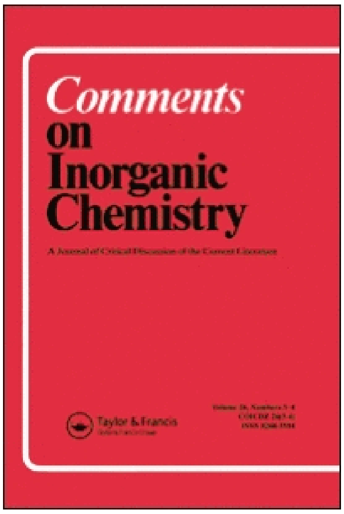

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Late Transition Metal Oxo and Imido Chemistry

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Late Transition Metal Oxo and Imido Chemistry

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The synthesis and reaction chemistry of second and third series late transition metal oxo and imido complexes are examined. The often serrendipitous syntheses are analyzed and catagorized into general types and according to the metal group. A brief survey of reaction chemistry reveals great diversity ranging from nucleophilic reactivity to oxygen atom and nitrene transfers.

Keywords: *oxo, imido, nitrogen ligands, oxygen ligands, platinum group metals, gold, late transition metals*

INTRODUCTION

The chemistry of late transition metal (Groups 9–11) covalent bonds to nitrogen and oxygen has been of interest to chemists for many years.[1-5] The reasons for this interest are varied but center primarily on catalytic chemistry and bioinorganic systems. Catalysis with late transition metals is vital to the chemical industry, and oxygen and nitrogen species

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bonded to metal complexes or metal surfaces are involved in many important processes.[6-14] The Wacker process,[15-17] and ethylene epoxidation on Ag[14] are two well-known examples where the mechanisms are still topics of debate despite many years of study.

Biological interest in late transition metal covalent bonds to nitrogen and oxygen originates from several areas. The anti-tumor activity of cis-$(NH_3)_2PtCl_2$ (cis-platin) and related complexes where hydrolysis is an important step in the activity of the drugs has spurred investigation into hydroxo Pt(II) and Pd(II) chemistry.[18,19] The reaction of molecular oxygen with Cu(I) complexes, of long-time interest in catalytic systems, has been advanced by interest in modeling Cu-containing proteins.[11,20–22] A remarkable result in this area is the recent observation of a reversible dioxygen-dioxo complex conversion.[23] There is also a general interest in metal covalent bonds to nitrogen and oxygen because of their involvement in several other biological systems including nitrogenase[24] and photosystem II.[25–27] Although these involve middle or early transition metals, their chemistry is still sufficiently mysterious that late transition metal complexes can give valuable insight into the workings of the biological systems.

Finally, there is a more fundamental interest in late transition metal-nitrogen and -oxygen covalent bonds, especially those involving the "soft" transition metals of the second and third series. Hard-soft acid-base theory[28,29] would predict an unfavorable interaction suggesting relatively weak bonds and high reactivity. Studies indicate that the supposition about weak bonding is incorrect and that in general M-O and M-N bonds of these metals are as strong as analogous M-C bonds.[30,31] High reactivity can be found as discussed below.

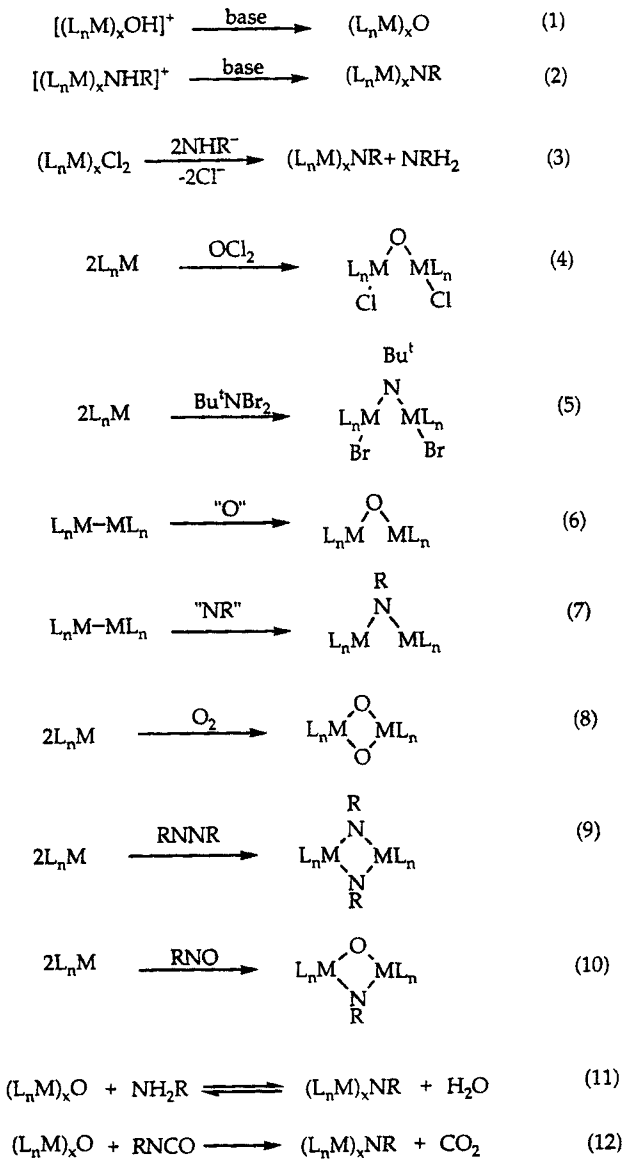
Our interest in late transition metal chemistry is focused on the second and third row metals Rh, Ir, Pd, Pt, Ag, and Au and primarily involves oxo (O^{2-}) and imido (RN^{2-}) complexes although in the process of preparing the oxo and imido complexes we have also examined the chemistry of hydroxo (OH^-) and amido (RHN^-) complexes. In this article, the synthesis and reaction chemistry of second and third series late transition metal oxo and imido complexes from Rh to Au is examined with emphasis on complexes prepared in our laboratories.

SYNTHESIS OF OXO AND IMIDO COMPLEXES

Early syntheses of second and third series late transition metal oxo complexes are largely serendipitous and generally give low yields. Serendipitous preparations of imido complexes are much rarer probably as a result of there being fewer common sources of the NR group, the greater basicity of the imido ligand (see below), and the reactivity of imido complexes with protic compounds including water. Rational syntheses of both oxo and imido complexes have more recently been developed. A problem with the synthesis of oxo and imido complexes is that the complexes can be difficult to characterize. Characteristic NMR signatures are absent and the often weak and broad nature of OH and NH ^{1}HNMR signals make it difficult to conclusively show that the oxo or imido ligands are present. X-ray crystal structure analysis can be similarly inconclusive as hydrogen atoms can be difficult to detect. Therefore, identification of oxo and imido complexes, especially those prepared serendipitously, must be viewed with some skepticism unless supported by other methods such as chemical reactivity and derivatization.

Preparative methods for imido and oxo complexes are outlined in Scheme 1. Water is a common source of oxo ligands and is responsible, in one form or another, for many of the serendipitous syntheses of oxo complexes. In planned syntheses, deprotonation of hydroxo complexes (Eq. (1)) is a favored route to oxo complexes and has produced Rh(I), Ir(I), Ir(III), and Pt(II) oxo complexes. Imido complexes have been prepared analogously by deprotonation of amido complexes (Eq. (2)) and Rh(I), Ir(I), Ir(III), and Pt(II) complexes have been reported. Equally as effective for the synthesis of imido complexes is the reaction of halo complexes with LiNHR (Eq. (3)). This reaction may well occur by formation of an intermediate amido complex which is then deprotonated by a second equivalent of LiNHR. An alternative is an alpha-abstraction type process from an intermediate diamido. Other oxo anion sources include nitrite and the gold oxo complex $[(LAu)_3(\mu\text{-}O)]^+$. Lower nitrogen oxides (N_2O and NO) are produced in the process of oxo ligand formation from nitrite.

