not normally open to the alkyls and hydrides. While their roles in many catalytic transformations are unclear, they represent unique opportunities as catalysts (or precursors) to carry out reactions that would be difficult to effect by other methods.

Abbreviations

DPPE	1,2-bis(diphenylphosphino)ethane
diphoe	*cis*-1,2-bis(diphenylphosphino)ethylene
DMPE	1,2-bis(dimethylphosphino)ethane
bpy	2,2′-bipyridine
phen	1,10-phenanthrene
TMEDA	*N,N′*-tetramethylethylenediamine
DMSO	dimethyl sulfoxide
DME	1,2-dimethoxyethane
pyr	pyridine
naphth	naphthalene
DMG-H	dimethylglyoxime
DPPP	1,3-bis(diphenylphosphino)propane

DPPB	1,4-bis(diphenylphosphino)butane
COE	*cis*-cyclooctene
Ts	*p*-toluenesulfonyl
salen	*N*,*N*′-disalicylideneethylenediamine
oifen	*N*,*N*′-bis(*o*-hydroxy-α-methylbenzylidene)-acetophenoneethylenediamine dianion
TFE	tetrafluoroethylene
THF	tetrahydrofuran
chiraphos	bis(diphenylphosphino)butane
prophos	1,2-bis(diphenylphosphino)propane
diop	2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane

References

(1) (a) Mehrotra, R. C.; Agarwal, S. K.; Singh, Y. P. *Coord. Chem. Rev.* **1985**, *68*, 101. (b) Malhotra, K. C.; Martin, R. L. *J. Organomet. Chem.* **1982**, *239*, 159. (c) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic: London, 1978.

(2) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643. (c) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973; p 169. (d) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, 1980.

(3) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993.

(4) (a) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603. (b) Bryndza, H. E.; Kretchmar, S. A.; Tulip, T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 977. (c) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805.

(5) (a) Fakley, M. E.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1444. (b) Almeida, J. F.; Pidcock, A. *J. Organomet. Chem.* **1981**, *209*, 415.

(6) Cooper, M. K.; Hair, N. J.; Yaniuk, D. W. *J. Organomet. Chem.* **1978**, *150*, 157.

(7) Aresta, M.; Nyholm, R. S. *J. Organomet. Chem.* **1973**, *56*, 395.

(8) (a) Motschi, H.; Pregosin, P. S.; Ruegger, H. *J. Organomet. Chem.* **1980**, *193*, 397. (b) Anklin, C.; Pregosin, P. S.; Bachechi, F.; Mura, P.; Zambonelli, L. *J. Organomet. Chem.* **1981**, *222*, 175.

(9) (a) Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1978**, *161*, 75. (b) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175*, 239. (c) Sinigalia, R.; Michelin, R. A.; Pinna, F.; Strukul, G. *Organometallics* **1987**, *6*, 728.

(10) (a) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738. (b) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.

(11) Britten, J. F.; Lippert, B.; Lock, C. J. L.; Pilon, P. *Inorg. Chem.* **1982**, *21*, 1936.

(12) Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939.

(13) Park, S.; Roundhill, D. M.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3974.

(14) Trogler, W. C.; Cowan, R. L. *Organometallics* **1987**, *6*, 2451.

(15) (a) Villain, G.; Kalck, P.; Gaset, A. *Tetrahedron Lett.* **1980**, *21*, 2901. (b) Gaset, A.; Constant, G.; Kalck, P.; Villain, G. *J. Mol. Catal.* **1980**, *7*, 355.

(16) Bhaduri, S.; Johnson, B. F. G.; Matheson, T. W. *J. Chem. Soc., Dalton Trans.* **1977**, 561.

(17) Coronas, J. M.; Polo, C.; Sales, J. *Inorg. Chim. Acta* **1981**, *48*, 77.

(18) Baranwal, B. P.; Mehrotra, R. C. *Aust. J. Chem.* **1980**, *33*, 37.

(19) Gregoriao, G.; Pregaglia, G.; Ugo, R. *Inorg. Chim. Acta* **1969**, *3*, 89.

(20) Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1370.

