



SYNTHESIS AND REACTIONS OF MONOMERIC LATE TRANSITION METAL ALKOXO, ARYLOXO AND HYDROXO COMPLEXES

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Abstract—Despite the fact that they are postulated as intermediates in many metal-catalyzed transformations, well-characterized complexes having bonds between late transition metals and alkoxo groups are not as well known as their alkylmetal analogues. Even fewer examples of monomeric late transition metal hydroxo complexes are available. This article summarizes recent published work from the author's group that has resulted in the synthesis of a number of rhodium, iridium, rhenium, osmium and ruthenium alkoxo and hydroxo complexes and has allowed investigation of their chemical properties.

Access to complexes having metal–carbon and metal–hydrogen σ -bonds has resulted from the realization that such materials can be most easily prepared for relatively electron-rich metal centers, as well as when “strong-field” ligands are present at the metal. This understanding has in large part been responsible for the explosion of research in organo-transition metal chemistry that has occurred during the past 40 years.¹

In view of the increasing knowledge of organo-metallic chemistry that is focused on M–C and M–H bonds, it is ironic that for metal fragments that form such bonds—especially in groups located on the right side of the periodic table, the so-called “late” transition metals—analogue complexes having covalent (as opposed to dative) metal–oxygen and metal–nitrogen bonds traditionally have appeared much less frequently in the literature. The result has been a common perception that for such metals, metal–heteroatom bond energies are relatively low. However, alkoxo- and hydroxometal complexes have been postulated as intermediates in many important transformations. These include metal-catalyzed organic oxidation reactions, the water–gas shift reaction, carboalkoxylation of alkenes, reductions of ketones and aldehydes to alcohols, metal-catalyzed hydrolysis of phosphates and amides, and enzymatic transformations such as the action of carbonic anhydrase.^{2–6}

Presumably because they are relatively electro-positive, “early” transition metals tend to form isolable metal alkoxides, aryloxides and amides (more accurately referred to as alkoxo-, aryloxo- and amidometal complexes) more readily than late metal systems.^{2,7} The overall situation with respect to early- and late-metal bonding has often been rationalized using the ideas of Pearson, who suggested that the “soft–soft” interactions characteristic of late transition metal fragments and carbon fragments should be more stabilizing than the “hard–soft” interactions associated with these metals and less polarizable atoms such as nitrogen, oxygen and fluorine. Because of the inaccessibility of late metal alkoxo and amido complexes, there has been correspondingly little known about whether M–O and M–N σ -bonds are capable of undergoing reactions, such as migratory insertions, α - and β -eliminations, etc., that have been established as very general processes for M–H and M–C systems.

We were interested in determining whether late metal–oxygen and metal–nitrogen σ -bonds are in fact less strong or accessible than metal–carbon bonds. Therefore, in the mid-1980s we initiated a program aimed at preparing direct M–O and M–N analogues of well-known metal alkyl complexes and examining their chemistry. The purpose of this paper is to summarize some of the con-

tributions that one group of individuals has made to the synthesis of complexes having metal–oxygen σ -bonds. Other investigators have also noted the trends summarized above, and have made significant contributions to the synthesis, structure and chemistry of alkoxometal complexes. Because this article is meant to summarize the research of one group, it does not contain extensive citations of the work of others. We direct the reader to the references in the primary papers cited in this article, as well as to the other contributions to this Symposium-in-Print, for summaries of the important contributions of other workers to this field.

Our work has focused on rhodium, iridium, rhenium, osmium and ruthenium complexes. Subsequent sections of this article are organized primarily by metal, although we have also tried to provide some feeling for the chronology of our investigations.