Two routes to oxo and imido complexes that are attractive but have not been reported are illustrated in Eqs. (4) and (5) of Scheme 1. The double oxidative addition of OCl_2 and Bu^tNBr_2 are shown. Bu^tNBr_2 is a remarkably stable red-orange solid[32] and seems an ideal reagent for the


[(LnM)xOH]+ base (LnM)xO (1)
[(LnM)xNHR]+ base (LnM)xNR (2)
(LnM)xCl2 2NHR- -2Cl- (LnM)xNR+ NRH2 (3)
2LnM OCl2 O LnM MLn Cl Cl (4)
2LnM ButNBr2 But N LnM MLn Br Br (5)
LnM–MLn "O" O LnM MLn (6)
LnM–MLn "NR" R N LnM MLn (7)
2LnM O2 O LnM MLn O (8)
2LnM RNNR R N LnM MLn N R (9)
2LnM RNO O LnM MLn N R (10)
(LnM)xO + NH2R (LnM)xNR + H2O (11)
(LnM)xO + RNCO (LnM)xNR + CO2 (12)

SCHEME 1

preparation of imido complexes. OCl_2 is unstable (explosive) and more difficult to prepare and isolate.[33]

Although oxygen atom and nitrene transfers to metal centers are attractive synthetic routes to oxo and imido complexes (Eqs. (6) and (7)), and have been effective for early transition metal complexes,[34] a mixed Pt/Re cluster,[35] and at least one copper complex,[36] no clear examples exist for second and third series late transition metal systems. Dioxygen as a donor of two oxygen atoms (Eq. (8)) is a reaction of special interest since this represents a critical step in the activation of molecular oxygen. The criteria for such a process are far from clear, but the observation of a reversible dioxo-dioxygen interconversion in a dinuclear copper system[23] and the formation of Re/Pt dioxo complexes from dioxygen[35] may lead to a better understanding and more general application of molecular oxygen in oxo complex synthesis. One example of Pd oxo complex formation from a Pd(0) complex and dioxygen has been communicated.[37] However, the complex has not been structurally characterized and its properties are incompatable with those of the Pt analog, synthesized by an alternate method (see below). Similarly, RNO and RNNR are potential oxygen atom and nitrene donors (Eqs. (9) and (10)).[34] Reactions that have yielded late transition metal oxo complexes where oxygen atom transfer may be operative involve the donors ozone, dioxygen, and Me_3NO. Yields, however, are low and oxidation of the metal center by electron transfer with oxo formation from water deprotonation is an alternative that should be considered in most cases. These reactions are discussed further below for specific examples.

Interconversions of oxo and imido complexes with isocyanates or by water or amine addition are also known (Eqs. (11) and (12)). The favored direction varies: in some cases the oxo complex is stable in the presence of amine and in others the imido complex is stable in the presence of water.[34] A complication in these interconversions is the potential reaction of the formed oxo or imido complex with excess water or amine. If the oxo or imido complexes are unstable in the presence of excess water or amine, hydroxo or amido complexes are obtained.

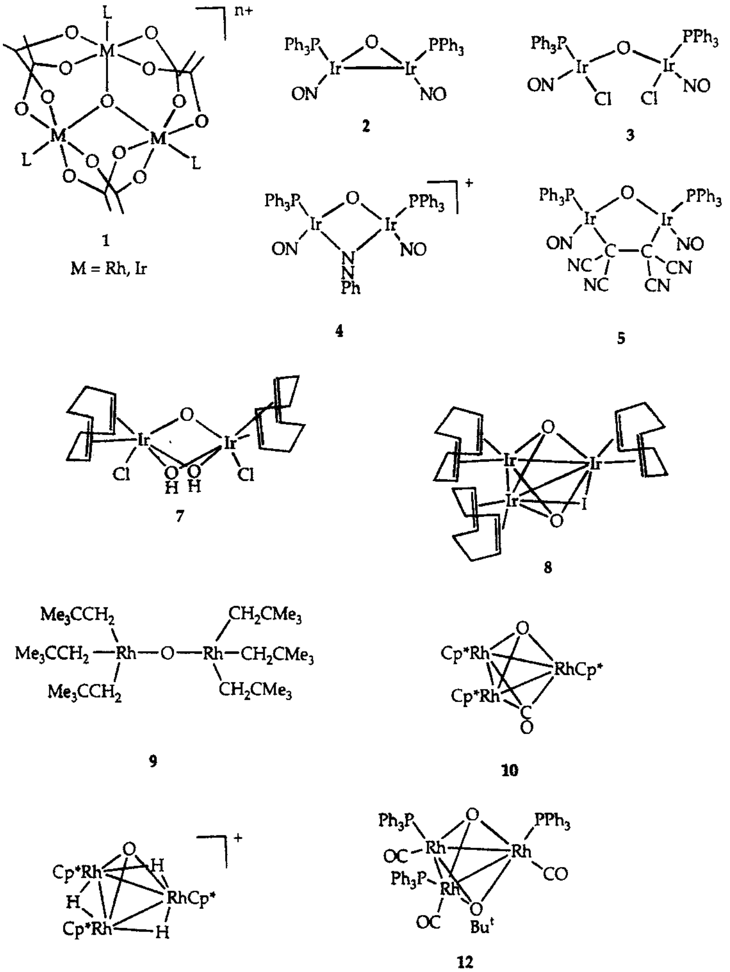
Rh and Ir

The first oxo complexes of Rh and Ir are the highly colored trinuclear acetates **1** (M =Rh, Ir) for which analogs exist earlier in the periodic table. These complexes are formed by ozonolysis of metal salts in the presence of acetic acid,[38] by Ag^+ treatment of the metal halides in acetate/acetic acid solutions,[38] or by acetic acid treatment of sintered IrO_2/BaO_2[39] and can be isolated with all three metal centers in the 3+ oxidation state or as mixed valence M(III, III, IV) complexes. The reaction chemistry of theses complexes is sparse and mostly limited to metal oxidation state changes and substitution reactions at the metal center. Reactivity at the oxo ligand is absent. Related complexes with sulfate[40] or nitrate[41] in place of acetate are known but not structurally characterized.

A low yield synthesis of the orange oxo complex $Ir_2(\mu\text{-}O)(NO)_2(PPh_3)_2$ **2** was reported in 1975 from the reaction of $Ir(CO)Cl(PPh_3)_2$ with $NaNO_2$.[42] A study of the reaction suggests the intermediacy of $Ir(CO)(NO_2)(PPh_3)_2$ and $[Ir(NO)_2(PPh_3)]_2$, the later complex eliminating N_2O (detected in the reaction mixture) in a low efficiency process to form the oxo complex.[43] The Ir-Ir bond of $Ir_2(\mu\text{-}O)(NO)_2(PPh_3)_2$ is susceptible to oxidative cleavage, and reaction with $HgCl_2$ gives $Ir_2(\mu\text{-}O)Cl_2(NO)_2(PPh_3)_2$ **3**.[42] ArN_2^+, $C_2(CN)_4$, and Ag^+ insert into the Ir-Ir bond yielding $[Ir_2(\mu\text{-}O)(\mu\text{-}N_2Ar)(NO)_2(PPh_3)_2]^+$ **4**, $[Ir_2(\mu\text{-}O)\{\mu\text{-}C_2(CN)_4\}(NO)_2(PPh_3)_2]$ **5**, and $[Ir_2(\mu\text{-}O)(\mu\text{-}AgTHF)(NO)_2(PPh_3)_2]^+$ **6**, respectively.[42,43] With the exception of **5**, these complexes all transfer their oxo oxygen atom to PPh_3 (see below).

Another example of an apparently serendipitous oxo synthesis is the reaction of $[(COD)Ir(\mu\text{-}Cl)]_2$ with dioxygen in the presence of water. Crystallographically characterized oxo-hydroxo complex, $Ir_2Cl_2(COD)_2(\mu\text{-}O)(\mu\text{-}OH)_2$ **7** is obtained in good yield.[44] A possible formation pathway is dioxygen addition to $[(COD)Ir(\mu\text{-}Cl)]_2$ to give the dioxo complex $[(COD)IrCl(\mu\text{-}O)_2]_2$ which is trapped by water. The oxo complex $[(COD)IrCl(\mu\text{-}O)_2]_2$ would be isoelectronic with known $[Cp^*Ir(\mu\text{-}O)_2]_2$ **17**. However, an electron transfer process is also possible. Superoxide anion is an effective base[45] and could deprotonate an hydroxo complex formed by hydrolysis of the chloride or its oxidized product. Support for an oxidation/hydration/deprotonation pathway is found in the low yield synthesis of the oxo complex $Ir_3(COD)_3(\mu\text{-}O)_2(\mu\text{-}I)$ **8** from the reaction of the Ir(II) complex $[(COD)IrI(\mu\text{-}I)]_2$ with AgOAc followed by chromotography on silica gel.[46]

Dioxygen also appears to be the source of the oxo ligand in $\{Np_3Rh\}_2(\mu\text{-}O)$ **9**.[47] This diamagnetic, green-black, Rh(IV) linear


1

M = Rh, Ir

2

3

4

5

7

8

9

10

11

12

STRUCTURES 1 — 12

dimer was isolated in 30% yield from the reaction of excess dioxygen exposed LiNp with $RhCl_3(THT)_3$. Dioxygen exposure of alkyllithium reagents is known to generate peroxides and alkoxides.[48] Me_3NO may also be used as the oxygen source in the pretreatment of the Li reagent.