(21) Vaska, L.; Peone, J., Jr. *J. Chem. Soc. D* **1971**, 418.

(22) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 3411.

(23) (a) Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. S. *Organometallics* **1985**, *4*, 2179. (b) Rees, W. M.; Atwood, J. D. *Organometallics* **1985**, *4*, 402. (c) Churchill, M. R.; Fettinger, J. C.; Rees, W. M.; Atwood, J. D. *J. Organomet. Chem.* **1986**, *308*, 361.

(24) Johnston, L. E.; Page, J. A. *Can. J. Chem.* **1969**, *47*, 4241.

(25) Newman, L. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 5314.

(26) Cetinkaya, B.; Lappert, M. F.; Torroni, S. *J. Chem. Soc., Chem. Commun.* **1979**, 843.

(27) Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1982**, *21*, 2089.

(28) (a) Hope, H.; Olmstead, M. M.; Murray, B. D.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 712. (b) Olmstead, M. M.; Power, P. P.; Sigel, G. *Inorg. Chem.* **1986**, *25*, 1027. (c) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 7563.

(29) Koch, S.; Millar, M. *J. Am. Chem. Soc.* **1982**, *104*, 5255.

(30) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546.

(31) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.

(32) Blackmore, T.; Bruce, M. I.; Davidson, P. J.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3153.

(33) (a) Allen, M.; Willis, C. J. *J. Am. Chem. Soc.* **1968**, *90*, 5343. (b) Boere, R. T.; Willis, C. J. *Inorg. Chem.* **1985**, *24*, 1059. (c) Boere, R. T.; Montgomery, C. D.; Payne, N. C.; Willis, C. J. *Inorg. Chem.* **1985**, *24*, 3680.

(34) (a) Fryzuk, M. D.; MacNeil, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3592. (b) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982**, *1*, 918. (c) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 355. (d) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1986**, *5*, 2469. (e) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Organomet. Chem.* **1987**, *332*, 345.

(35) (a) Beck, W.; Bauder, M. *Chem. Ber.* **1970**, *103*, 583. (b) Beck, W.; Bauder, M.; LaMonnica, G.; Ugo, R. *J. Chem. Soc. A* **1971**, 113. (c) Pizzotti, M.; Cenini, S.; Porta, F.; Beck, W.; Erbe, J. *J. Chem. Soc., Dalton Trans.* **1978**, 1155.

(36) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006.

(37) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027.

(38) Tani, K.; Tanigawa, E.; Tatsuno, Y.; Otsuka, S. *J. Organomet. Chem.* **1985**, *279*, 87.

(39) Milstein, D.; Calabrese, J. C.; Williams, J. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387.

(40) Braga, D.; Sabatino, P.; Di Bugno, C.; Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1987**, *334*, C46.

(41) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 973.

(42) (a) Monaghan, P. K.; Puddephatt, R. J. *Inorg. Chim. Acta* **1982**, *65*, L59. (b) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444.

(43) Appleton, T. G.; Hall, J. R.; Neale, D. W.; Williams, M. A. *J. Organomet. Chem.* **1984**, *276*, C73.

(44) Akl, N.; Tayim, H. A. *J. Organomet. Chem.* **1985**, *297*, 371.

(45) (a) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (b) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.

(46) Leading references include: (a) Schlodder, R.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Am. Chem. Soc.* **1974**, *96*, 6893. (b) Graziani, M.; Lenarda, M.; Ros, R.; Belluco, U. *Coord. Chem. Rev.* **1975**, *16*, 35. (c) Lenarda, M.; Ros, R.; Traverso, O.; Pitts, W. D.; Baddley, W. H.; Graziani, M. *Inorg. Chem.* **1977**, *16*, 3178.

(47) (a) Yamamoto, T.; Miyashita, S.; Naito, Y.; Komiya, S.; Ito, T.; Yamamoto, A. *Organometallics* **1982**, *1*, 808. (b) Yoshinori, H.; Yamamoto, T.; Yamamoto, A.; Komiya, S.; Kushi, Y. *J. Am. Chem. Soc.* **1986**, *108*, 385.

(48) Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180.

