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PERSPECTIVE

Oxo and imido ligands in late transition metal chemistry

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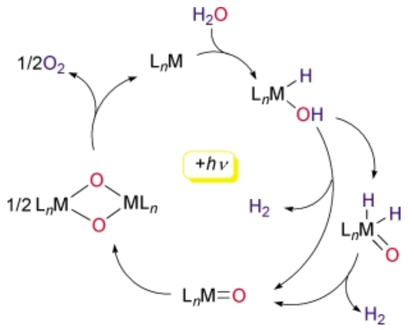
Our results on the chemistry of second and third series late transition metal oxo (O^{2-}) and imido (RN^{2-}) complexes are presented from a semi-historical perspective. Synthetic results are discussed followed by reaction chemistry and properties of the complexes.

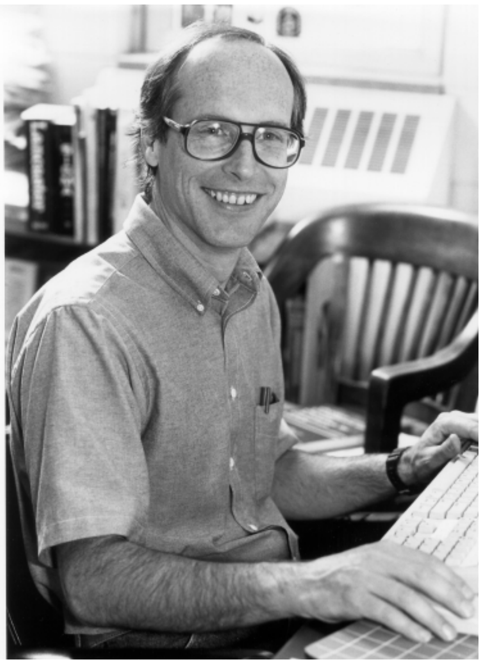
Introduction

I first became interested in late transition metal oxo (O^{2-}) and imido (RN^{2-}) complexes in late 1979 when I was near graduation and beginning to think about an NSF postdoctoral fellowship proposal. This was the decade of the oil embargo and energy sources were a hot topic. The Wrighton research group was studying photovoltaic solar energy conversion by water splitting to dioxygen and dihydrogen. I had the idea of using solution complexes to do the same thing *via* oxo and hydrido complexes formed by the oxidative addition of water to a metal center (Scheme 1). I was in the Schrock research group and was familiar with the tendency of early transition metals to form strong bonds with oxygen. These metals therefore seemed unlikely candidates for the needed release of molecular oxygen by reductive elimination of two oxo ligands. I proposed studying late transition metal oxo, hydroxo, and aquo chemistry for possible application to a solution phase photo-driven water splitting process. At the time there had been no concerted effort to synthesize nor to study the chemistry of late transition metal oxo complexes. My proposal was not funded that year and so my work in late transition metal chemistry had to wait. Later, as an assistant professor at the University of Missouri I took up the topic again.



Scheme 1

Paul Sharp was born and raised in California. He received his BS degree in Chemistry from UC Berkeley in 1975. While at Berkeley he began his research career in the laboratories of Professor Raymond working in X-ray crystallography. Following a tour of Europe and North Africa he entered the graduate program in Chemistry at MIT. His graduate work with Professor Schrock included methylidene and methylidyne complexes of Ta and W, low-valent W phosphine chemistry, and W–W quadruple bonds. Following the award of his PhD degree in 1980 he moved to UT Austin for postdoctoral work with Professor Allen Bard on electrochemistry in liquid SO_2. In 1982 he accepted a position at the University of Missouri at Columbia where he has been ever since and now holds the position of Professor of Chemistry.



Paul R. Sharp

There are of course many more reasons than water splitting to be interested in the chemistry of the oxo ligand bonded to late transition metal centers. If the isoelectronic imido ligand is included an even greater area of chemistry is encompassed. Late transition metals are catalysts in many reactions involving the assembly and/or disassembly of nitrogen and oxygen containing species.[1–6] An industrially important example is the oxidation of ammonia to nitric oxide (eqn. (1)). The metal

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O \qquad (1)$$

gauze catalyst is composed primarily of Pt. Dioxygen is cleaved on the surface into oxygen "adatoms" in the surface chemist's vocabulary or oxo ligands in the coordination chemist's vocabulary. Hydrogen atoms are transferred from ammonia to oxygen adatoms generating surface OH (hydroxo), water, and species such as NH_2 (amido), NH (imido), and N (nitrido). These nitrogen species couple with other oxygen adatoms ultimately giving NO. Similar processes occur in the Rh/Pd catalyzed conversion of CO and nitrogen oxides (NO_x) to CO_2 and N_2 in pollution control (eqn. (2)).

$$2NO + 2CO \xrightarrow{Rh} N_2 + 2CO_2 \qquad (2)$$

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Biological interest in late transition metal oxo and imido chemistry originates from several areas.[7] The reaction of molecular oxygen with Cu(I) complexes, of long standing importance in catalytic systems, has been advanced by interest in modeling Cu containing proteins.[3,8–12] A remarkable result in this area is the observation of a reversible dioxygen–dioxo complex conversion.[13,14] There is also a general interest in metal covalent bonds to nitrogen and oxygen because of their involvement in other biological systems including nitrogenase[15–21] and photosystem II.[22–25] 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.

In addition, there is a 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[26,27] predicts 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 for these metals are as strong as analogous M–C bonds.[28,29] However, high reactivity is found in many cases as discussed in following sections.

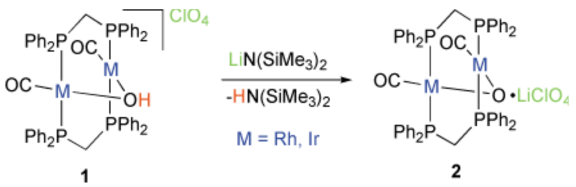
When we began our work there were already reports of second and third series late transition metal oxo complexes. However, their syntheses were largely serendipitous and generally gave low yields. Imido complexes were much rarer probably as a result of there being fewer common sources of the NR group and the greater reactivity of imido complexes with protic compounds (see below). A complication in serendipitous and intentional syntheses of oxo and imido complexes is characterization. Characteristic NMR signatures for oxo and imido ligands are absent and the commonly weak and broad nature of OH and NH ^{1}H NMR signals make it difficult to conclusively show that the oxo or imido ligands are present and not their protonated forms. X-Ray crystal structure analysis can be similarly inconclusive as hydrogen atoms can be difficult to detect and crystallographic problems can lead to erroneous assignments.[30] Consequently, 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.

Syntheses

One of the first tasks in this area was the development of rational synthetic methods for late transition metal oxo and imido complexes. Deprotonation of hydroxo and amido complexes, especially cationic ones, seemed a reasonable approach. The synthesis of a terminal oxo complex by deprotonation of the Co(III) complex $[TpCo(OH)]^+$ (Tp = tris(pyrazolyl)borate) was naively chosen for our first synthetic effort. Work in Theopold's group has shown that had we succeeded in preparing Co(III) terminal oxo complexes (doubtful) they would not have lasted long. Such complexes are extremely reactive and readily abstract hydrogen atoms.[31,32] More reasonable would have been Rh(III) and Ir(III) complexes though even with these a terminal oxo complex is unlikely as shown by work in Bergman's group on the Cp* complexes $[Cp^*Ir(\mu\text{-}O)]_2$.[33,34] The terminal imido complex Cp*IrNR has been isolated but only with bulky R groups.[34–36]

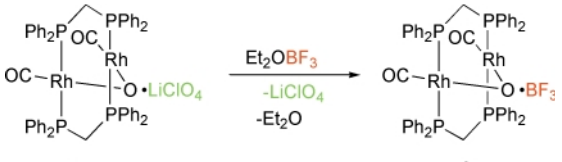
The rarity of terminal late transition metal oxo and imido complexes is due to the electron-rich character of these elements. A terminal oxo or imido ligand requires π-bond donation to vacant metal d-orbitals that are generally lacking for electron-rich late transition metals in common oxidation states. (See ref. 37 for a unique terminal Ir(V) oxo complex.) Bridging oxo and imido complexes without π-bonds were more reasonable targets and we shifted our efforts to developing rational syntheses for these.