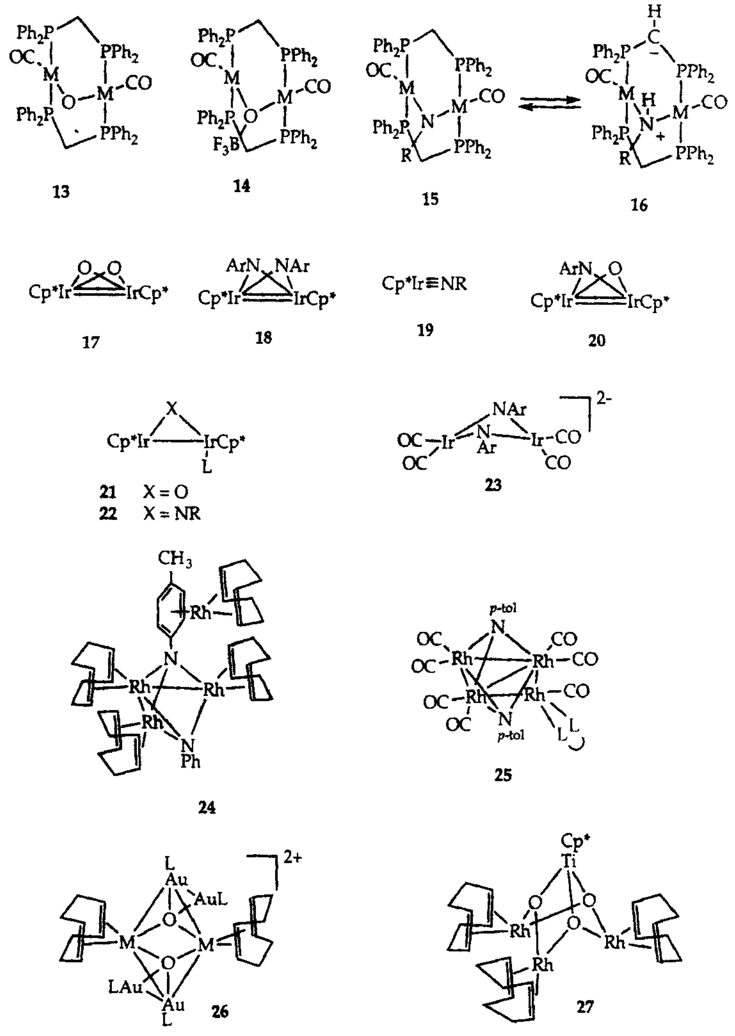
The unusual nature of this complex, problems with the crystal structure determination, and the lack of reaction studies leave some doubt as to the correct formulation of this complex.

Decarbonylation of $Cp^*Rh(CO)_2$ with Me_3NO in boiling acetone gives high yields of $[Cp^*Rh(CO)]_2$. However, a small amount of purple $(Cp^*Rh)_3(\mu\text{-}CO)(\mu\text{-}O)$ **10** is also isolated from the reaction mixture.[49] The oxo ligand is presumably formed by oxygen atom transfer from Me_3NO. Structural characterization reveals the expected O and CO capped Rh triangle. The analogous red-black imido complex, $(CpRh)_3(\mu\text{-}CO)(\mu\text{-}NSiMe_3)$, is reported to be produced from the reaction of $(CpRh)_3(\mu\text{-}CO)_2$ with N_3SiMe_3, but the imido complex has not been structurally characterized.[50]

Refluxing an Pr^iOH solution of $[Cp^*{}_2Rh_2(\mu\text{-}OH)_3][OH]$ gives moderate yields of the oxohydrido complex $[(Cp^*Rh(\mu\text{-}H)]_3(\mu\text{-}O)]^+$ **11**.[51] The hydride ligands are likely produced by β-hydride elimination from an intermediate isopropoxide complex while the oxo group is formed by hydroxide deprotonation of an hydroxo ligand. Another trinuclear Rh oxo complex, $[\{Rh(CO)(PPh_3)\}_3(\mu\text{-}O)(\mu\text{-}OBu^t)]$ **12**, is isolated in low yield from the reaction of $RhCl(CO)(PPh_3)$ with $KOBu^t$.[52] Water contamination is the probable source of the oxo ligand.

The first synthesis of a second and a third series late transition metal oxo complex by deprotonation of hydroxo complexes yields the A-Frame oxo complexes $M_2(\mu\text{-}O)(CO)_2(\mu\text{-}dppm)_2$ **13** (M = Rh, Ir, dppm = bis(diphenylphosphino)methane).[53] The oxo complexes contain remarkably basic oxo ligands and are isolated with associated LiX salts probably through oxo-Li coordination as is found in Pt oxo complexes. The salt-free Rh derivative is prepared by hydrolysis of the analogous imido complex and is structurally characterized.[54] A BF_3 adduct, structurally characterized $[Rh_2(\mu\text{-}OBF_3)(CO)_2(\mu\text{-}dppm)_2]$ **14** is prepared by displacement of LiX with BF_3.[53]

Analogous imido complexes $M_2(\mu\text{-}NR)(CO)_2(\mu\text{-}dppm)_2$ **15** are obtained from the reaction of $M_2Cl_2(CO)_2(\mu\text{-}dppm)_2$ (M = Rh, Ir) with LiNHR.[54,55]As with the analogous oxo complexes **13**, the imido nitrogen is highly basic, only more so. The lower electronegativity of nitrogen results in a lower acidity for the amido N-H, and alternate deprotonation of the dppm methylene group may occur giving the amido complexes $M_2(\mu\text{-}NHR)(CO)_2(\mu\text{-}dppm)(\mu\text{-}dppm\text{-}H)$ **16**. Complex **16** is the sole deprotonation product with R = Me, but in the case of R = aryl, tautomeric equilibrium mixtures of the imido and amido com-



STRUCTURES 13 — 27

plexes may be obtained. The equilibrium ratio is sensitive to the aryl group and shifts according to the aryl group electron donating ability following a Hammett free energy relationship. An estimate of the $\Delta G^{\ddagger}$

for the proton transfer equilibrium gives a value of 40 kJ/mol (M = Rh, R = p-MeC_6H_4) and is consistent with the long hydrogen bonding distance (2.2 Å) observed in the structure of the amido complex with R = Me (Fig. 1). The high donor ability of the imido nitrogen lone pair is reflected in the structure of **15** (M = Ir, R = p-tol) where a short N-C distance (1.35 Å) suggests delocalization of the lone pair into the ring π-orbitals. This delocalization has consequences for the reactivity of the complexes as discussed below.