(49) (a) Vleck, A. A.; Hanzlik, J. *Inorg. Chem.* **1967**, *6*, 2053. (b) Vleck, A., Jr.; Klima, J.; Vleck, A. A. *Inorg. Chim. Acta* **1983**, *69*, 191.

(50) Ghedini, M.; Dolcetti, G.; Giovannitti, B.; Denti, G. *Inorg. Chem.* **1977**, *16*, 1725.

(51) (a) Ferguson, G.; Parvez, M.; Monaghan, P. K.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 267. (b) Ferguson, G.; Monaghan, P. K.; Parvez, M.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1669.

(52) Alcock, N. W.; Golding, B. T.; Mwesigye-Kibende, S. *J. Chem. Soc., Dalton Trans.* **1985**, 1997.

(53) Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1014.

(54) Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150.

(55) Leading references to oxidation reactions that may proceed through peroxymetallacycle intermediates follow: (a) Mimoun, H.; Seree de Roch, I.; Sajus, L. *Tetrahedron* **1970**, *26*, 37. (b) Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 883. (c) Mimoun, H.; Perez Machirant, M. M.; Seree de Roch, I. *J. Am. Chem. Soc.* **1978**, *100*, 5437. (d) Tang, R.; Mares, F.; Neary, N.; Smith, D. E. *J. Chem. Soc., Chem. Commun.* **1979**, 274. (e) Igersheim, F.; Mimoun, H. *Nouv. J. Chim.* **1980**, *4*, 161. (f) Mimoun, H. *J. Mol. Catal.* **1980**, *7*, 1. (g) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047. (h) Bregeault, J.-M.; Mimoun, H. *Nouv. J. Chim.* **1981**, *5*, 287. (i)

Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734. (j) Grassi, A.; Longo, P.; Musco, A.; Porzio, W.; Scrivanti, A. *J. Organomet. Chem.* **1985**, *289*, 739.

(56) As will be seen in the Reactivity section of this review, the terms *reversible* and *irreversible*, as used above, are almost certainly kinetic terms, suggesting the microscopic reverses of some reactions are exceedingly slow. In some cases thermodynamic considerations may play a role in determining the outcome of σ-ligand metathesis reactions.

(57) (a) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3028. (b) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750. (c) Arnold, D. P.; Bennett, M. A.; Crisp, G. T.; Jeffery, J. C. *Adv. Chem. Ser.* **1982**, *No. 196*, 195. (d) Bennett, M. A.; Rokicki, A. *Aust. J. Chem.* **1985**, *38*, 1307. (e) Bennett, M. A. *J. Organomet. Chem.* **1986**, *300*, 7.

(58) (a) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130. (b) Kim, Y.-J.; Osakada, K.; Yamamoto, T.; Yamamoto, H. P-107 presented at the *VI Int. Symp. Homogen. Catal.*; *Organometallics*, in press.

(59) Jeffery, E. A. *Aust. J. Chem.* **1973**, *26*, 219.

(60) Friedrich, K.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944.

(61) Keim, W. *J. Organomet. Chem.* **1968**, *14*, 179.

(62) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563.

(63) Brown, C. K.; Georgiou, D.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 929.

(64) Komiya, S.; Taneichi, S.; Yamamoto, A.; Yamamoto, T. *J. Chem. Soc. Jpn.* **1980**, *53*, 673.

(65) Jones, R. A.; Wilkinson, G.; Colquohoun, I. J.; McFarlane, W.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1980**, 2480.

(66) (a) Michelin, R. A.; Ros, R.; Strukul, G. *Inorg. Chim. Acta* **1979**, *37*, L491. (b) Strukul, G.; Ros, R.; Michelin, R. A. *Inorg. Chem.* **1982**, *21*, 495. (c) Strukul, G.; Michelin, R. A.; Orbell, J. D.; Randaccio, L. *Inorg. Chem.* **1983**, *22*, 3706.

(67) Booth, B. L.; Haszeldine, R. N.; Neuss, G. R. H. *J. Chem. Soc., Dalton Trans.* **1982**, 37.