The beautiful dppm ($Ph_2PCH_2PPh_2$) A-frame chemistry developed by several groups seemed ideal for our purposes.[38] Bridging Rh, Ir, Pd, and Pt sulfido complexes,[39–42] isoelectronic to target oxo and imido complexes, were known and cationic Rh and Ir bridging hydroxo complexes $[M_2(\mu\text{-}OH)(CO)_2(\mu\text{-}dppm)_2]^+$ **1** (eqn. (3)), ripe for deprotonation, had been reported.[43,44] We began with metal salt "loans" from Johnson Matthey and the cationic hydroxo complexes were prepared and treated with the base $LiN(SiMe_3)_2$ (eqn. (3)). Our first indications of success were the observations of a single new product by ^{31}P NMR spectroscopy and a low energy shift of the CO bands in the IR spectra. The new products were soluble in toluene consistent with the formation of a neutral oxo complex. However, IR spectra of the solid isolated from toluene showed bands that appeared to be those of the perchlorate counterion from the hydroxo complex. The $LiClO_4$ produced in the deprotonation should not have been soluble in toluene. The solution to this puzzle was finally realized when hydrolysis of the solid isolated from toluene regenerated the hydroxo complex complete with the perchlorate counterion. The oxo complexes were acting as rather exotic phase transfer agents for the $LiClO_4$ by coordination of the Li ion to the oxo ligand giving product **2** (eqn. (3)). This was supported by the addition of BF_3, which yielded a precipitate of $LiClO_4$ and a new product that an X-ray analysis revealed to be the BF_3 adduct **3** (eqn. (4)).[45]



(3)

1 **2**

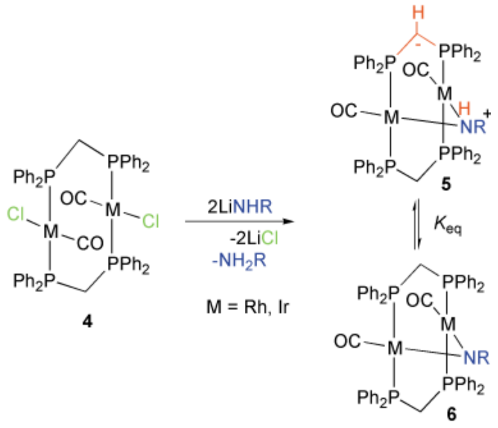


(4)

2 **3**

Coordination of Li ions to μ-oxo complexes generated by deprotonation with Li bases has now been well-established (see below).

With knowledge of the oxo complexes we began an effort to prepare the imido analogs. The amido analogs of the hydroxo complexes were not known and an alternative route to deprotonation was needed. The "face-to-face" dichloro complexes $[MCl(CO)(\mu\text{-}dppm)]_2$ **4** (M = Rh, Ir)[39,46] were chosen for reaction with LiNHR (Scheme 2). With R = Me and M = Rh a



Scheme 2

smooth reaction occurred requiring 2 equivalents of LiNHMe. An orange toluene soluble product was isolated. IR spectroscopy showed a low energy shift of the CO bands but not as large a shift as was expected. ^{31}P NMR spectroscopy displayed an unexpectedly complex pattern. The reason for these unexpected results was revealed by an X-ray crystal structure analysis, which showed the zwitterionic amido complex **5** where the dppm methylene group had been deprotonated instead of the bridging amido ligand. We had actually anticipated this possibility but did not recognize it when it occurred! Switching to R = Ph gave a product which had a very broad ^{31}P NMR signal indicating a fluxional system. Low temperature ^{31}P NMR spectroscopy and ambient temperature IR spectroscopy revealed an equilibrium mixture of the anticipated imido complex **6** and its tautomer, the zwitterionic amido complex, **5**. Other derivatives quickly followed and demonstrated the generality of the synthesis. The equilibrium between the imido and amido forms is controlled by the donor properties of the R group and the equilibrium constants can be fitted to a Hammett free energy relationship.[47,48]

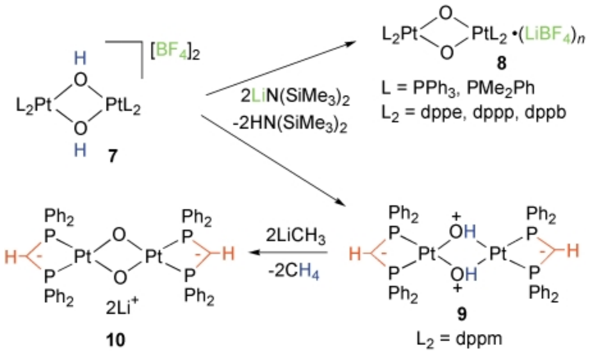
The Ir analogs were later prepared and the R = Et derivative, like the Rh, R = Me complex, was completely in the amido form **5**.[49] In contrast, the aryl derivatives appeared to be completely in the imido form **6** and the only indication that the amido forms were present was a broadening of the ^{31}P NMR signal at ambient temperature. Low temperature NMR spectroscopy showed only a sharpening of the ambient temperature singlet for the imido form. IR spectra similarly showed only bands for the imido form indicating that the concentration of the amido form was very low. The implication of these observations is that the Rh imido complexes **6** are more basic than the Ir analogs. This is discussed more fully in the section on basicity (see below).

Simultaneously with the Rh and Ir A-frame deprotonation work we began investigating the possibility of oxygen atom insertion into the Pt–Pt bond of $[PtCl(\mu\text{-dppm})]_2$.[50] Insertion of a sulfur atom from S_8 or other sulfur atom donors had given the isoelectronic sulfido complex $[Pt_2(\mu\text{-S})Cl_2(\mu\text{-dppm})_2]$.[42] With a kind gift of $(NH_4)_2PtCl_6$ from Dick Schrock, $[PtCl(\mu\text{-dppm})]_2$ was prepared and its reactions with known oxygen atom donors (Me_3NO, *N*-methylmorpholine-*N*-oxide, iodobenzene) were examined. The donors either did not react or gave intractable mixtures. Mercuric oxide, prepared from $HgCl_2$ and NaOH, also did not yield an oxo complex although an interesting $HgCl_2$ adduct was produced.[51] Almost in desperation, a solution of ozone was added to $[PtCl(\mu\text{-dppm})]_2$. Surprisingly, this did not totally destroy the complex and a yellow solid with spectroscopic data very similar to the sulfido complex was isolated as the major product. Unfortunately, this complex could never be obtained pure or in crystalline form and its proposed identity as $[Pt_2(\mu\text{-O})Cl_2(\mu\text{-dppm})_2]$ could never be confirmed. James later reported evidence for the low temperature formation of the unstable Pd analog $[Pd_2(\mu\text{-O})Cl_2(\mu\text{-dppm})_2]$[52] and very recently, arylsulfonylimido complexes have been isolated from azide reactions of $[PdCl(\mu\text{-dppm})]_2$.[53]