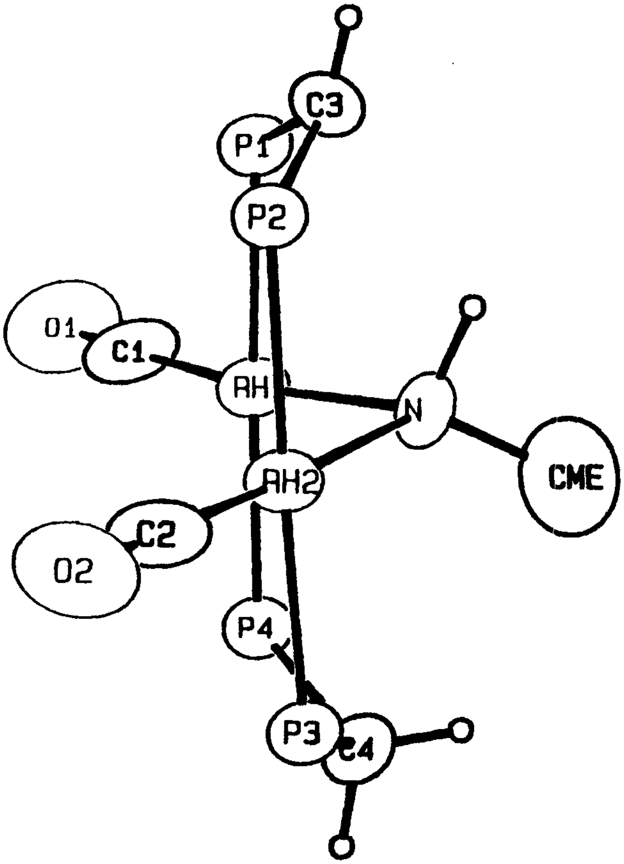


FIGURE 1 ORTEP drawings of the cationic portions of $[Rh_2(\mu\text{-}NHMe)(CO)_2(\mu\text{-}dppm\text{-}H)(\mu\text{-}dppm)]BF_4$ **16** (phenyl rings omited)

The imido complex **15** ($M = Rh$, $R = Ph$) may be hydrolyzed to adduct free, structurally characterized $Rh_2(\mu\text{-}O)(CO)_2(\mu\text{-}dppm)_2$ **13**($M = Rh$). However, this is a case where further reaction of the oxo complex competes with the imido to oxo conversion, and mixtures of the oxo complex **13** and $[Rh_2(\mu\text{-}OH)(CO)_2(\mu\text{-}dppm)_2]^+$ are obtained.

Deprotonation and dehydration of $[Cp^*Ir(\mu\text{-}OH)_3]OAc$ with $LiNR_2$ yields the Ir(III) oxo complex $[Cp^*Ir(\mu\text{-}O)]_2$ **17**.[56] This complex is also produced from the reaction of $[Cp^*IrCl_2]_2$ and Ag_2O in water followed by lyophilis of the initially obtained uncharacterized product.[57] The uncharacterized product is probably $[Cp^*Ir(\mu\text{-}OH)_3]OH$[58] which during lyophilis undergoes deprotonation of a bridging HO group by the OH^- counterion and elimination of water from two bridging OH ligands. The analogous imido complexes are prepared by reacting $[Cp^*IrCl(\mu\text{-}Cl)]_2$ with LiNHR or by dehydrochlorination of $Cp^*IrCl_2(NH_2R)$ and are isolated as monomeric Cp^*IrNR **19** ($R = Bu^t$, $SiMe_2Bu^t$, $2,6\text{-}Me_2C_6H_3$, $2,6\text{-}Et_2C_6H_3$, $2,6\text{-}Pr^i{}_2C_6H_3$) with bulky R groups.[57,59] Monomeric Cp^*IrNR **19** ($2,6\text{-}Me_2C_6H_3$, $2,6\text{-}Pr^i{}_2C_6H_3$) and dimeric $[Cp^*Ir(\mu\text{-}NR)]_2$ **18** ($R = Ph$, $2,6\text{-}Me_2C_6H_3$, $2,6\text{-}Et_2C_6H_3$) are obtained by treating Cp^*IrNBu^t with aryl amines. Monomeric **19** are the apparent kinetic products and are thermally converted to dimeric **18** for R groups of intermediate bulk. The dimerization is catalyzed by water via the oxo-imido dimers $Cp^*{}_2Ir_2(\mu\text{-}O)(\mu\text{-}NR)$ **20**. The monomers show linear Ir-N-R structures with short Ir-N bond distances indicating multiple bonding between the Ir and N atoms.[59] No other monomeric second or third series late transition metal imido or oxo complexes are known, and complexes showing multiple bonding between the metal and oxo or imido ligand are rare. Attempts to extend this chemistry to Rh have failed probably as a result of the more facile reduction of Rh(III) as compared to Ir(III).[60,61]

Oxo-imido interconversion has been well studied in this system.[57] Oxo-imido dimers $Cp^*{}_2Ir_2(\mu\text{-}O)(\mu\text{-}NR)$ **20** are formed by partial hydrolysis of the imido complexes but are only present in small equilibrium amounts for all but $R = Bu^t$, indicating that the imido form is favored for aryl imido complexes. Consistent with this, the oxo complex $[Cp^*Ir(\mu\text{-}O)]_2$ **17** reacts with aryl amines first to give **20** and then $[Cp^*Ir(\mu\text{-}NR)]_2$ **18**. Complexes **18–20** transfer an NR or O group to phosphines (L) giving dinuclear complexes $Cp^*{}_2Ir_2(\mu\text{-}X)L$ (**21**, $X = O$; **22**, $X = NR$) with asymmetric bridging oxo and imido ligands.[57,59]

Deprotonation of the amido complexes $[Ir(\mu\text{-}NHAr)_2(CO)_2]_2$ with RLi gives the anionic imido complexes $[Ir(\mu\text{-}NAr)_2(CO)_2]_2^{2-}$ **23**.[62] Li counterion association with the imido groups is suggested by Li NMR data. The Li ions are readily replaced by LAu^+ producing $[Ir(\mu\text{-}NAr)_2(CO)_2]_2(AuL)_2$ where again NMR data indicates bonding of the LAu^+ fragments to the imido nitrogen atoms.

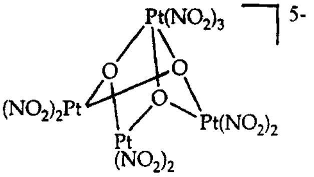
The reaction of $[(diene)Rh(\mu\text{-}Cl)]_2$ with LiNHAr gives the imido complex $[\{(diene)Rh\}_3(\mu\text{-}NAr)_2][Rh(diene)]$ **24** (diene = COD, TFB, Ar = $p\text{-}MeC_6H_4$).[63] The structure of the COD derivative shows an open triangle of Rh atoms bicapped by the two imido groups. The fourth Rh center is η^6-coordinated to one of the rings of the imido groups. In contrast to other imido complexes, the CO reaction chemistry of **24** is remarkably limited to the Rh centers.[64] Room temperature CO addition results in displacement of three of the four dienes and formation of $[\{(CO)_2Rh\}_3(\mu\text{-}NAr))_2][Rh(diene)(CO)]$ **25** (L_2 = diene) with the fourth Rh center, complexed by the remaining diene and a CO ligand, bonding to an edge of the Rh3 triangle. Slow loss of CO from the Rh(diene)(CO) fragment causes it to migrate back to the imido ring while CO addition at 55°C results in displacement of the last diene and formation of $[\{(CO)_2Rh\}_3(\mu\text{-}NAr)_2][Rh(CO)_3]$ **25** (L_2= 2CO).

Mixed M/Au (M = Rh, Ir) oxo complexes, $[(diene)M\{\mu\text{-}O(AuL)_2\}]_2^{2+}$ **26** (diene = COD, NBD) are isolated from the reaction of $[(LAu)_3(\mu\text{-}O)]^+$ with $[(diene)M(\mu\text{-}Cl)]_2$. The structure of the Rh and Ir NBD complexes show a rare 4-coordinate oxo group in a trigonal pyramidal geometry. This unusual oxygen geometry results from Au-Au and Au-M bonding.[65]

Complexes with oxo ligands bridging between a late transition metal and an early transition metal are known but are generally not considered here. However, an exception is made for $Cp^*Ti\ [(COD)Rh(\mu_3\text{-}O)]_3$ **27**, prepared from the reaction of $[(COD)Rh(\mu\text{-}OH)]_2$ with Cp^*TiMe_3.[66] This reaction may be considered an hydroxo group deprotonation reaction where the deprotonating agent is the methyl group of Cp^*TiMe_3. The core structure is very similar to the Pt oxo complex **28** described below.