EARLY EXPERIMENTS: METAL ENOLATES; ALKOXORHODIUM AND ALKOXOIRIDIUM COMPLEXES

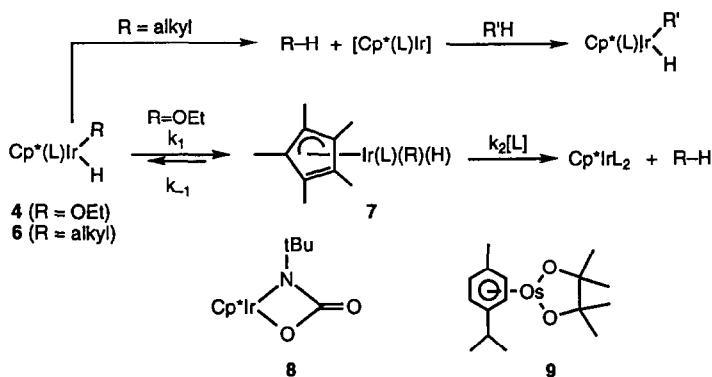
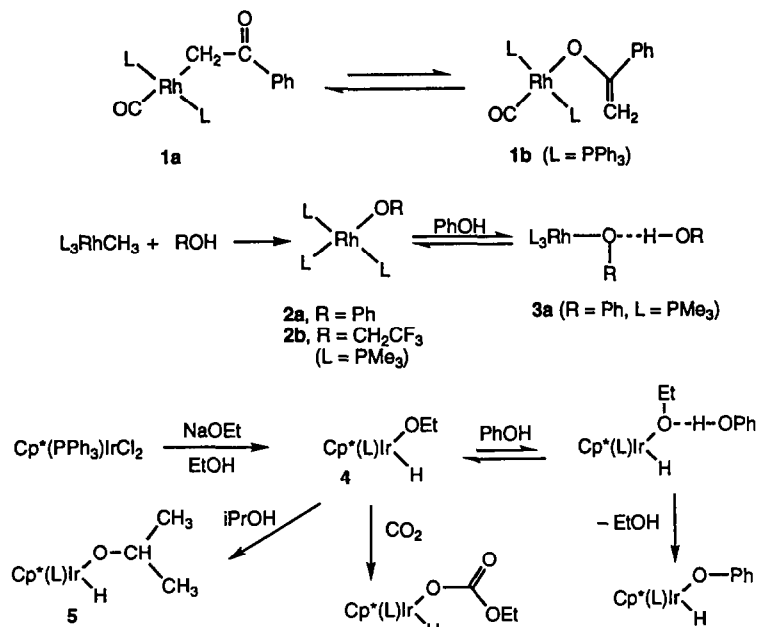
Some of our early experiments with alkoxometal complexes grew out of a collaborative project, undertaken with C. H. Heathcock and his group, that was designed to examine the chemistry of metal enolates. Metal enolates are potentially fluxional, and so can choose to be in a carbon- or oxygen-bound form. True to the general perceptions of the bonding preferences of early and late transition metals mentioned above, most of the late metal enolates that were examined preferred to exist in carbon-bound forms.^{8,9}

One exception, however, was the square planar rhodium enolate $(\text{CO})(\text{PPh}_3)_2\text{Rh}(\text{CH}_2\text{COPh})$ (**1**), which exists in a dynamic equilibrium containing both the oxygen-bound and carbon-bound forms **1a** and **1b** (Scheme 1).⁹ This result suggested that we might be able to use a related metal fragment to gain access to late metal complexes with M—O bonds. As shown in Scheme 1, we were able to obtain phenoxo and trifluoroethoxo complexes **2a** and **2b**, but we were not able to prepare stable simple alkoxo complexes in this series, presumably because of steric congestion or their tendency to undergo rapid β -elimination.¹⁰ One important result of this work was the understanding that phenoxo and electron-withdrawing metal alkoxo complexes appeared to be more stable than their simple alkoxometal relatives, despite the fact that one might expect the corresponding stabilized free anions to dissociate from the metal more easily than simple alkoxides. Another interesting finding was that phenoxo-rhodium complexes were capable of unusually

strong hydrogen bonding to another hydroxyarene molecule (Scheme 1). Thermodynamic studies placed the strength of the hydrogen bond in **3a** at the unusually high level of $14.0 \text{ kcal mol}^{-1}$ in cyclohexane solution.