Naturally, the question arose as to whether the techniques used to produce the Rh and Ir A-frame complexes would work in other systems. We began investigating two other systems, the Cp*M(III) (M = Rh, Ir)[54,55] and L_2M(II) (M = Pt, Pd)[56,57] systems. Cationic dimeric hydroxo complexes for deprotonation were known for both systems. Before we had progressed very far into the Cp*M(III) system, I heard from Eric Mattaa (K State) about unpublished deprotonation chemistry of Cp*Ir hydroxo complexes in the well-known Bergman group at UC Berkeley. Competition with such a distinguished researcher was a frightening prospect for an assistant professor! With trepidation I telephoned Bob Bergman and in the simplest fashion we agreed to avoid overlap by his group working with Cp*Ir complexes and my group with Cp*Rh complexes. The chemistry of the two metal systems turned out to be sufficiently different that duplication was not an issue. While deprotonation/dehydration of $[(Cp^*Ir)_2(\mu\text{-OH})_3]^+$ yielded the oxo complex $[Cp^*Ir(\mu\text{-O})]_2$,[33,34] all attempts to deprotonate analogous $[(Cp^*Rh)_2(\mu\text{-OH})_3]^+$ resulted in deeply colored intractable mixtures.[58] Similarly, treatment of $[Cp^*IrCl_2]_2$ with LiNHR yielded the unique terminal imido complex Cp*IrNR with bulky R groups and dimeric $[Cp^*Ir(\mu\text{-NR})]_2$,[34–36] with less bulky R groups while similar reactions with $[Cp^*RhCl_2]_2$ again yielded deeply colored intractable mixtures.[58] In one case, the amido analog of the hydroxo complex $[(Cp^*Rh)_2(\mu\text{-NHR})_3]^+$ was isolated. Despite many attempts we were unable to convert this complex or related complexes to an imido complex. This difference between Rh and Ir is probably due to the more facile reduction of Rh and a lower acidity for the hydroxo and amido ligands bonded to Rh (see section on basicity). Other groups have also attempted the preparation of Cp*Rh(III) imido complexes without success.[59,60]

The more facile reduction of Rh was turned to an advantage by the synthesis of the deep blue Rh(II) dimer $[Cp^*Rh(\mu\text{-Cl})]_2$.[61,62] This complex was readily formed by the reduction of $[Cp^*Rh(\mu\text{-Cl})Cl]_2$ with Na, Na/Hg, or cobaltacene and contains a reactive Rh–Rh bond. Reaction of this complex with dioxygen and nitrosobenzene was explored as a possible route to oxo and imido complexes. Interesting dioxygen and nitrosobenzene complexes were produced but they did not yield oxo or imido complexes.

We were more successful with the Pt(II) series of complexes $[L_2Pt(\mu\text{-OH})]_2^{2+}$. A number of these hydroxo complexes with different L had been prepared and studied partly because of interest in the hydrolysis chemistry of the chemotherapy drug cisplatin (*cis*-$(NH_3)_2PtCl_2$). Phosphine ligand complexes were selected for their flexibility and the convenience of ^{31}P NMR spectroscopy for product characterization and reaction monitoring. The triphenylphosphine complex $[(Ph_3P)_2Pt(\mu\text{-OH})]_2(BF_4)_2$ (**7**, L = PPh_3)[56] was the first to be deprotonated to oxo complex **8** (Scheme 3). Again, $LiN(SiMe_3)_2$ was used as the base and the product, which fortunately crystallized nicely, was shown by X-ray diffraction to be the $LiBF_4$ adduct $[(Ph_3P)_2Pt(\mu\text{-O})]_2\cdot LiBF_4$ (Fig. 1[63,64]). Li ion coordination is not essential for the stability of these complexes and salt free $[(Ph_3P)_2Pt(\mu\text{-O})]_2$ was isolated when $NaN(SiMe_3)_2$ or $KN(SiMe_3)_2$ was used as the base.[65]



Scheme 3

Other hydroxo complexes $[L_2Pt(\mu\text{-OH})]_2^{2+}$ **7** (L = PMe_2Ph, L_2 = dppm ($Ph_2PCH_2PPh_2$), dppe ($Ph_2P(CH_2)_2PPh_2$), dppp ($Ph_2P(CH_2)_3PPh_2$), dppb ($Ph_2P(CH_2)_4PPh_2$)) were also easily deprotonated (Scheme 3).[66,67] With the exception of the dppm complex the deprotonations of the hydroxo complexes and the properties of the resulting dioxo complexes were similar to the PPh_3 complex. The dppm complex was unique in that dppm methylene group deprotonation occurred prior to hydroxo group deprotonation (Scheme 3). Resulting $[(dppm\text{-}H)Pt(\mu\text{-OH})]_2$ **9** was further deprotonated to the anionic oxo complex $[(dppm\text{-}H)Pt(\mu\text{-O})]_2Li_2$ **10**. As a neutral complex the

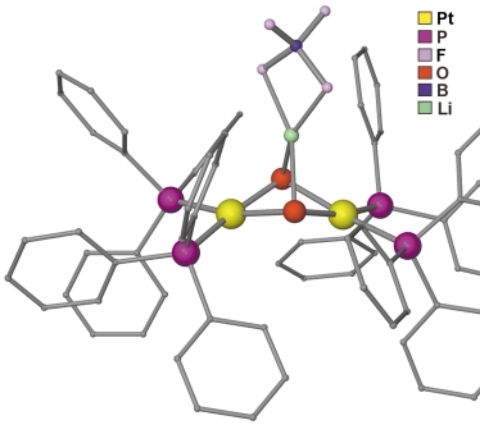
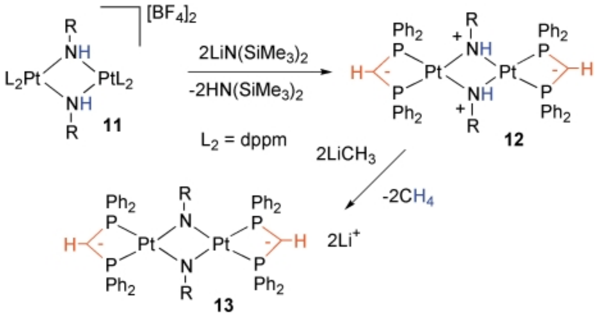


Fig. 1 Drawing of $[(Ph_3P)_2Pt(\mu\text{-}O)]_2\cdot LiBF_4$ **8** ($L = PPh_3$).

deprotonation of $[(dppm\text{-}H)Pt(\mu\text{-}OH)]_2$ was more difficult and LiMe was required. X-Ray diffraction with crystals from thf showed coordination of $Li(thf)_2$ ions to the oxo ligands.

Expansion to the imido analogs was sought but first the amido complexes had to be made. These were readily prepared by treatment of the hydroxo complexes with amines. Since our work on the A-frame systems had shown us that alkyl imido complexes could be extremely basic we used aryl amines in these reactions. The mixed hydroxo amido complexes $[(L_2Pt)_2(\mu\text{-}NHAr)(\mu\text{-}OH)]^{2+}$ were prepared with $L = PPh_3$. Bidentate phosphine complexes gave diamido complexes $[L_2Pt(\mu\text{-}NHAr)]_2{}^{2+}$ and, with NH_3, the parent complex $[L_2Pt(\mu\text{-}NH_2)]_2{}^{2+}$. With the exception of the dppm complexes, all attempts to deprotonate the amido groups of these complexes were unsuccessful. There was no reaction with $LiN(SiMe_3)_2$ and with stronger bases such as MeLi reduction to Pt metal was observed.[68]

As with the oxo complexes the dppm case was unique. Treatment of $[(dppm)Pt(\mu\text{-}NHR)]_2{}^{2+}$ **11** (R = Ph, 4-tol, H) with strong bases yielded first the dppm deprotonation products $[(dppm\text{-}H)Pt(\mu\text{-}NHR)]_2$ **12** (Scheme 4). Complexes **12** were further deprotonated with LiMe to give our first Pt imido complexes $[(dppm\text{-}H)Pt(\mu\text{-}NR)]_2Li_2$ **13** (R = Ph, 4-tol, H). An X-ray structure determination with crystals from thf (R = Ph) showed coordination of a single Li ion to the two imido ligands (Fig. 2[63,64]).[68,69]