(68) Sigel, G. A.; Bartlett, R. A.; Decker, D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 1773.

(69) (a) Griffith, W. P.; Rossetti, R. *J. Chem. Soc., Dalton Trans.* **1972**, 1449. (b) Nielson, A. J.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1978**, 1501.

(70) Cesari, M.; Neri, C.; Perego, G.; Perrotti, E.; Zazzetta, A. *J. Chem. Soc., Chem. Commun.* **1970**, 276.

(71) (a) Caddy, P.; Green, M.; Howard, J. A. K.; Squire, J. M.; White, N. J. *J. Chem. Soc., Dalton Trans.* **1981**, 400. (b) Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151. (c) Howard, J. L.; Hamor, M. J.; Hamor, T. A.; Caughey, W. S. *J. Am. Chem. Soc.* **1965**, *87*, 2312. (d) Riche, C.; Chiaroni, A.; Perree-Fauver, M.; Gaudemer, A. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1868. (e) Flohr, H.; Pannhorst, W.; Retey, J. *Helv. Chim. Acta* **1978**, *61*, 1565.

(72) Murray, B. D.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 4584.

(73) Bryndza, H. E.; Calabrese, J. C.; Kretchmar, S. A.; Tam, W.; Tulip, T. H., manuscript in preparation.

(74) Montgomery, C. D.; Payne, N. C.; Willis, C. J. *Inorg. Chem.* **1987**, *26*, 519.

(75) The results of similar measurements in aqueous media will be discussed below.

(76) These experiments cannot, however, rule out an oxidative pathway involving sequential stereoselective oxidative addition and stereoselective reductive coupling steps. Such an oxidative mechanism seems unlikely since platinum(IV) dimethyl alkoxide derivatives (similar to this postulated oxidative addition intermediate) are quite stable with respect to reductive elimination as shown by Puddephatt.[42a,b]

(77) Bernard, K. A.; Atwood, J. D. *Organometallics* **1987**, *6*, 1133.

(78) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1985**, *4*, 1145.

(79) Fryzuk, M. D.; MacNeil, P. A.; McManus, N. T. *Organometallics* **1987**, *6*, 884.

(80) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 682.

(81) Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543.

(82) Jones, R. F.; Fisher, J. R.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2550.

(83) The acid source in this reaction has not been established.

(84) Appleton, T. G.; Bennett, M. A. *J. Organomet. Chem.* **1973**, *55*, C88.

(85) Otsuka classified these complexes by their "anionic character" according to the rates of these reactions. The anionic character of the hydroxide was greater for palladium than for platinum and decreased in the order R = Ph > $H{=}CCl_2 > CCl{=}CCl_2 > C_6F_5$.

(86) A dissociative exchange mechanism would be zero order in $[CD_3OD]$ because, after rate-limiting methoxide dissociation, a faster-than-diffusion-controlled exchange of deuterium between CD_3OD and CH_3O^- would result in methoxide exchange without CD_3OD participation in any rate-determining steps.

(87) It is recognized that "essentially thermoneutral" includes reactions with equilibrium constants of 150 (or even larger for the ruthenium hydroxide and dihydrogen) which might appear "irreversible" and can certainly be used for synthetic purposes without even employing an excess of the H–X reagent. However, the amounts of energy involved in these equilibria are actually quite small (<3 kcal·mol^{-1}).

(88) Given the previous observations "irreversible" is clearly a misleading term. In this context it is meant to convey a reaction in which only products can be detected under all reaction conditions (i.e., no ruthenium hydroxide or HCN could be detected when the cyanide was dissolved in 50/50 THF/H_2O).

(89) (a) Bryndza, H. E.; Domaille, P. J.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *Polyhedron*, accepted for publication. (b) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *J. Am. Chem. Soc*, submitted for publication.

(90) This evaluation requires that the only bond strengths changing in the equilibrium are the four directly involved in the σ-ligand metathesis. Put another way, the Pt–C bond in the amide is about as strong as the Pt–C bond in the methoxide. This assumption was tested and found valid as shown in ref 89.