We next turned to the coordinatively saturated $\text{Cp}^*(\text{L})\text{IrX}_2$ system in hope that its 18-electron configuration would prevent β -elimination and thus allow access to complexes with simple alkoxo groups. This turned out to be successful, at least in special cases. Treatment of $\text{Cp}^*(\text{PPh}_3)\text{IrCl}_2$ with sodium ethoxide in ethanol gave complex **4**. Not only does this material possess a simple late metal M—OR functionality, it also has a hydride attached to the metal, providing a new member of a very rare class of materials, the alkoxo hydrides (perhaps stabilized relative to their square planar rhodium analogues because of the 18-electron iridium center). We subsequently were also able to prepare phenoxo hydrides and phenoxo alkyls in this series, although we have not yet obtained access to alkoxo alkyls. We performed an X-ray diffraction study of the iso-propoxido analogue **5**, obtaining one of the few structurally characterized monomeric late transition metal alkoxo complexes at the time.¹¹ Although some metal alkoxo complexes had been found to have unusually short C—O distances, the isopropoxy C—O distance in **5** is similar to that of the corresponding alcohol.

The synthesis of **4** provided a late metal system whose behavior could be compared directly with that of the corresponding alkyl hydride complexes $\text{Cp}^*(\text{PR}_3)\text{Ir}(\text{R})(\text{H})$, which we had prepared earlier in our C—H activation studies.^{12,13} The two types of systems behave quite differently. Studies of the reactivity of **4** established that in spite of the covalent nature of the Ir—O bond (suggested by the solid state structure of **5**), its chemistry reflected the anion-like nature of the alkoxo ligand. Thus, it was shown to undergo alkoxide interchange with esters and nucleophilic ring-opening of anhydrides, just as one would expect for NaOEt . We were also able to utilize exchange reactions with thiols to prepare analogous thiolate complexes and examine their chemistry.¹⁴ Among the most interesting reactions of **4** were its reactivity toward carbon dioxide and other heterocumulenes. This again emphasizes the apparent anion-like character of the coordinated alkoxy group and its dissimilarity to the Ir—R fragment. A most dramatic difference was observed on thermolysis of **4** in the presence of compounds capable of trapping reactive intermediates (Scheme 2). It has been established that heating $\text{Cp}^*(\text{PR}_3)\text{Ir}(\text{R})(\text{H})$ complexes (**6**) leads to unimolecular reductive elimination, followed by reaction of the resulting coordinatively unsaturated species



so generated with an alkane or arene. In the case of **4**, however, kinetic studies established that reductive elimination to give Cp^*IrL (or its solvate) does not occur. Instead, a reactive intermediate is formed, without elimination of ROH , that is trapped by phosphine to extrude ROH in a second step. After ruling out a number of possibilities for the reactive species, we were left with the conclusion that this intermediate is the $\eta^3\text{-Cp}^*$ complex **7**. Although it at first seemed unlikely that such a “ring-slipped” intermediate could have a lifetime long enough to allow phosphine trapping (k_2) to compete with $\eta^3\text{-}\eta^5$ re-coordination of the Cp^* ring (k_{-1}), other studies in the iridium series (*vide infra*) provided evidence that such a property might be characteristic of Cp^* rings attached to metal centers that also have OR or NR_2 groups bound to them.^{15,16}

Contemporaneously with our studies on M—O complexes, we attempted to prepare late transition metal complexes with single and multiple metal–nitrogen bonds. A serendipitous success in this area was the finding that treatment of $[\text{Cp}^*\text{IrCl}_2]_2$ with $t\text{BuNHLi}$ led to the simple monomeric imido complex $\text{Cp}^*\text{Ir}\equiv\text{NtBu}$.¹⁷ Isoelectronic imidoosmium complexes were prepared by an analogous route.^{18,19} In both series, reactions of the imido complexes were carried out that led to metal centers, to which were attached two heteroatom ligands, that were quite stable with (formally) 16-electron electronic configurations (e.g. **8** and **9**). This contrasts quite strongly with the analogous system **6** containing simple alkyl groups, which have PMe_3 ligands that resist dissociation even at temperatures near 180°C . It seems likely that stabilization of the iridium centers in **8** and **9** is provided by π -donation