Scheme 4

The oxo and imido results with the dppm ligand were remarkable not so much for the fact that the dppm ligand was deprotonated but for the fact that the complexes survived further deprotonation with MeLi. MeLi reduced all the other phosphine ligand hydroxo and amido complexes. Survival could have been due to the enhanced donation from the deprotonated dppm ligand, or to the very small bite angle of dppm, or to both of these factors. Bite angle effects are well known in reaction chemistry and catalysis.[70,71] Of particular relevance is the suppression of reductive elimination from Ni(II) complexes by small bite angle phosphine ligands indicating a stabilization of Ni(II) over Ni(0).[72]

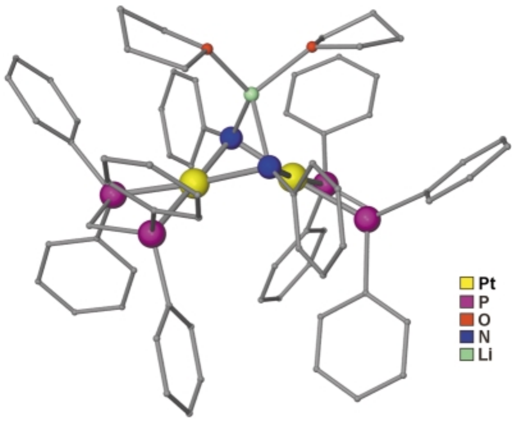


Fig. 2 Drawing of the anionic portion of $[(dppm\text{-}H)Pt(\mu\text{-}NPh)]_2Li_2$ **13** (R = Ph)·6thf.

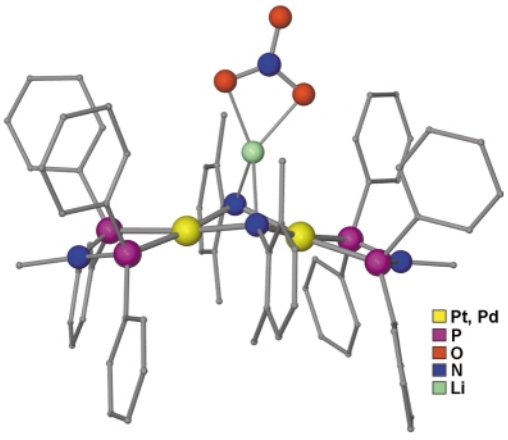
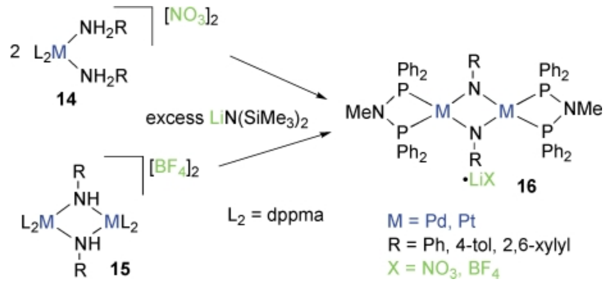


Fig. 3 Drawing of $[(dppma)M(\mu\text{-}NAr)]_2$ **16** (M = Pd or Pt, Ar = 2,6-xylyl).

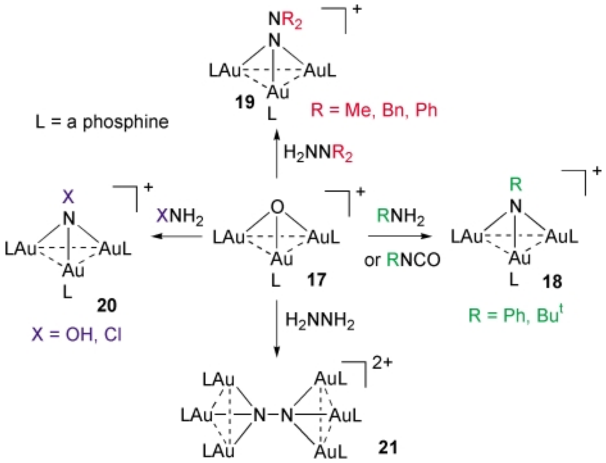
To further investigate bite angle effects in our system the dppma ($Ph_2PN(Me)PPh_2$) ligand, which is not readily deprotonated, was selected for the preparation of imido complexes. Both the dimeric amido complexes **14** and the monomeric amine complexes **15** deprotonated cleanly with $LiN(SiMe_3)_2$ yielding imido complexes $[(dppma)Pt(\mu\text{-}NAr)]_2\cdot LiX$ **16** (Scheme 5, Fig. 3[63,64]). The deprotonation with $LiN(SiMe_3)_2$ was surprising since this base had no effect on other phosphine ligand amido complexes. This led us to suspect that the dppma ligand complexes contain more acidic amido groups. This possibility is discussed in the section below on basicity.



Scheme 5

The reductive stability of the Pt(dppm) (or dppm-H) complexes was noted above. Unfortunately this did not translate to Pd and all of our attempts to prepare Pd oxo and imido complexes failed with the apparent formation of Pd metal. The facile formation of the Pt dppma imido complexes **16** renewed our hope for Pd and we began dppma Pd chemistry. This worked beautifully and led to the isolation of the second known and the first rationally prepared Pd imido complexes **16** (Scheme 5, Fig. 3[63,64]). The Pd and Pt complexes are isomorphous and isostructural.

We also studied oxo and imido complexes in the Group 11 triad. The large scale Ag catalyzed air epoxidation of ethene[1,6] and advances in Au catalyzed oxidation and NO_x reactions[73] highlight the importance of these metals. The Au oxo complex $[(LAu)_3(\mu\text{-}O)]^+$ **17** ($L = Ph_3P$)[74] (Scheme 6), one of the few high yield late transition metal oxo complexes available at the time we began our work, attracted our attention. Simple adaptation of the original syntheses of the Ph_3P derivative, the reaction of LAu^+ (generated *in situ* from LAuCl and Ag^+) with hydroxide ion or the reaction of LAuCl, Ag_2O, and $NaBF_4$, produced analogs $[(LAu)_3(\mu\text{-}O)]^+$ **17** with a variety of phosphine ligands.[75,76] Oxo complexes **17** were useful reagents for the preparation of a number of compounds (Scheme 6). Imido analogs $[(LAu)_3(\mu\text{-}NR)]^+$ **18** were readily prepared either by reaction of $[(LAu)_3(\mu\text{-}O)]^+$ with amines or isocyanates.[77,78] Here our work converged with that of the Schmidbaur group.[76,79,80] Fortunately, our interests were divergent. We were interested in the oxo and imido ligand chemistry while the Schmidbaur group was interested in the clustering of gold atoms around p-block elements. Hydroxylamine, 1,1-substituted hydrazines, and chloramine reacted similarly to amines and gave heteroatom substituted imido complexes **19** and **20**.[81,82] With hydrazine, the first Group 11 dinitrogen complexes $[(LAu)_6(\mu\text{-}N_2)]^{2+}$ **21** were obtained.[78,83,84]



Scheme 6

The oxo complex $[(LAu)_3(\mu\text{-}O)]^+$ **17** also proved useful as an oxide ion source and oxo/halo exchange reactions yielded numerous new oxo complexes (Scheme 7). Oxo/chloro exchange of $[L'_2M(\mu\text{-}Cl)]_2$ with $[(LAu)_3(\mu\text{-}O)]^+$ yielded $[L'_2M\{\mu\text{-}O\text{-}(AuL)_2\}]_2^{2+}$ **22** (M = Rh, Ir; L'_2 = cod, nbd).[85] The oxo ligand in these complexes is in an unusual trigonal pyramidal coordination environment evidently as a result of bonding interactions between the Au and Rh or Ir centers (Fig. 4[63,64]). A different product, $[(Ph_3P)_2Rh(\mu\text{-}OH)(AuPPh_3)]_2^{2+}$ **23**, was obtained from the exchange reaction with $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$. Presumably, an oxo complex similar to **22** was produced but was protonated by an unknown proton source to give hydroxo complex **23**.