Pd and Pt

Serendipitous preparations of Pt and Pd oxo complexes have been fewer than those for Rh and Ir. A particularly interesting example is the thermolysis of $K_2Pt(NO_2)_4$.[67] From the decomposition process at 325 °C it



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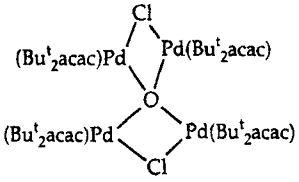

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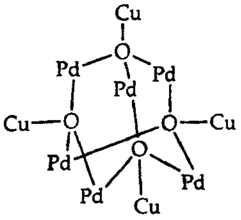

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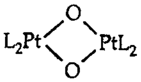

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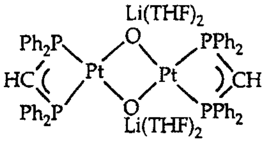

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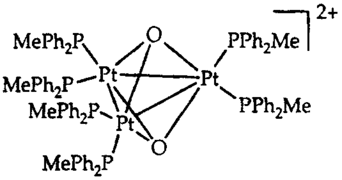

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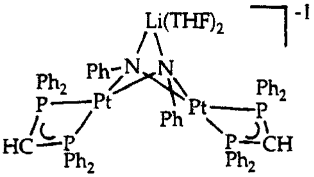

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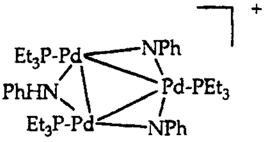

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STRUCTURES **28** — **38**

is possible to obtain yellow crystals of the tetranuclear oxo complex $K_5[Pt_4(NO_2)_9(\mu\text{-}O)_3]$ **28**. The structure is closely related to the Rh/Ti complex **27** and consists of a six-membered ring of three Pt(II)-O units. The ring is capped by a Pt(IV) bonding to the three ring oxo ligands.

Reaction of $[Pd(Bu^t{}_2acac)(OMe)]_2$ with dioxygen in chlorinated solvents yields the first example of a μ^4-oxo Pd complex, red $[(Bu^t{}_2acac)_4Pd_4Cl_2(\mu^4\text{-}O)]$ **29**.[68] The role of the dioxygen and chlorinated solvent are unclear, but electron transfer processes are a possibility. The complex is proposed as a model for solid PdO which contains similar units. The mixed Pd-Cu oxo complex $Pd_6Cu_4Cl_{12}O_4(HMPA)_4$ **30** contains μ^4-oxo ligands bonding to both Pd and Cu.[69] The adamantane-like metal-oxo core structure is shown. The HMPA ligands are terminally bonded to the Cu centers and the twelve chlorine atoms μ^2-bridge the Pd and Cu centers. Complex **30** is isolated from the reaction of dioxygen with a mixture of CuCl and $PdCl_2(MeCN)_2$ in HMPA. Cu(I) complexes are known to react with dioxygen to give oxo complexes,[11,12,23,70–73]and this may be the source of the oxo ligand in this mixed Pd/Cu system.

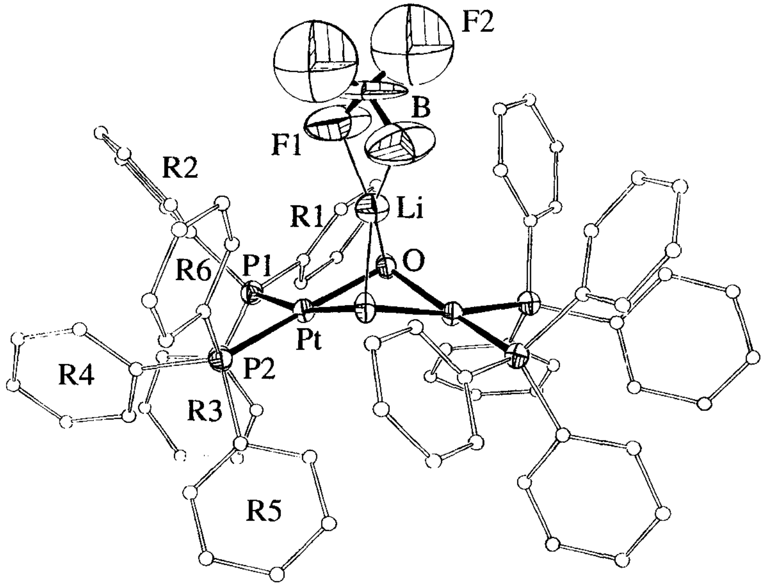
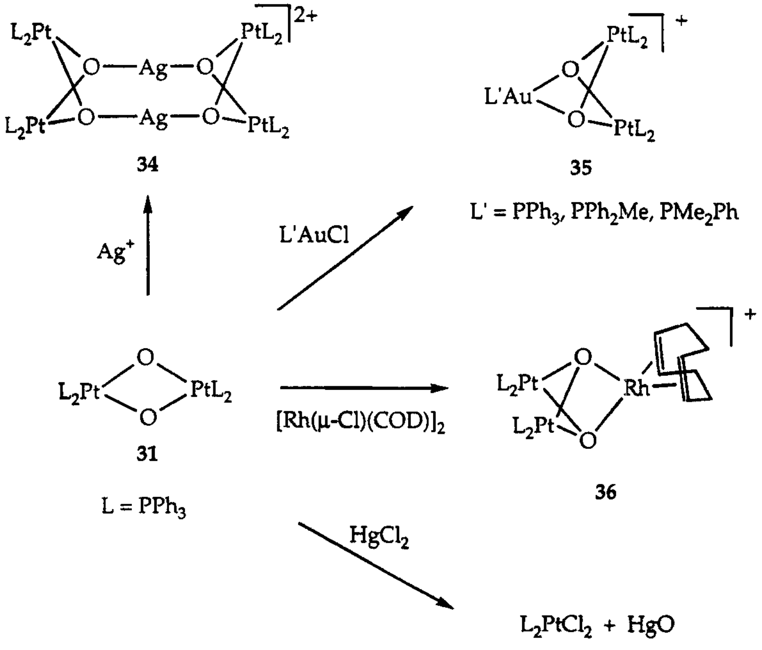


FIGURE 2 ORTEP drawing of $[(PPh_3)_2Pt(\mu\text{-}O)]_2{\bullet}LiBF_4$ **31•LiBF$_4$**

As with Rh and Ir, hydroxo complex deprotonation is an effective entry into Pt oxo chemistry. The dinuclear dioxo complexes $[L_2Pt(\mu\text{-}O)]_2$ **31** (L = a phosphine) that result from the deprotonation of $[L_2Pt(\mu\text{-}OH)]_2^{2+}$are strongly basic and are associated with LiX salts generated in the deprotonations.[74] Structural characterization reveals the bonding of the Li ions to the oxo ligands (Fig. 2) If the phosphine is the chelating phosphine dppm, deprotonation of the dppm methylene occurs prior to the hydroxo group deprotonation. The structurally characterized anionic dioxo complex $[(dppm\text{-}H)Pt(\mu\text{-}O)]_2[Li(THF)_2]_2$ **32** results from deprotonation of both the dppm ligand and the hydroxo groups. Attempts to prepare Pd complexes analogous to **31** and **32** by similar reactions result in the formation of Pd metal and oxidized phosphines. The formation of a Pd analog of **31** from the reaction of dioxygen with the Pd(0) dimer $[Pd(Cy_2CH_2CH_2PCy_2)]_2$ has been communicated.[37] The complex has not been structurally characterized and its stability in MeCN would indicate a greatly decreased basicity over the analogous Pt complexes **31**.

Solution decomposition of **31** ($L = PMePh_2$) yields the structurally characterized trinuclear oxo complex $[(L_2Pt)_3(\mu\text{-}O)_2]^{2+}$ **33**, a rare example of a late transition metal bicapped dioxo complex. Heterometallic analogs of **33** are formed by the reaction of $[L_2Pt(\mu\text{-}O)]_2$ **31**with Ag, Au, and Rh complexes (Scheme 2).[75] Instead of adduct formation, the reaction of **31** with $HgCl_2$ gives HgO and L_2PtCl_2 via oxo/chloro exchange as is observed in reactions of the gold oxo complex **45** with metal halides. Sulfido analogs of the heterometallic complexes are also known.[76–78]

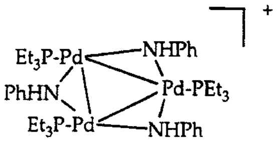
Only two imido complexes from this group are known. Treatment of $[(dppm)Pt(\mu\text{-}NHAr)]_2^{2+}$ with strong bases yields first the dppm deprotonation product $[(dppm\text{-}H)Pt(\mu\text{-}NHAr)]_2$.[79] This complex is further deprotonated with LiMe to $[(dppm\text{-}H)Pt(\mu\text{-}NAr)]_2(Li)2$. An X-ray structure determination with crystals from THF shows the structure **37** with one THF coordinated Li ion bridging the two imido ligands. The second imido complex, trinuclear $[Pd^3(\mu\text{-}NPh)^3(\mu\text{-}NHPh)^2(PEt_3)_3]^+$ **38**, is isolated from the reaction of $[PhN_3NHCH_2CH_2NH]^{2-}$ with $(PEt_3)_2PdCl_2$.[80] Formation of intermediate $(PEt_3)_2Pd{=}NPh$ was proposed, but given the highly basic nature of the dimeric Pt oxo complexes $[L_2Pt(\mu\text{-}O)]_2$ **31**, such an intermediate seems unlikely. Calculations also indicate that L_2PtNR is unstable with respect to elimi-