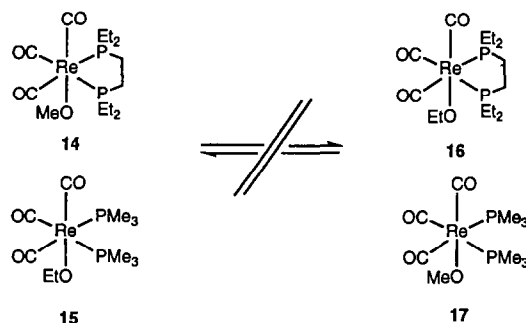
from the attached heteroatoms, reducing their need to acquire a new donor ligand to reach an 18-electron electronic configuration.^{20,21} These results make the relatively long apparent lifetime of the η_3 -Cp* intermediate **7** discussed earlier seem more plausible, since the ring-slipped intermediate might be stabilized substantially by π -donation to the metal from the ethoxy group.¹⁵

ALKOXORHENIUM AND ARYLOXORHENIUM COMPLEXES

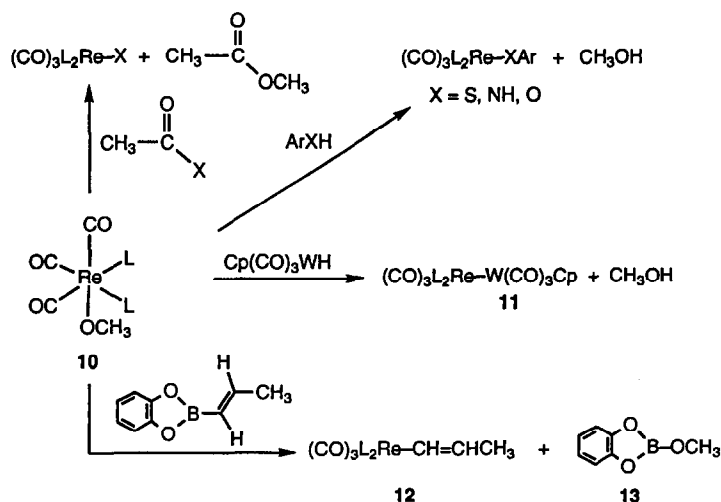
A different access to coordinatively saturated aryloxides and alkoxides was found in a series of octahedral rhenium complexes. Treatment of the alkyl complex $(\text{CO})_3(\text{PPh}_3)_2\text{Re}-\text{R}$ with phenols or treatment of the triflate $(\text{CO})_3(\text{L})_2\text{ReOSO}_2\text{CF}_3$ ($\text{L} = \text{PMe}_3$, chelating diphosphine or diarsine) with sodium alkoxides provided good yields of the series of complexes $(\text{CO})_3(\text{L})_2\text{ReOR}$ ($\text{R} = \text{Ph}$, *p*-substituted aryl, CH_3 , CH_2CH_3 , $\text{CH}(\text{CH}_3)_2$).²² As in the iridium system discussed above, the rhenium complexes exhibited anionic behavior. The methoxo complex **10**, for example (Scheme 3), attacks the carbonyl groups of anhydrides, activated esters and acid chlorides.^{23,24} The complex was also reactive toward the electrophilic small molecules CO_2 and CS_2 , but it did not react readily with CO . In addition, **10** undergoes an extensive series of exchange reactions. Some of these were expected based on the chemistry of the better known early metal alkoxo complexes: e.g. the reaction of **10** with phenols, amines and thiols to give phenoxo, amido and thiolato complexes. Some were more unusual, however, such as the reaction of **10** with $\text{Cp}(\text{CO})_3\text{WH}$ to give heterodinuclear complex **11** and the reaction with a vinyl boron

compound to give vinylrhenium complex **12** and borate **13**.

In spite of the fact that much of this chemistry appears to be characteristic of nucleophilic methoxide, we have consistently failed to obtain evidence for the intermediacy of this species as a free ion. Thus, a kinetic study of the reaction of **10** with CS_2 gave strictly second-order kinetics, providing no direct evidence for an intermediate such as free ions or a long-lived ion pair in which the rate of return to **10** would be competitive with the rate of reaction of the intermediate with CS_2 .^{23,25} Perhaps most dramatic is the negative crossover experiment shown in Scheme 4: a solution of the diethylphosphinoethane-substituted ethoxo complex **14** and the bis-trimethylphosphine-substituted methoxo complex **15** in benzene solution at room temperature produced no exchange products **16** and **17**. In our opinion, even quite small instantaneous concentrations of Re^+ and OR^- ions (or even solvent-separated ion pairs) should have led to a reasonable rate of crossover. We therefore conclude that the extensive nucleophilic chemistry of **10** is the result of a highly polarized (but still covalent)



Scheme 4.