Pt(cod)Cl_2 also underwent exchange with $[(LAu)_3(\mu\text{-}O)]^+$ **17** and the mixed Pt/Au oxo complexes $[Pt(cod)\{(\mu\text{-}O)(AuL)_2\}_2]^{2+}$ **24** and $[Pt(cod)(\mu\text{-}O)(AuL)]_2^{2+}$ **25** were obtained (Scheme 7).[86] Considering the isolobal relationship of LAu^+ and H^+ these complexes can be viewed as aura–aqua and aura–hydroxo Pt complexes. With excess Pt(cod)Cl_2 exchange gives $[Pt_4(cod)_4Cl_2(\mu\text{-}O)_2]^{2+}$ **26** (Fig. 5). Complex **26** is moisture sensitive and in wet CH_2Cl_2 gave crystals of the Pt hydroxo oxo complex $[Pt_4(cod)_4(\mu\text{-}OH)(\mu\text{-}O)_2]^{3+}$ **27** (eqn. (5)).

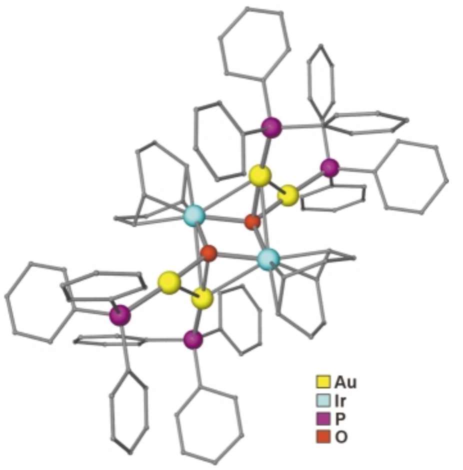


Fig. 4 Drawing of $[(cod)Ir\{\mu\text{-}O(AuPPh_3)_2\}]_2^{2+}$ **22** (M = Ir, L'_2 = cod, $L = PPh_3$).

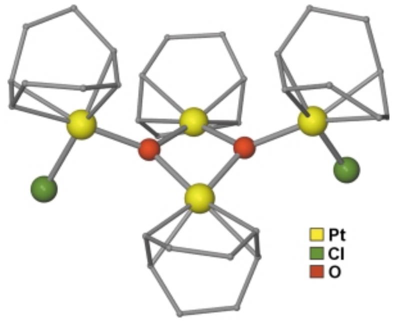
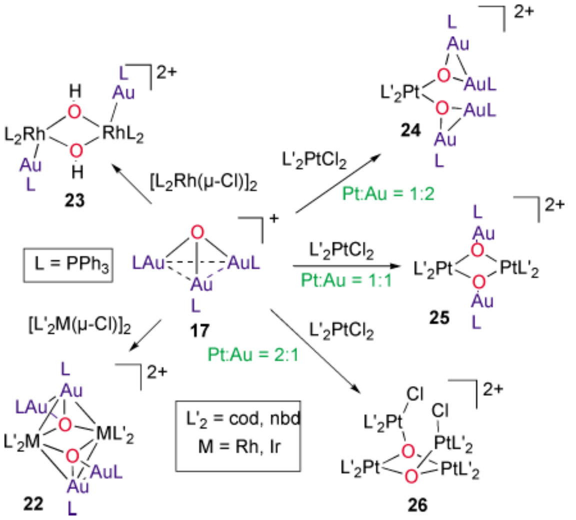
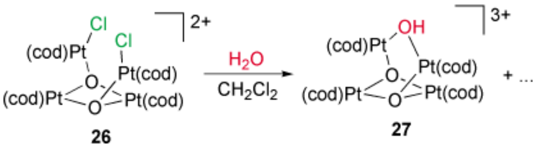


Fig. 5 Drawing of $[Pt_4(cod)_4Cl_2(\mu\text{-}O)_2]^{2+}$ **26**.



Scheme 7



(5)

We first became aware of the oxo/chloro exchange chemistry of $[(LAu)_3(\mu\text{-}O)]^+$ **17** when we observed exchange with L′AuCl.[75] Given the important oxidation chemistry of silver surfaces we had hoped that similar exchange chemistry with $[LAgCl]_4$ would give silver oxo complexes. Unfortunately, mixtures of $[LAgCl]_4$ and $[(LAu)_3(\mu\text{-}O)]^+$ gave only black

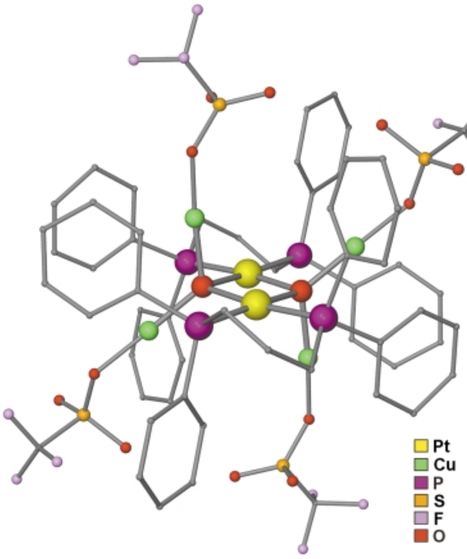


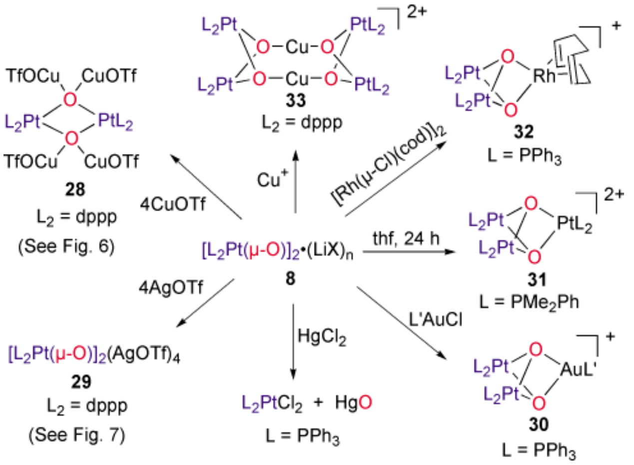
Fig. 6 Drawing of $[(dppp)Pt(\mu\text{-}O)]_2 \cdot 4CuOTf$ **28**.

precipitates and silver oxo complexes remain elusive. (See below for heterometallic Pt/Ag oxo complexes.)

Properties and reaction chemistry of oxo and imido complexes

Oxo and imido complexes as ligands

The propensity of the oxo and imido complexes to coordinate to Li ions suggested using these complexes as ligands. The Pt complexes were particularly attractive (and still are!) since they can serve as bidentate ligands. Mingos,[87–89] and more recently Hor[90] have shown that the analogous sulfido complexes are effective bidentate ligands. Our oxo complexes are equally effective although clearly with some differences due to the harder oxo ligand. For example, the sulfido complexes do not coordinate to Li ion. Complexes prepared from $[L_2Pt(\mu\text{-}O)]_2$ **8** are shown in Scheme 8.[91,92] Most have been structurally characterized by single crystal X-ray diffraction. The 4 equivalents AgOTf and CuOTf reactions are interesting in yielding analogous μ_4-oxo complexes **28** and **29** but with different structures (Figs. 6 and 7[63,64]). The Cu complex **28** contains linear 2-coordinate Cu centers with an approximate tetrahedral array about the μ_4-oxo groups. In contrast, the Ag complex **29** contains both planar 3-coordinate and tetrahedral 4-coordinate Ag centers. The two 4-coordinate Ag centers are bonded, like the Cu analog, to an oxo ligand and an η^1-triflate anion. The tetrahedral coordination sphere is completed by η^1-coordination of two phenyl rings from the phosphine ligands. Two bridging triflate anions and the Pt_2O_2 core link the two 3-coordinate Ag centers.