SCHEME 2

nation of LNR.[81] An alternative formulation of the product as $[Pd_3(\mu\text{-}NHPh)_3(PEt_3)_3]^+$ **39**, containing all amido groups, would also fit the data and would be consistent with a number of other Pt and Pd complexes containing a triangular array of metal atoms with bridging monoanionic ligands.[82–86]

Base hydrolysis of $Pt(dppm)Cl_2$ yields the trinuclear oxo complex $[\{Pt(PMePh_2\}_3(\mu\text{-}OPPh_2)_3(\mu\text{-}O)]^+$ **40**.[87] The $PMePh_2$, and Ph_2PO^- ligands arise from the base cleavage of a P-C bond of the dppm ligand. The oxo ligand is presumably produced by deprotonation of an intermediate hydroxo complex. A similar process likely occurs in the formation of $Pt_4Cl_2(DMSO)_6(\mu\text{-}O)_2$ **41**, produced when a solution of K_2PtCl_4 and NaOMe in MeOH/DMF/DMSO is slowly evaporated in air for 2 weeks. Methoxide is the proposed reducing agent for formation of the Pt(I) centers.[88]



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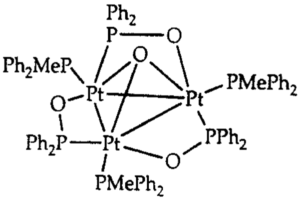

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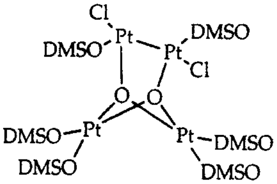

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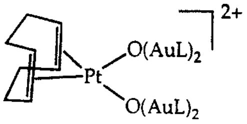

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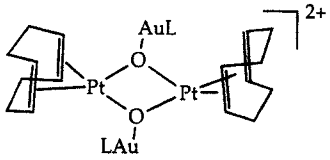

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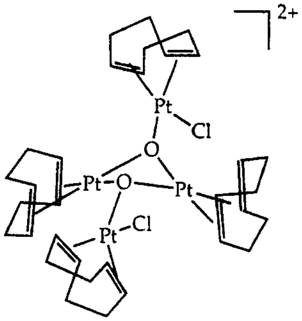

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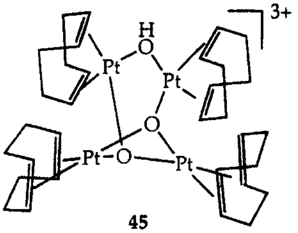

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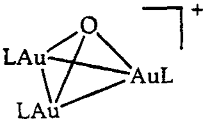
STRUCTURES **39** — **45**



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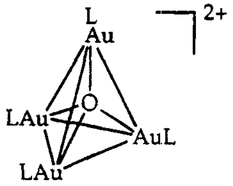

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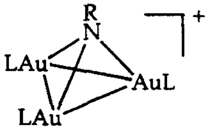

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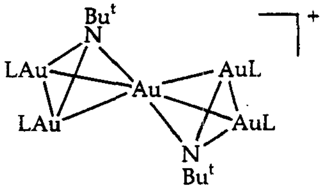

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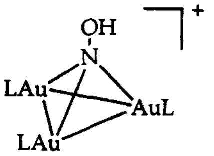

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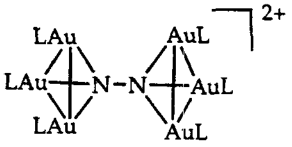

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STRUCTURES 46 — 51

Oxo/halo exchange reactions between $[(LAu)_3(\mu\text{-}O)]^+$ and $Pt(COD)Cl_2$, similar to those discussed above for Rh and Ir, yield the mixed Pt/Au oxo complexes $[Pt(COD)\{(\mu\text{-}O)(AuL)_2\}_2]^{2+}$ **42** and $[Pt(COD)(\mu\text{-}O)(AuL)]_2{}^{2+}$ **43**.[89] These complexes can be viewed as aura-aqua and aura-hydroxo Pt complexes. If a higher Au:Pt ratio is used, $[Pt_4(COD)_4Cl_2(\mu\text{-}O)_2]^{2+}$ **44** may be isolated. All of these complexes have considerable potential for synthetic elaboration. For example, dissolving **44** in wet CH_2Cl_2 gives crystals of the Pt hydroxo oxo complex $[Pt_4(COD)_4(\mu\text{-}OH)(\mu\text{-}O)_2]^{3+}$ **45**. Reduction of **44** might be expected to give $[Pt_4(COD)_4(\mu\text{-}O)_2]^{2+}$, a cationic COD analog of **41**.

Au and Ag

There are no structurally characterized homometallic Ag oxo complexes. Homometallic Au oxo complexes are restricted to complexes of the class $[(LAu)_3(\mu\text{-}O)]^+$ **46** where L = phosphine. These complexes are most readily prepared from LAu^+ (generated in situ from LAuCl and Ag^+) and hydroxide or from LAuCl, Ag_2O, and $NaBF_4$.[90–95] Complexes **46** are very useful reagents for the preparation of a large number of compounds. Only reactions that give oxo or imido complexes are discussed here.

The reaction of **46** and LAu^+ gives the μ^4-oxo complex $[(LAu)_4(\mu\text{-}O)]^{2+}$ **47**[96]and, as discussed above, with Rh, Ir, and Pt chloro diene complexes the heterometallic oxo complexes $[(diene)M\{\mu\text{-}O(AuL)_2\}]_2{}^{2+}$ **26** (M = Rh, Ir; diene = COD, NBD), $[Pt(COD)\{(\mu\text{-}O)(AuL)_2\}_2]^{2+}$ **42**, and $[Pt(COD)(\mu\text{-}O)(AuL)]_2{}^{2+}$ 43. The imido complexes, $[(LAu)_3(\mu\text{-}NR)]^+$ **48**, are readily prepared by treatment of $[(LAu)_3(\mu\text{-}O)]^+$ with amines or isocyanates.[97–100] The related complex, $[\{(LAu)_2(\mu\text{-}NBu^t)\}_2Au]^+$ **49** was unexpectedly isolated from the reaction of LAuCl with $LiNHBu^t$.[101] Hydrazines and hydroxyl amines react similarly to amines with **46** and give many interesting complexes including the structurally characterized hydroxylamine complex **50**[102] and the first group 11 dinitrogen complex $[(LAu)_6(\mu\text{-}N_2)]^{2+}$**51**.[98,103,104]

PROPERTIES AND REACTION CHEMISTRY OF OXO AND IMIDO COMPLEXES

Basicity

A common characteristic of late transition metal oxo and imido complexes is charge polarization in the metal-oxygen and metal-nitrogen bonds. This may result in substantial accumulation of negative charge density at the heteroatom and high basicity of the oxo or imido complex. Although basicity in non-aqueous systems is difficult to access, reactivity of the complexes at the oxo or imido ligand with electrophiles can give approximate ideas of relative basicity. The limited data suggest that the basicity depends on (1) the number of metals bonded to the ligand, (2) the nature of the ancillary ligands, and (3) the metal center oxidation state. These factors can be readily rationalized in terms of the acceptor properties of the metal centers. The more metal centers bonded to the oxo or imido ligand, the more charge transfer from the formally 2-ligand. Similarly, the more acidic the ancillary ligands or the higher the metal oxidation state, the better the metal center at charge acceptance.