Scheme 3.

metal—oxygen bond that reacts directly with electrophiles. The ability of these molecules to form strong hydrogen bonds with phenols is also consistent with a significant degree of M—O charge polarization in their ground states.

TETRAKIS(PHOSPHINE) ARYLOXORUTHENIUM AND ANILIDORUTHENIUM COMPLEXES

Concurrent with our studies on the rhenium complexes described above, we also found it possible to prepare several tetrakis(trimethylphosphine) ruthenium complexes with metal—oxygen single bonds. Simple alkoxo complexes proved elusive in this series, but once again the higher stability of the ArO—M (and ArNH—M) interactions allowed us to isolate and study the chemistry of complexes having phenoxo and anilido ligands. Because complexes with analogous M—C bonds were also available, this project yielded insight into the comparative chemistry of Ru—O, Ru—N and Ru—C bonds in similar environments.

Our first experiments involved the synthesis of the benzyne complex **18** (Scheme 5) and its ring-opening reactions with weak acids.^{26,27} Treatment with aniline and *p*-cresol led, via (phenyl)(XR)Ru complexes **19a** and **19b** (only **19a** was isolable), to the cyclometallated complexes **20a** and **20b**. Similarly, ring opening occurred cleanly with ethylene complex **21** and cyclometallated phosphine complex **22** to give *cis*-anilido-ruthenium and (aryloxo) (hydrido)ruthenium complexes **23** and **24**, respectively.²⁸ More recently we have explored analogues of these complexes having two bis(dimethylphosphino)ethane (DMPE) ligands coordinated to the ruthenium center in place of four PMe₃ groups;^{29,30} this has led in several cases to *trans*- rather than *cis*-oriented H and X groups, and has allowed us to characterize structurally *trans*-(DMPE)₂Ru(OAr)(H) (Ar = *p*-CH₃C₅H₄).²⁹

In analogy to the ethoxo(hydrido)iridium complex discussed earlier, treatment of **23** and **24** with a dative ligand (in this case, CO) promoted overall reductive elimination of aniline and *p*-cresol. Our inability to observe or isolate a CO adduct such as L₂(CO)₂Ru(H)(OAr) prevented attempts to elucidate the detailed mechanism of this reaction, but reductive elimination of aniline from **23** is markedly faster than the corresponding elimination of *p*-cresol from **24**. It is not clear whether this is due to the conditions necessary for a second CO substitution reaction or to an inherent difference in rates of the two reductive elimination processes.²⁸

As in the rhenium series, the aryloxo- and anilidoruthenium complexes undergo rapid exchange