Scheme 8

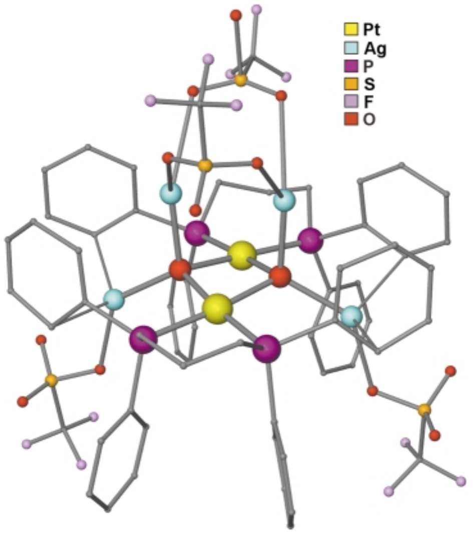


Fig. 7 Drawing of $[(dppp)Pt(\mu\text{-}O)]_2 \cdot 4AgOTf$ **29**.

Complex formation with $[L_2Pt(\mu\text{-}O)]_2$ **8** was not always observed in its reactions with metal salts. Treatment of **8** with $HgCl_2$ gave oxo/chloro exchange and a precipitate of yellow HgO (Scheme 8). This type of reaction is possible whenever a highly stable oxo complex can form from transfer of the oxo ligand.

Though much less developed, the imido complexes $[L_2Pt(\mu\text{-}NR)]_2$ **16** also function as ligands. Lithium ion coordination is evident from the structures of the imido complexes and LAuCl reacted readily with $[L_2Pt(\mu\text{-}NR)]_2$ **16** to produce the LAu^+ adduct **34** (eqn. (6)).[93] Other complexes are expected but the coordination chemistry will be more limited than with the oxo complexes as a result of the presence of only one lone pair and the steric influence of the imido R group.

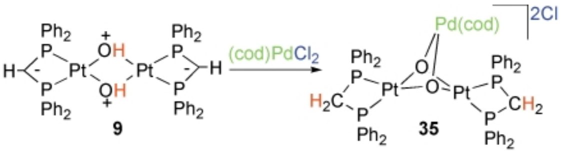
(6)

The diene oxo complexes **22** and **24**–**26** (Scheme 7) prepared by oxo/chloro exchange discussed above can be considered to be composed of dioxo complexes $[(cod)Pt(\mu\text{-}O)]_2$ or $[(diene)M(\mu\text{-}O)]_2^{2-}$ (M = Rh, Ir) coordinated to the cationic fragments LAu^+ or $(cod)PtCl^+$. This suggests the possibility that, like the phosphine oxo complexes in Scheme 8, the free parent diene dioxo complexes $[(cod)Pt(\mu\text{-}O)]_2$ or $[(diene)M(\mu\text{-}O)]_2^{2-}$ (M = Rh, Ir) should exist. We have tried to prepare the Pt complex by Cl^- displacement of LAu^+ from $[(cod)Pt(\mu\text{-}OAuL)]_2$ **25** without success. Deprotonation of $[(cod)Pt(\mu\text{-}OH)]_2^{2+}$ should also be a possible route but we have been unable to prepare this hydroxo complex. The hydroxo complexes $[(diene)M(\mu\text{-}OH)]_2$ (M = Rh, Ir) are known and may yield the anionic oxo complexes $[(diene)M(\mu\text{-}O)]_2^{2-}$ if deprotonated under the appropriate conditions.

Basicity

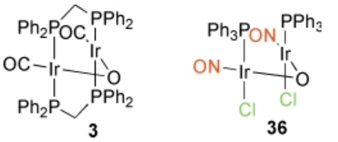
Many of our oxo and imido complexes behave as Brønsted strong bases. (We have sometimes referred to the μ-oxo complexes as soluble analogs of Li_2O.) This reflects the polar nature of the M–O and M–N bonds. Strong Brønsted basicity is also observed for oxygen atoms on the surface of late transition metals.[6] Factors that contribute to this polarization are not clearly understood. We are just now beginning a program to measure pK_a values for the hydroxo and amido complexes so that we may make careful comparisons and determine the involved parameters. In the meantime, observed features of the syntheses of the complexes, their properties, and their reactions suggest that the following factors are important in the base strength of our oxo and imido complexes. (1) The number of metals bonded to the oxo or imido ligand, (2) the nature of the metal ancillary ligands, and (3) the location of the metal in the second or third transition metal series. We may also say that imido complexes are more basic than analogous oxo complexes as would be expected given the lower electronegativity of nitrogen.

Some of these factors can be readily rationalized. The more metal centers bonded to the oxo or imido ligand the more charge transfer from the formally dianionic ligand and the lower the basicity of the complex. This is evident from the general protic sensitivity of the μ-oxo and -imido complexes. The μ_3-oxo and -imido complexes are much less sensitive. A striking example of this effect is the reaction of the deprotonated dppm hydroxo complex [(dppm-H)Pt(μ-OH)]$_2$ **9** with (cod)PdCl$_2$ (eqn. (7)). The isolated adduct **35** is an oxo complex where the hydroxo proton has transferred from the less basic μ_3-oxo ligand to the now more basic dppm-H ligand.



(7)

Ancillary ligands are important for their effect on the metal center. The more π-acidic the ancillary ligands the better the metal center at charge acceptance. This is nicely illustrated by comparing the protic sensitivity of the Ir A-frame complex **3** with the analogous nitrosyl complex **36**[94] (Scheme 9). The A-frame complex **3** is highly sensitive to protonation while **36** is water stable. The major differences between these two complexes is the substitution of the strongly π-acidic NO ancillary ligand in **36** for the less π-acidic CO ancillary ligand in **3** and the replacement of a phosphorus ligand in **3** with a chloro ligand in **36**. Both of these changes are expected to decrease the electron density on the Ir center and increase its ability to accept electron density from the oxo ligand.

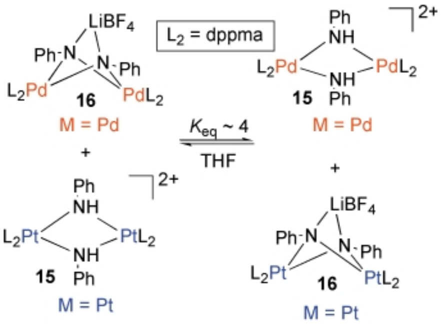


Scheme 9

The facile deprotonation of the dppma amido complexes suggests that the dppma ligand increases the acidity of the amido ligand over that of the other phosphine complexes. Two contributing dppma factors could be the small natural bite angle and a decreased donation to the Pt center as a result of the electronegative nitrogen bridge. Comparisons of CO IR bands of analogous dppm and dppma complexes indicate little difference in the donor properties of these two diphosphine ligands[95] suggesting that the nitrogen bridge is not a factor. Calculations on the L$_2$Pt fragment show that the bite angle does have a strong effect.[70,96,97] The greatest effect is on the HOMO energy which increases with decreasing bite angle of the diphosphine. Since this would be a vacant acceptor orbital in the L$_2$Pt^{2+} fragment a decreasing bite angle should result in less electron density transfer from the oxo and imido ligands to the Pt(II) center and decreased acidity, opposite to what we seem to observe. The calculations are, however, consistent with the observed lower tendency to reduction with the small bite angle dppma and dppm-H complexes.

Our conclusion of greater acidity for the dppma complexes is based on our ability to deprotonate the amido complexes with LiN(SiMe$_3$)$_2$. This base did not react with the other phosphine ligand amido complexes. However, the deprotonation reactions are typically done in thf or dme where the protonated form, the amido or amine complex, has low solubility. It is possible that the difference in the deprotonation reactions is at least partly due to solubility differences between the protonated forms. Further discussion of bite angle effects will have to await the completion of careful pK_a measurements in solvents (dmso) where all species are soluble.