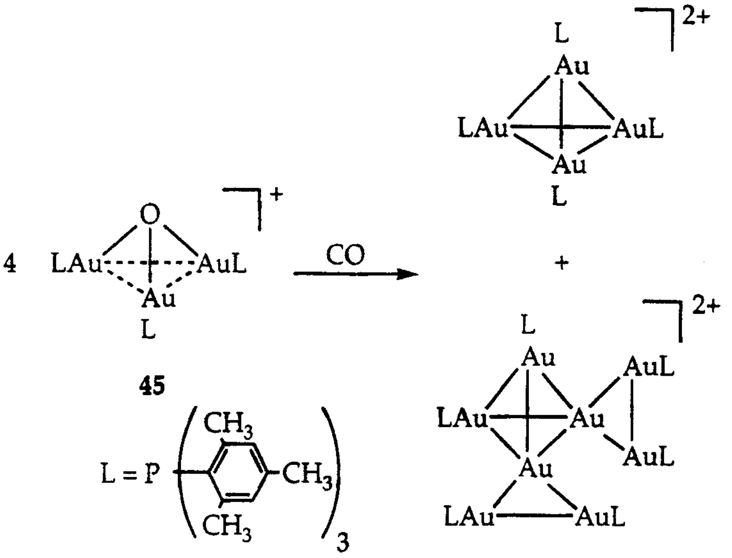
Another factor in the basicity of the complexes appears to be whether the metal is in the second or third transition metal series. This is suggested by the equilibria of the A-frame imido complexes **15** with the amido complexes **16**.[54,105] The equilibrium lies much more towards the amido complex **16** for Rh than for Ir, indicating that the Rh bonded imido ligand is more basic than the Ir bonded imido ligand. This is presumably a result of the greater electronegativities of the third series metals over the second series metals of the same group and suggests that other second series oxo and imido complexes will be more basic than their third series analogs.[106]

Greater basicity for second series metal oxo and imido complexes may be involved in the inability of our group[60,107] and others[61] to synthesize Rh and Pd analogs of the oxo and imido complexes $[Cp^*Ir(\mu\text{-}O)]_2$ **17**, $[Cp^*IrNR]_x$ (x = 1, 2) **18** and **19**, and $[L_2Pt(\mu\text{-}O)]_2$ **31**. The critical step in the synthesis of these complexes is deprotonation of intermediate hydroxo or amido complexes. Reduced acidity of the amido and hydroxo ligands in the case of Rh and Pd may allow other reaction pathways (e.g., reduction) to become dominant, and the analogous oxo and imido complexes are not obtained.

O and NR Transfers

One of the interesting prospects for late transition metal oxo and imido complexes is oxygen atom and nitrene transfer to unsaturated substrates. Many of the known oxo and imido complexes react with CO in this way.[56,59,79,75,93,98,105,108] The OXO product, CO_2, is released from the metal center, but often the RNCO, formed from the imido complexes, remains bound, at least transiently.[59,105,108] The result of the CO reactions is a reduction of the metal centers with possible formation of CO complexes or clusters. Since Au has a low affinity for CO, the reaction of the gold oxo complexes with CO yields CO free gold clusters (Scheme 3).[93,98] Pt and Ir have higher CO affinities and give CO complexes. For example, $[L_2Pt(\mu\text{-}O)]_2$ **31** and $[(PPh_3)_2Pt_2(\mu\text{-}O)_2$

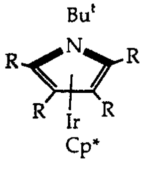
$Au(PPh_3)]^+$ give $L_2Pt(CO)_2$ and $[(PPh_3)_3Pt_3(\mu\text{-}CO)_3Au(PPh_3)]^+$, [75,79] respectively and $[Cp^*Ir(\mu\text{-}O)]_2$ **17** reacts with CO to give CO_2 and $(Cp^*Ir(\mu\text{-}CO)]_2$.[56]



SCHEME 3

Oxygen atom and nitrene transfers to phosphines are also known. The earliest example is that of the Ir oxo complex **2** which oxidizes PPh_3 to $OPPh_3$.[42] Curiously, the reaction is zero order in Ph_3P and first order in **2** (first order overall) with a rate constant that increases with solvent polarity.[43] The derivatives **3–6** (but not **5**) also transfer their oxo oxygen to PPh_3 following first order kinetics in oxo complex and in phosphine (second order overall).

Only one of the oxo oxygens from $[Cp^*Ir(\mu\text{-}O)]_2$ **17** is transferred to PR_3.[56] The remaining oxo group bridges asymmetrically suggesting multiple bonding to one of the Ir centers in **21**. There is apparently no further reaction of **21** with phosphines. The analogous imido complexes **18** and **19** react similarly, transferring a nitrene to the phosphine.[57,59] The mixed oxo/imido complex **20** preferentially transfers the oxo oxygen atom.



R = CO_2Me

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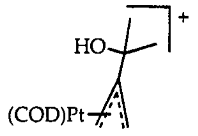

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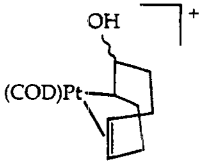

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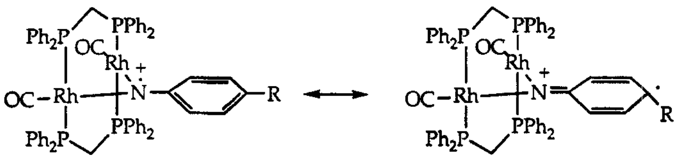

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STRUCTURES 52 — 55

OPPh$_3$ also forms in the reaction of $[(COD)Pt(\mu\text{-}O)AuPPh_3)]_2^{2+}$ **43** with PPh$_3$. The metal containing product is $[(Ph_3P)_3Pt\text{-}AuPPh_3]^+$. No intermediates are detected in the reaction, suggesting that phosphine oxidation is at least as rapid as COD displacement from **43**.[89]

Alkene and alkyne oxidation by oxygen atom or nitrene transfer is a particularly desirable reaction for oxo and imido complexes. Very few examples exist. The imido complex Cp*IrNBu^t **19** reacts with the activated alkyne RCCR (R = CO_2Me) to give Cp*Ir($R_4C_4NBu^t$) **52**.[59] Under somewhat extreme conditions, 1-decene is oxidized to the ketone 2-decanone by the Pd-Cu oxo cluster **30**.[69] Finally, $[Pt_4(COD)_4(\mu\text{-}OH)(\mu\text{-}O)_2]^{3+}$ **45** reacts with a variety of unactivated alkenes (C_2H_4, C_2Me_4, COE, COD)[89]. Unfortunately, the reactions are complex, yielding a variety of products with all but COD. Acetaldehyde is detected in the ethylene reaction, and crystals of the hydroxy allyl complex **53** have been isolated from the C_2Me_4 reaction. COD gives **54** as the major product. These results suggest that oxo complexes may be

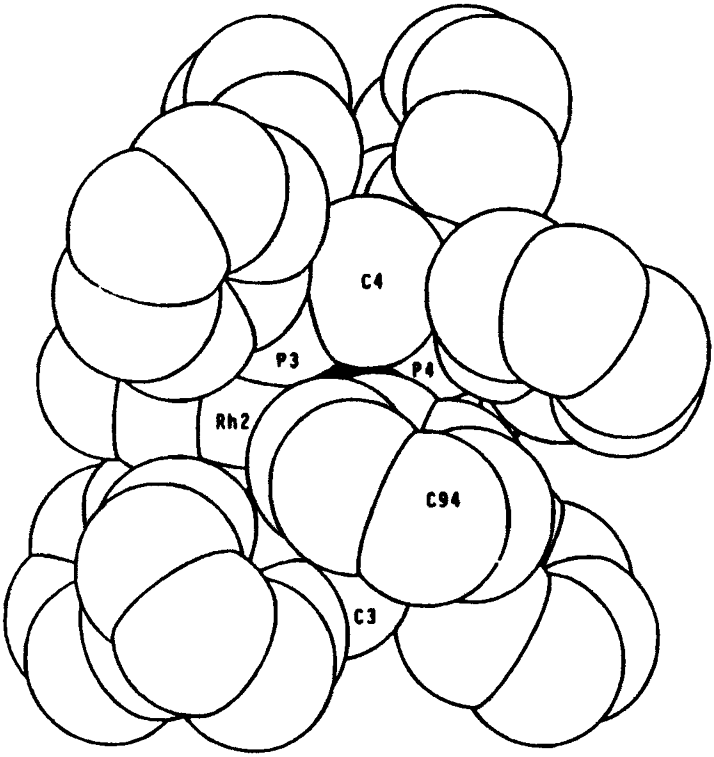
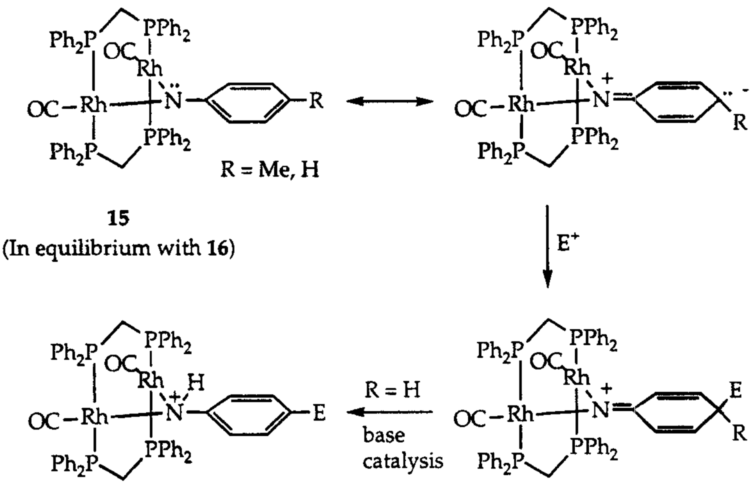