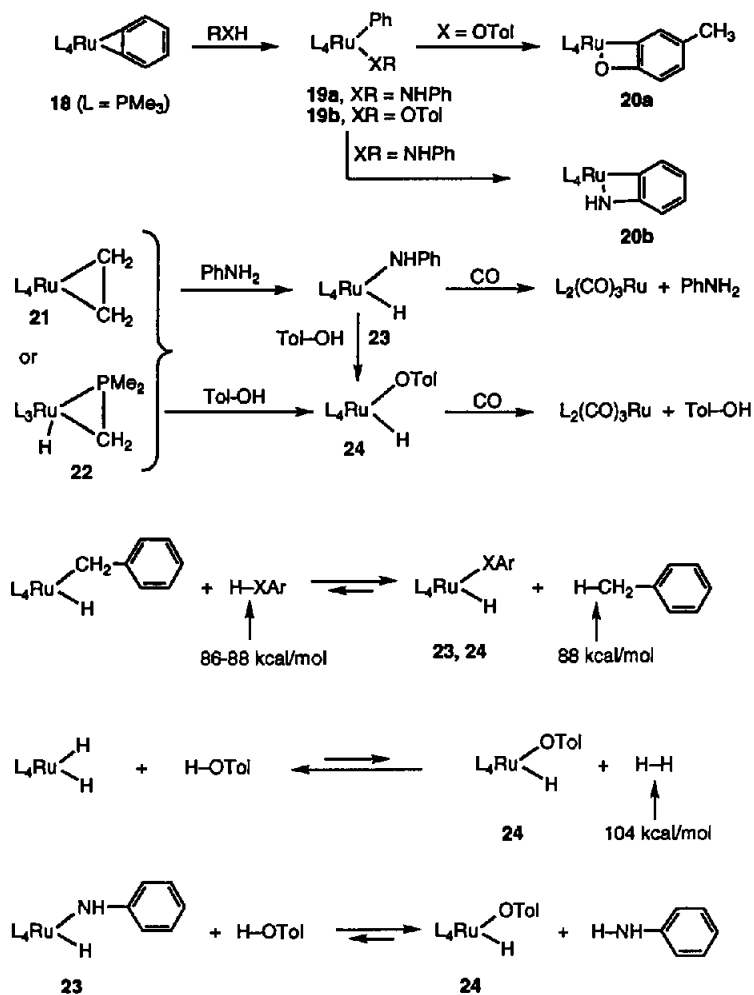
reactions with other proton donors. However, the position of equilibrium for these reactions depends dramatically on the organic fragments involved. Thus, the interchange of the benzyl hydride (PMe₃)₄Ru(H)(CH₂Ph) with either aniline or *p*-cresol lies substantially on the side of toluene and the aryloxo and anilido hydrides (Scheme 5). Reaction of (PMe₃)₄RuH₂ with *p*-cresol, on the other hand, lies to the left as written in Scheme 5, which is confirmed by the generation of the dihydride and free cresol upon treatment of the aryloxo hydrido complex **24** and H₂. Finally, exchange of the anilido hydrido complex **23** with *p*-cresol lies to the right, giving aryloxo complex **24** and aniline. Because the C—H, O—H and N—H bond energies in toluene, *p*-cresol and aniline are all comparable (87 ± 3 kcal mol⁻¹), these results establish the following trends in bond strengths: L₄(H)Ru—H > L₄(H)Ru—OAr > L₄(H)Ru—NHPPh > L₄(H)Ru—CH₂Ph. This trend clearly contradicts the classical assumption that late metal M—C bonds are necessarily stronger than M—N and M—O bonds.

The availability of oxa- and azametallacycles **20a**, **20b** and the corresponding carbocycle **20c** allowed us to compare the behavior of these three isoelectronic molecules in CO and CO₂ migratory insertion reactions (Scheme 6).³¹ Carbon monoxide gave exclusive insertion into the aryl-ruthenium bond leading, in each case, to products of general structure **25**. Carbon dioxide reacted with carbon- and oxygen-containing metallacycles **20a** and **20c** also with M—C insertion, leading to **26** (X = O, CH₂). With the cyclometallated anilido complex **20b**, however, **28**, the product of apparent CO₂ insertion into the M—N bond, was obtained.

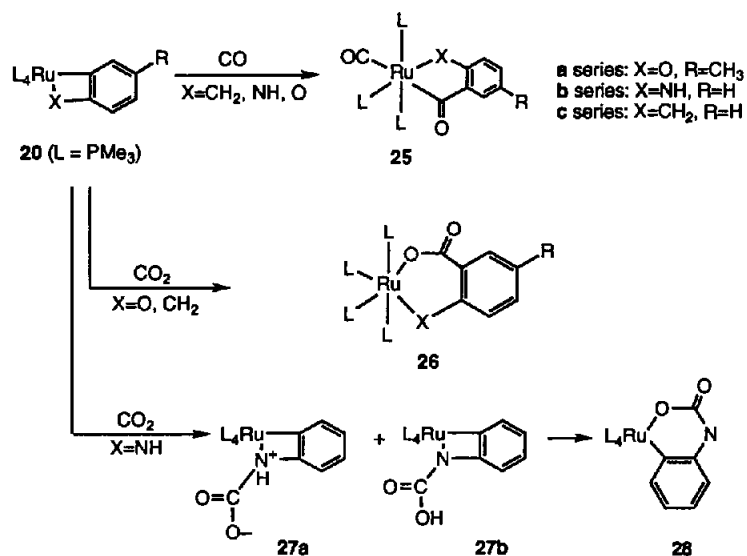
Kinetic and NMR-monitoring studies provided further insight into the unique behavior of **20b**. Evidence was obtained that the M—C insertion reactions of **20c** proceed by loss of phosphine, followed by coordination of CO or CO₂, and then migratory insertion and re-coordination of phosphine. In the nitrogen case, however, intermediates **27a** and **27b** were formed without initial PMe₃ loss, and then these complexes rearranged to **28**. We therefore concluded that it is the higher inherent nucleophilicity of nitrogen that allows it to react directly with the relatively electrophilic CO₂ molecule, and this process overtakes the slower phosphine loss/migratory insertion pathway that appears to favor carbon migration.