(91) A direct comparison of an L_nM-CH_3 homolytic bond strength to an L_nM-OCH_3 bond strength would find them the same since the H–C bond strength in methane is (fortuitously?) the same as the H–O bond strength in methanol. Similar reasoning shows the corresponding L_nM-OH bond to be approximately 15 kcal·mol^{-1} stronger than those bonds mentioned above.

(92) Vaska, L.; Chen, L. S.; Senoff, C. V. *Science (Washington, D.C.)* **1971**, *174*, 587.

(93) While it is clear that K_a values measured in aqueous solutions do not accurately reflect dissociation constants in organic solvents, such as toluene or THF, where these equilibria were studied, the example serves to illustrate the relative ease of ligand heterolytic dissociation in a hypothetical solvent system. The use of K_a values appropriate to different solvent systems *may* change the ratio of line 6, Scheme II; however, any such changes, by definition, will also alter the ratio of K_1/K_2 in exactly the same way so that $K_{1solv}/K_{2solv} = K_a(HOMe)_{solv}/K_a(HNMePh)_{solv}$.

(94) Milburn, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 54.

(95) Desai, A. G.; Milburn, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 1958.

(96) Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191.

(97) Strukul, G.; Michelin, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 7563.

(98) Yoshida, T.; Otsuka, S. *Adv. Chem. Ser.* **1982**, *No. 196*, 135.

(99) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134.

(100) Diamond, S. E.; Mares, F. *J. Organomet. Chem.* **1977**, *142*, C55.

(101) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, C17.

(102) Milstein, D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3773.

(103) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110.

(104) Fernandez, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A. *J. Organomet. Chem.* **1986**, *316*, 343.

(105) Arnold, D. P.; Bennett, M. A.; Bilton, M. S.; Robertson, G. B. *J. Chem. Soc., Chem. Commun.* **1982**, 115.

(106) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. (b) Diversi, P.; Ingrosso, G.; Lucherini, A. *J. Chem. Soc., Chem. Commun.* **1978**, 735.

(107) Milstein, D. *J. Am. Chem. Soc.* **1986**, *108*, 3525.

(108) The stated uncertainty of the thermochemical estimates cited is several kcal·mol^{-1}, a large enough difference to prevent observation or isolation of a hydroxymethyl species in these systems.

(109) Bernard, K. A.; Rees, W. M.; Atwood, J. D. *Organometallics* **1986**, *5*, 390.

(110) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1982**, *1*, 1540.

(111) Fryzuk, M. D.; MacNeil, P. A. *J. Am. Chem. Soc.* **1984**, *106*, 6993.

(112) These experiments cannot distinguish between a direct reductive coupling and dissociation of methoxide followed by attack on the acyl carbon atom. However, the π-acid effects seem most in line with reductive coupling.

(113) Milstein, D. *J. Chem. Soc., Chem. Commun.* **1986**, 817.

(114) Yamamoto, T. *J. Am. Chem. Soc.* **1980**, *102*, 3758.

(115) See, for example: (a) Kullberg, M. L.; Kubiak, C. P. *Inorg. Chem.* **1986**, *25*, 26. (b) Kullberg, M. L.; Lemke, F. R.; Powell, D. R.; Kubiak, C. P. *Inorg. Chem.* **1985**, *24*, 3589. (c) Kullberg, M. L.; Kubiak, C. P. *C1 Mol. Chem.* **1984**, *1*, 171. (d) Kullberg, M. L.; Kubiak, C. P. *Organometallics* **1984**, *3*, 632.

(116) Clark, H. C.; Dixon, K. R.; Jacobs, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 1346.

(117) von Werner, K.; Beck, W. *Chem. Ber.* **1972**, *105*, 3947.

(118) Minghetti, G.; Bonati, F.; Banditelli, G. *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*, 415.

(119) Bennett, M. A. *J. Mol. Catal.* **1987**, *41*, 1.

(120) Bennett, M. A.; Rokicki, A. *J. Organomet. Chem.* **1983**, *244*, C31.

(121) Bennett, M. A.; Rokicki, A. *Organometallics* **1985**, *4*, 180.