Greater basicity of analogous second over third series transition metal oxo or amido complexes is suggested by the greater extent of internal dppm deprotonation (Scheme 2) for the Rh over the Ir A-frame complexes **6**. Since this is an internal deprotonation solubility is not involved and the only assumption is that the dppm methylene bridge acidity is the same in the Rh and Ir complexes. The synthesis of the Pd imido complexes **15** provided an opportunity to test another second/third series pair. Mixing the Pd imido complex **16** and the Pt amido complex **15** resulted in proton transfer and equilibrium with the Pt imido complex dominating (Scheme 10). Poor solubility of the protonated forms **15** is a complication in the equilibrium but if we make the reasonable assumption that the Pd and Pt amido complexes **15** have similar solubility then greater basicity for the second series metal complex is again indicated.



Scheme 10

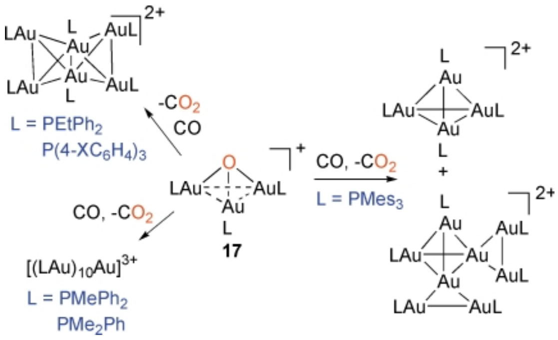
Lower basicity for the third series metal complexes implies that third series metal fragments are more strongly electron withdrawing or, from the Pauling model, more electronegative. Unfortunately, group electronegativity values for transition metal fragments are largely unknown. One might expect group electronegativity trends in analogous fragments to follow element electronegativity trends. However, transition metal electronegativities are rather nebulous and the relative ranking of second and third transition metal series group pairs varies from scale to scale.[98] Acidity differences between second and third series group pairs have also been observed in transition metal hydride chemistry. However, the trend is the reverse of that observed here and the third series metal complexes are less acidic than the second series analogs.[99–101]

Greater basicity for the second series metal is also inconsistent with the proposal that there are π–π repulsive interactions between filled metal orbitals and the N or O lone pair(s) of oxo and imido ligands.[102] In this view the π–π repulsive interactions push up the energy of the heteroatom lone pairs causing them to be more basic. Since third series metals are usually considered the stronger π-bases they are predicted to give the more basic complexes, opposite to that observed. Holland, Bergman, and Andersen have concluded that π–π repulsive interactions are weak at best.[103,104]

High basicity for second series metal oxo and imido complexes may be involved in the inability of our group and others[59,60] to synthesize Rh analogs of the Ir oxo and imido complexes $[Cp^*Ir(\mu\text{-}O)]_2$ and $[Cp^*IrNR]_x$ ($x = 1, 2$) and in our difficulty in preparing Pd imido complexes with phosphine ligands other than dppma. A critical step in the synthesis of these complexes is hydroxo or amido ligand deprotonation. Reduced acidity of the amido and hydroxo ligands in the case of Rh and Pd allows other reaction pathways (*e.g.* reduction) to become dominant.

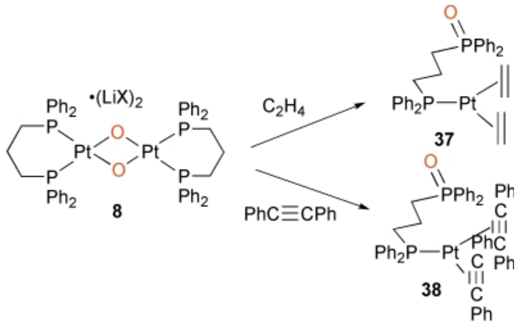
O and NR transfers

One of the interesting prospects for late transition metal oxo and imido complexes is oxygen atom and nitrene transfer to unsaturated substrates. Many of our oxo and imido complexes reacted with CO in this way.[49,69,78,79,91,105] The oxo product, CO_2, was released from the metal center but RNCO, formed from the imido complexes, remained bound, at least transiently. The result of transfer is a reduction of the metal centers and formation of CO complexes or clusters. Since Au has a low affinity for CO the reaction of gold oxo complexes **17** with CO provided a useful synthetic route to CO free gold clusters (Scheme 11).[78,79] Pt and Rh have higher CO affinities and gave CO complexes as exemplified by $[L_2Pt(\mu\text{-}O)]_2$ **8** and $Rh_2(\mu\text{-}O)(CO)_2(\mu\text{-dppm})_2$ **2** which when treated with CO gave $L_2Pt(CO)_2$ and $Rh_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$, respectively.[69,91] Oxygen atom transfer to phosphines was also observed. Triphenylphosphine oxide and $[(Ph_3P)_3Pt\text{–}AuPPh_3]^+$ form in the reaction of $[(cod)Pt(\mu\text{-}O)AuPPh_3]_2{}^{2+}$ **25** with PPh_3.[86]



Scheme 11

Alkene and alkyne oxidation by oxygen atom or nitrene transfer is a particularly desirable reaction for late transition metal oxo and imido complexes. Very few examples exist.[36,106] Treatment of the oxo complex $[L_2Pt(\mu\text{-}O)]_2$ **8** (L_2 = dppp) with ethene or diphenylethyne did result in oxygen atom transfer. However, the transfer was to the phosphine ligand and not to ethene or diphenylethyne! The 3-coordinate Pt(0) complexes **37** and **38** (Scheme 12) were the final products.[69] This system is currently under investigation and recent results indicate that the reaction is catalyzed by trace amounts of water suggesting mediation of the reaction by hydroxo species. The dppma imido complexes **16** also react with alkenes but the products have not yet been characterized.



Scheme 12

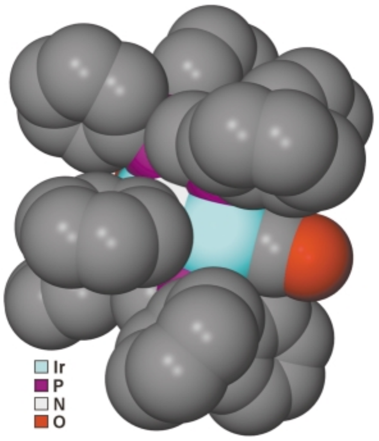
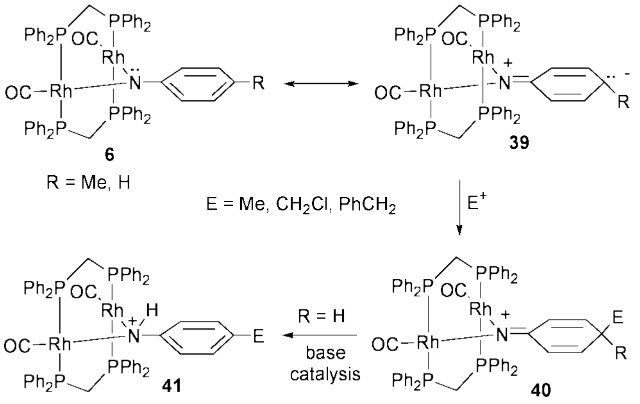


Fig. 8 Space-filling drawing of $Ir_2(\mu\text{-}NR)(CO)_2(\mu\text{-dppm})_2$ **6** (M = Ir, R = 4-tol). The ring methyl group has been omitted.