FIGURE 3 Space-filling drawing of the cationic portion of $[Rh_2(\mu\text{-}NPh(CO)_2(\mu\text{-}dppm)_2]BF_4$ **15** (nitrogen phenyl ring omited). Darkened area represents the imido nitrogen atom

involved in known alkene oxidation reactions promoted by late transition metal systems. The study of a broader range of reactive oxo and imido complexes will give a better understanding of the requirements for alkene and alkyne oxidation by late transition metal oxo and imido complexes.

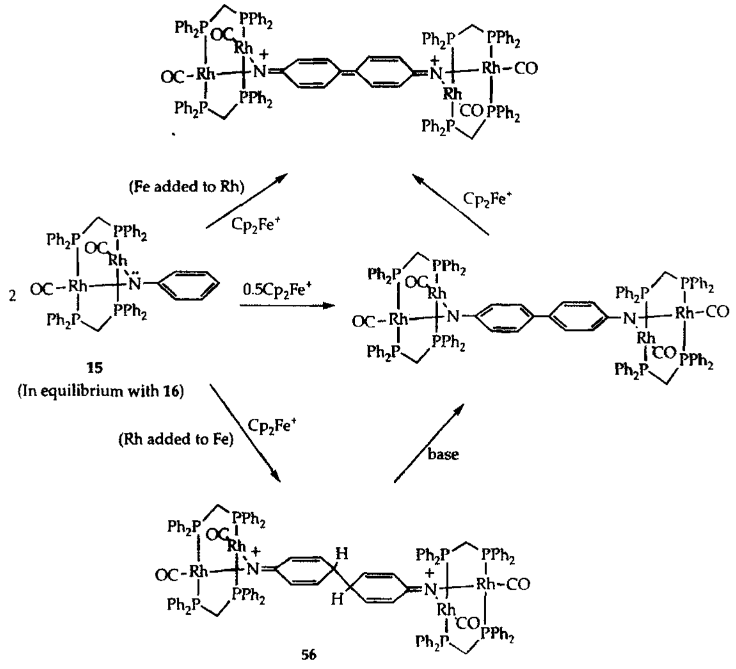
Miscellaneous

The reaction chemistry of many of the oxo and imido complexes indicates nucleophilic behavior, especially for the μ^2-imido and μ^2-oxo complexes. Metal electrophiles and H^+ add to the oxygen and nitrogen of many of the imido and oxo complexes. This reactivity has been used for the preparation of heterometallic oxo complexes (Scheme 2).[75] Carbon electrophiles also add to the nitrogen and oxygen atoms of oxo and imido groups with the exception of the dppm A-frame aryl imido complexes **15**. In these complexes the dppm phenyl rings and methylene group inhibit access to the imido nitrogen atom (Fig. 3) promoting kinetic attack on the aryl imido ring. The ring is electron rich from delocalization of the imido nitrogen atom lone pair into the ring, and *para* ring addition occurs (Scheme 4).[109] That steric factors play a part in this chemistry is supported by the observation that the analogous dmpm complexes, with methyl groups in place of the phenyl groups on the phosphine ligands, show only small amounts of ring addition products.



SCHEME 4

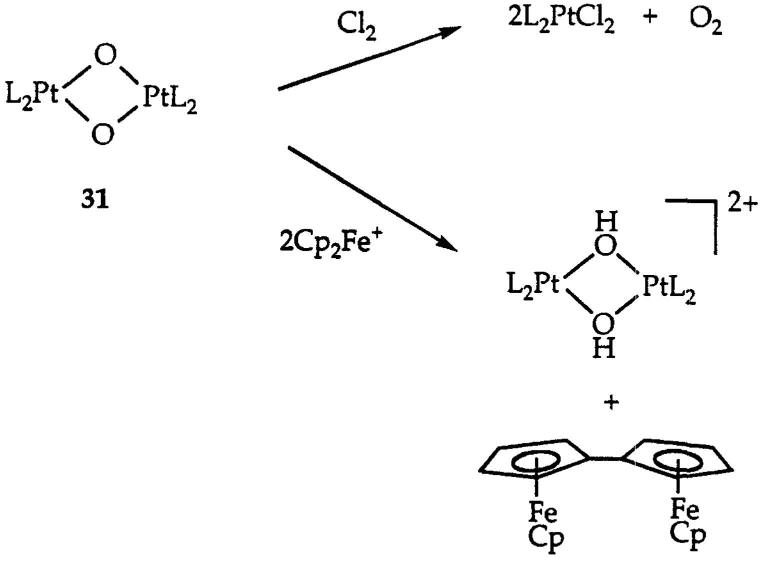
The observation of ring addition and the implied high electron density of the A-frame complexes **15** indicate possible oxidation chemistry for these complexes. Facile oxidation is observed by CV with only partial chemical reversibility observed for the phenyl complex. Bulk oxidation with ferricinium ion gives the products shown in Scheme 5.[110] The products depend on the order of addition and on the reactant ratio. The key step is the one electron oxidation of the imido complex to the radi-



SCHEME 5

cal cation **55** which has a high degree of radical density in the ring. Radical coupling through the para position of the ring yields the observed dimer **56** which is susceptible to deprotonation and oxidation. This type of reaction chemistry, related to that of N,N-substituted anilines,[111-114] has not been reported for any other imido system but may be expected whenever a heteroatom aryl ligand with lone pair electrons (M-OAr, M_2-NAr, M-NHAr) is bonded to an electron rich metal complex in an environment where access to the heteroatom is inhibited. Terminal Pt aryl amido complexes do show similar ring coupling chemistry.[115]

Oxidation of oxo complexes is also possible. Halogen addition to the Pt dioxo complexes **31** gives molecular oxygen and Ph_3PO in ratios that depend on the halogen.[75,79,116] Increasingly larger amounts of Ph_3PO and decreasing amounts of molecular oxygen are obtained in the order Cl_2, Br_2, I_2. Formation of molecular oxygen from oxo complexes is rare[117,118] and may have relevance to biological dioxygen evolving systems.[25–27] Attempted oxidation of **31** with ferricinium gave very different results (Scheme 6).[79] The products are the hydroxo complex $[L_2Pt(\mu\text{-OH})]_2^{2+}$ and CpFe(fulvalene)FeCp, evidently as a result of deprotonation of the ferricinium Cp ring by **31** followed by coupling of the deprotonated ferricinium radicals. Further study of oxo and imido complex oxidation is needed to understand these different types of reactivity.



SCHEME 6

CONCLUSIONS

Late transition metal oxo and imido complexes of Rh, Ir, Pt, and Au are a fascinating group of compounds. Although a number of serendipitous preparations are known, a growing number have been prepared by planned synthesis. The complexes display a wide range of reactivities showing in many cases strong polarization of the M-O and M-N bond and nucleophilic character for the oxo and imido ligands. A small number of oxo and imido complexes react with activated and unactivated alkenes and alkynes to give new C-O and C-N bonds showing promise for these complexes in alkene and alkyne derivatization. Among the topics still in need of study in this area are the criteria for C-O and C-N coupling reactions, the factors controlling basicity, and the controlled use of O_2, RNO, and RNNR as sources for oxo and imido ligands. Finally, in closing I quote the words of Fred Basolo[119]: "... any oxo-platinum metal complex is potentially a better oxygen atom transfer agent than are oxo-metal complexes of oxophilic early transition metal[s]."

Acknowledgments

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