(122) Although Bryndza and Kretchmar have reported reductive elimination chemistry from (DPPE)Pt(CO_2Me)$_2$ which takes place along with CO deinsertions at elevated temperatures.

(123) Bryndza, H. E. *Organometallics* **1985**, *4*, 1686.

(124) Churchill, M. R.; Fettinger, J. C.; Rees, W. M.; Atwood, J. D. *J. Organomet. Chem.* **1986**, *304*, 227.

(125) (a) Costa, G.; Mestroni, G.; Pellizer, G. *J. Organomet. Chem.* **1968**, *15*, 187. (b) Costa, G.; Mestroni, G.; Pellizer, G.; Tauzher, G.; Licari, T. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 515.

(126) (a) Michelin, R. A.; Strukul, G.; Bresciani-Pahor, N.; Zangrando, E.; Randaccio, L. *Inorg. Chim. Acta* **1984**, *84*, 229 (b) Ros, R.; Carturan, G.; Graziani, M. *Transition Met. Chem.* **1976**, *1*, 13.

(127) Flynn, B. R.; Vaska, L. *J. Am. Chem. Soc.* **1973**, *95*, 5081.

(128) Yoshida, T.; Thorn, D. L.; Okano, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 4212.

(129) Bryndza, H. E. *Organometallics* **1985**, *4*, 406.

(130) Ros, R.; Renaud, J.; Roulet, R. *J. Organomet. Chem.* **1976**, *104*, 393.

(131) Michelin, R. A.; Ros, R. *J. Organomet. Chem.* **1979**, *169*, C42.

(132) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *202*, 107.

(133) (a) Alcock, N. W.; O'Sullivan, R. D.; Perkins, A. W. *J. Chem. Soc., Chem. Commun.* **1980**, 1216. (b) O'Sullivan, R. D.; Parkins, A. W.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1986**, 571.

(134) Some leading references to this longstanding controversy follow: (a) Henry, P. M. *J. Am. Chem. Soc.* **1964**, *86*, 3246. (b) Henry, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 1595. (c) Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135. (d) Green, M.; Hancock, R. I. *J. Chem. Soc. A* **1967**, 2054. (e) Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1968**, 464. (f) Stille, J. K.; Fox, D. B. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 157. (g) Stille, J. K.; Devakaruni, R. *J. Am. Chem. Soc.* **1978**, *100*, 1303. (h) Stille, J. K.; Divakarumi, R. *J. Organomet. Chem.* **1979**, *169*, 239. (i) Henry, P. M. *Palladium-Catalyzed Oxidation of Hydrocarbons*; D. Reidel: Dordrecht, The Netherlands, 1980; Vol. 2. (j) Backvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959. (k) Clark, H. C.; Goel, A. B.; Goel, S. *J. Organomet. Chem.* **1981**, *216*, C25. (l) Gragor, N.; Henry, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 681. (m) Gragor, N.; Henry, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 681. (n) Green, M.; Sashan, J. K. K.; Al-Najjar, I. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1565. (o) Wan, W. K.; Zaw, K.; Henry, P. M. *J. Mol. Catal.* **1982**, *16*, 81. (p) Zaw, K.; Lautens, M.; Henry, P. M. *Organometallics* **1983**, *2*, 197.

(135) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; Chapter 6, p 104. In succeeding pages this author also discusses the related situation involving acetoxylation of simple olefins and dienes, which, while quite important, lies outside the admittedly artificial boundaries of this review.