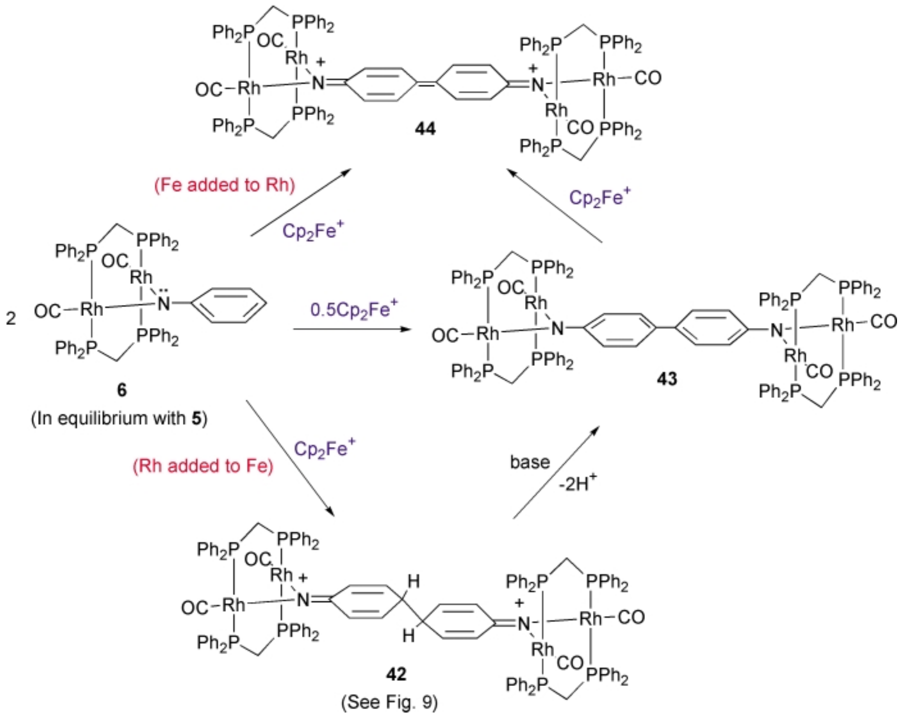
The oxo complex $[Pt_4(cod)_4Cl_2(\mu\text{-}O)_2]^{2+}$ **26** or its hydrolysis product $[Pt_4(cod)_4(\mu\text{-}OH)(\mu\text{-}O)_2]^{3+}$ **27** reacted with unactivated alkenes (C_2H_4, C_2Me_4, C_8H_{14}, cod).[86,107] Unfortunately, the reactions are complex yielding a variety of products. Acetaldehyde was detected in the ethylene reaction and crystals of the hydroxy allyl complex $[(cod)Pt\{\eta^3\text{-}(CH_2)_2C\text{–}CMe_2(OH)\}]^+$ were isolated in low yield from the C_2Me_4 reaction.

Nucleophilic reactivity

Our first indication that there was interesting nucleophilic reactivity associated with the imido complexes was the observation that the Rh imido complexes **6** (R = Ph) reacted slowly with the solvent CH_2Cl_2 to give the CH_2Cl ring addition product **40** (Scheme 13).[108,109] Other carbon electrophiles reacted similarly to give ring addition products. Addition to the phenyl ring was unexpected since proton sources had resulted in protonation at the basic imido nitrogen. The reason for the different reactivity of carbon electrophiles is steric. The dppm phenyl rings and methylene groups inhibit access of the larger carbon electrophile to the imido nitrogen atom. This can be seen in Fig. 8[63,64] where the nitrogen atom is just visible in the space-filling drawing of the Ir imido complex $[Ir(\mu\text{-}NR)(CO)(\mu\text{-dppm})]_2$ **6** (M = Ir, R = 4-tol). Denied access to the imido nitrogen the electrophile attacks the aryl imido ring made electron-rich by delocalization of the imido nitrogen atom lone pair into the ring (**39** in Scheme 13). Electron delocalization into the ring is reflected in short N–C distances observed in the structure of the imido complex.[49] That steric factors play a part in this chemistry is supported by the observation that the less sterically demanding dmpm ($Me_2PCH_2PMe_2$) analogs gave only small amounts of ring addition products. The ring addition products **40** are kinetic products as was demonstrated



Scheme 13



Scheme 14

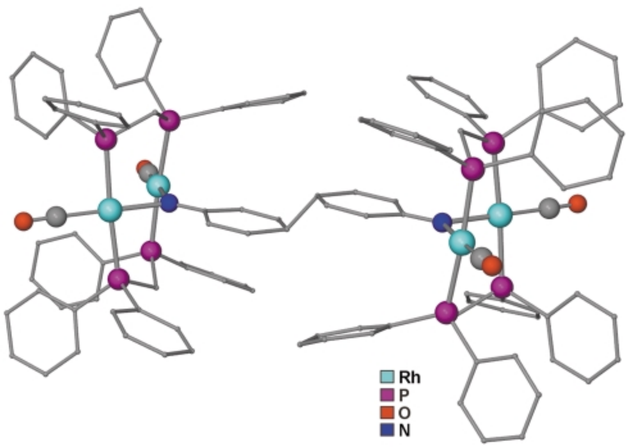
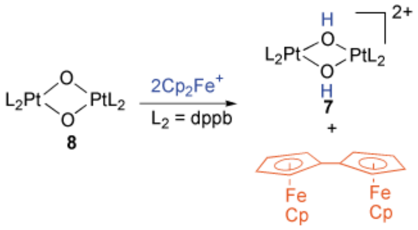


Fig. 9 Drawing of $[Rh_2(CO)_2(\mu\text{-dppm})_2(\mu\text{-}NC_6H_5C_6H_5N)Rh_2(CO)_2\text{-}(\mu\text{-dppm})_2]^{2+}$ **42**.

by the facile base-catalyzed rearrangement of the phenyl derivatives to the amido complexes **41** (Scheme 13).

In any electrophile–nucleophile reaction an SET process must be considered. For the ring addition reactions this implied redox chemistry for the A-frame complexes. Facile oxidation of the imido complexes **6** was observed by CV with only partial chemical reversibility for the R = phenyl complex. Bulk oxidation of **6** (R = phenyl) with ferrocenium gave the products shown in Scheme 14.[110] The products depended on the order of addition and on the reactant ratio. The key step is the one-electron oxidation of the imido complex **6** to a radical cation that has a high degree of radical density in the ring. Radical coupling through the *para* position of the ring yields the observed dimer **42** (Fig. 9[63,64]) that is susceptible to deprotonation and oxidation to give **43** and **44**. 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 should be possible whenever a heteroatom aryl ligand with lone pair electrons (M–OAr, M_2–NAr, M–NHAr) is bonded to an electron rich metal center that is not a π-acceptor. A terminal Pt aryl amido complex does show similar ring coupling chemistry.[115]

Reaction of $[L_2Pt(\mu\text{-}O)]_2$ **8** (L_2 = dppp) with ferrocenium gave very different results from the A-frame imido complexes (Scheme 15).[69] The products were the hydroxo complex $[L_2Pt(\mu\text{-}OH)]_2^{2+}$ and CpFe(fulvalene)FeCp. This process may involve a Pt(III) oxo complex which abstracts a hydrogen atom from Cp_2Fe. A Ni(III) oxo complex that readily abstracts hydrogen atoms was recently reported.[116] Further study of oxo and imido complex oxidation is needed to understand these different types of reactivity.



Scheme 15

Conclusions

Our work and that of others on late transition metal oxo and imido complexes has revealed a rich and interesting chemistry. Hydroxo and amido complex deprotonation and chloro/oxo exchange have proven for us to be the most useful synthetic routes to oxo and imido complexes. Our complexes display a range of reactivities showing strong polarization of the M–O and M–N bond. This is reflected in the strong basicity of many of the complexes and is similar to the basicity observed for oxygen atoms on the surface of late transition metals.[6] The degree of basicity of the complexes appears to be controlled by the acceptor properties of the metal centers bonded to the oxo or imido ligands. Qualitative trends suggest that important factors in the acceptor properties of the metal center include donor/acceptor properties of the ancillary ligands, ancillary ligand bite angle, and the location of the metal in the second or third transition metal series. Confirmation of these effects will require a quantitative measurement of pK_a values for the complexes. Oxygen atom and nitrene transfers from oxo and imido complexes were observed showing promise for these complexes in oxidation chemistry. Among the topics still in need of further study in this area are the careful elucidation of factors that control the basicity of the complexes and oxygen atom and nitrene transfers.

Acknowledgements

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