(136) A few leading references to these important reactions follow. (a) Flabe, J. *Carbon Monoxide in Organic Synthesis*; Springer-Verlag: New York, 1970. (b) Pino, P.; Piacenti, F.; Bianchi, M. "Hydrocarboxylation of Olefins". In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, p 233. (c) Stone, F. G. A.; West, R., Eds. *Advances in Organometallic Chemistry*; Academic: New York, 1979; Vol. 17. (d) Bittler, K.; von Kutepow, N.; Neubaur, D.; Reis, H. *Angew. Chem., Int Ed. Engl.* **1968**, 7, 329. (e) Fenton, D. M. *J. Org. Chem.* **1973**, *38*, 3192. (f) Piacenti, F.; Bianchi, M.; Lazzaroni, R. *Chim. Ind. (Milan)* **1968**, *50*, 318. (g) Knifton, J. F. *J. Org. Chem.* **1976**, *41*, 2885. (h) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1963**, *85*, 2779. (i) Ellwood, P. *Chem. Eng.* **1969**, 148. (j) Roth, J. F.; Craddock, J. H.; Hershman, A.; Paulik, F. E. CHEMTECH. **1971**, *1*, 600. (k) Grove, H. D. *Hydrocarbon Proc.* **1972**, 76. (l) Paulik, F. E. U.S. Patent 3 769 329. (m) Cassar, L.; Foa, M. *J. Organomet. Chem.* **1977**, *134*, C15. (n) Forster, D. *Adv. Organomet. Chem.* **1979**, *17*, 255. (o) Ohshiro, Y.; Hirao, T. *Heterocycles* **1984**, *22*, 859. (p) Alper, H.; Hashem, K.; Heveling, J. *Organometallics* **1982**, *1*, 775. (q) Alper, H.; Woell, J. B.; Despeyroux, B.; Smith, D. J. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1270. (r) Alper, H.; Daniele, L. *Tetrahedron Lett.* **1985**, *26*, 5639. (s) Alper, H.; Leonard, D. *J. Chem. Soc., Chem. Commun.* **1985**, 511. (t) Ferguson, S. B.; Alper, H. *J. Mol. Catal.* **1986**, *34*, 381.

(137) (a) Head, R. A.; Tabb, M. I. *J. Mol. Catal.* **1984**, *26*, 149. (b) Zahalka, H. A.; Alper, H.; Sasson, Y. *Organometallics* **1986**, *5*, 2497.

(138) (a) Yoshida, T.; Okano, T.; Otsuka, S. *ACS Symp Ser.* **1981**, *No. 152*, 79. (b) Choudhury, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1885. (c) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941.

(139) (a) Alper, H.; Arzoumanian, Petrignani, J.-F.; Saldana-Maldonado, M. *J. Chem. Soc., Chem. Commun.* **1985**, 340. (b) Kamiya, Y.; Kawato, K.; Ohta, H. *Chem. Lett.* **1980**, 1549. (c) Alper, H.; Urso, F.; Smith, D. J. H. *J. Am. Chem. Soc.* **1983**, *105*, 6737.

(140) (a) Kobayashi, T.; Tanaka, M. *J. Organomet. Chem.* **1982**, *231*, C12. (b) Murahashi, S.-I.; Yoshimura, N.; Tsumiyama, T.; Kojima, T. *J. Am. Chem. Soc.* **1983**, *105*, 5002.

(141) (a) Tam, W. *J. Org. Chem.* **1986**, *51*, 2977. (b) Hallgren, J. E.; Matthews, R. O. *J. Organomet. Chem.* **1979**, *135*, 135. Durand, D.; Lasson, C. *Tetrahedron Lett.* **1969**, *80*, 2329. (c) Hallgren, J. E.; Lucas, G. M. *J. Organomet. Chem.* **1981**, *212*, 135. (d) Ozawa, F.; Soyama, H.; Yamamoto, A. *Tetrahedron Lett.* **1982**, *23*, 3383. (e) Ozawa, F.; Yanagihara, H.; Yamamoto, A. *J. Org. Chem.* **1986**, *51*, 415. (f) Hallgren, J. E.; Lucas, G. M.; Matthews, R. O. *J. Organomet. Chem.* **1981**, *204*, 135. (g) Kobayashi, T.; Tanaka, M. *J. Organomet. Chem.* **1982**, *233*, C64. (h) Fenten, D. M.; Steinwand, P. J. *J. Org. Chem.* **1974**, *39*, 701. (i) Graziani, M.; Uguagliati, P.; Carturan, G. *J. Organomet. Chem.* **1971**, *27*, 275. (j) Hallgren, J. E.; Matthews, R. O. *J. Organomet. Chem.* **1979**, *175*, 135. (k) Ozawa, F.; Sugimoto, T.; Yuasa, Y.; Santra, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 683. (l) Ozawa, F.; Soyama, H.; Yanagihara, H.; Aoyama, I.; Takino, H.; Izawa, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1985**, *107*, 3235. (m) Koch, P.; Perrotti, E. *J. Organomet. Chem.* **1974**, *81*, 111. (n) des Abbayes, H.; Bulop, A. *J. Chem. Soc., Chem. Commun.* **1978**, 1090. (o) Tsiji, J.; Iwamoto, N. *J. Chem. Soc., Chem. Commun.* **1966**, 380. (p) Yamamoto, A.; Yamamoto, T.; Ozawa, F. *Pure Appl. Chem.* **1985**, *57*, 1799. (q) Alper, H.; Hartstock, F. W. *J. Chem. Soc., Chem. Commun.* **1985**, 1141. (r) Alper, H.; Vasapollo, G.; Hartstock, F. W.; Mlekuz, M.; Smith, D. J. H.; Morris, G. E. *Organometallics* **1987**, *6*, 2391.

(142) (a) Appleton, T. G.; Chisholm, M. H.; Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 1786. (b) Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1978**, *154*, 323. (c) Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1979**, *174*, 221. (d) Rivetti, F.; Romano, U. *Chim. Ind.* (*Milan*) **1980**, 62. (e) Fenton, D. M.; Steinwand, P. J. *J. Org. Chem.* **1974**, *39*, 714. (f) Burk, P. L.; Van Engen, D.; Campo, K. S. *Organometallics* **1984**, *3*, 493.

(143) (a) Delgado-Lieta, E.; Luke, M. A.; Jones, R. F.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 839. (b) Jung, C. W.; Garrou, P. E. *Organometallics* **1982**, *1*, 658. (c) Tani, K.; Suwa, K.; Otsuka, S. *ACS Symp. Ser.* **1982** *No. 185*, 283. (d) Tani, K.; Suwa, K.; Tanigawa, E.; Yoshida, T.; Okano, T.; Otsuka, S. *Chem. Lett.* **1982**, 261. (e) Tani, K.; Tanigawa, E.; Tatsuno, Y.; Otsuka, S. *Chem. Lett.* **1986**, 737. (f) Barratt, D. S.; Cole-Hamilton, D. J. *J. Organomet. Chem.* **1986**, *306*, C41. (g) Sanchez-Delgado, R. A.; Valencia, N.; Rosa-Linda, M.-S.; Antida, A.; Medina, M. *Inorg. Chem.* **1986**, *25*, 1106. (h) Morton, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 248. (i) Itagaki, H.; Saito, Y. *J. Mol. Catal.* **1987**, *41*, 209.

(144) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Chem. Commun.* **1979**, 870.

(145) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 2803.

(146) (a) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3030. (b) Diamond, S. E.; Grant, B.; Tom, G. M.; Taube, H. *Tetrahedron Lett.* **1974**, 4025. (c) Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723.

(147) Some reports of olefin hydration in acrylonitrile were described using $L_2PtR(OH)$ catalysts and were characterized as quite irreproducible. In light of the more recent information cited above, it is likely that small amounts of hydride impurities or byproducts were resulting in the olefin hydrations in those cases.

(148) Or put another way, it appears that an oxidation-state change for platinum may be necessary during olefin hydration and may not be required during nitrile hydrolysis.

(149) Jensen, C. M.; Trogler, W. C. *Science* (*Washington, D.C.*) **1986**, *233*, 1069.

(150) Strukul, G.; Michelin, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1538.

(151) The actual catalysts for these transformations are somewhat in question. The mechanism of catalyst deactivation is especially interesting as this seems to take place under conditions where the suspected catalysts can be reisolated.

(152) (a) Eberhardt, G. G.; Tadros, M. E.; Vaska, L. *J. Chem. Soc., Chem. Commun.* **1972**, 290. (b) Yoshida, T.; Okano, T.; Saito, K.; Otsuka, S. *Inorg. Chim. Acta* **1980**, *44*, L135.

(153) Burton, J. T.; Puddephatt, R. J. *Can. J. Chem.* **1986**, *64*, 1890.