OXAMETALLACYCLOBUTANES

A special class of transition metal alkoxo complexes in which we have been interested for some time is 2-oxametallacyclobutanes—four-membered



Scheme 5.



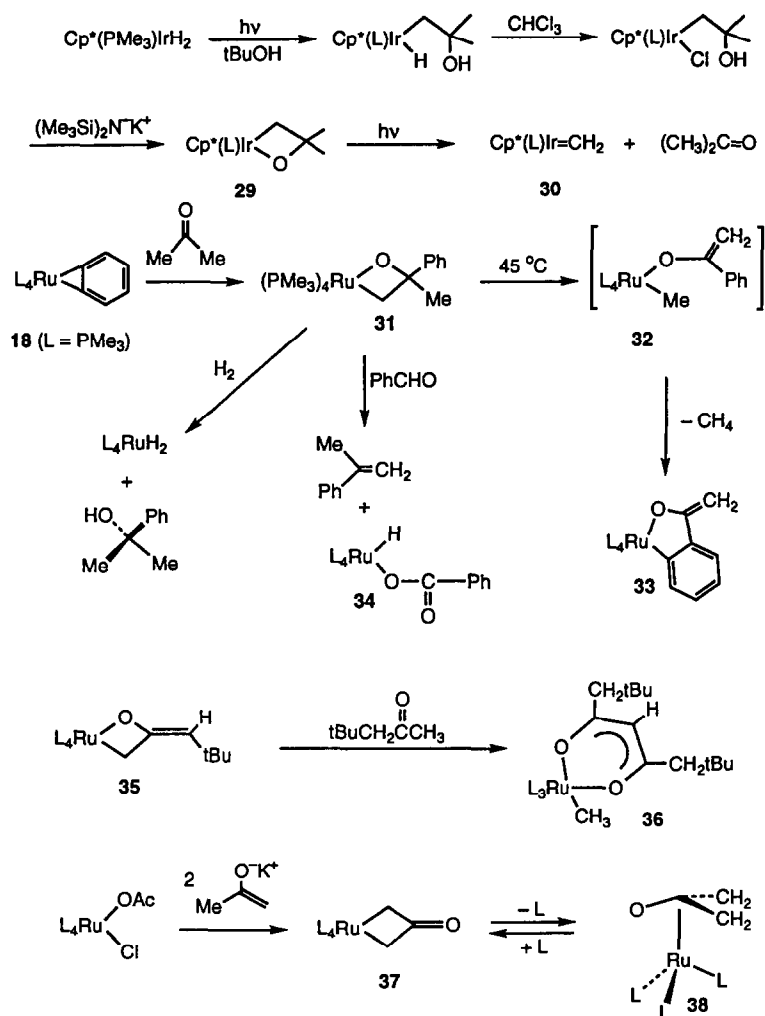
Scheme 6.

ring complexes with adjacent metal and oxygen atoms in the ring. As with late transition metal alkyls and the corresponding alkoxides, many examples of metallacyclobutanes have been known for some time, but the corresponding mono-oxa analogues are much less well known. Besides being of interest in themselves, the chemistry of these materials is relevant to metal-catalyzed alkene oxidation reactions. Although the possible intermediacy of 2-oxametallacyclobutanes in cytochrome P-450 catalyzed epoxidation of alkenes is controversial,³² there is mounting evidence that (oxo)oxametallacyclobutanes may be involved in metal-mediated dihydroxylation reactions.³³

As with simple alkoxides, our early attempts to synthesize 2-oxametallacyclobutanes focused on iridium(III) complexes. In this work we successfully prepared complex **29** by the route illustrated at the top of Scheme 7 (a similar sequence also led to the nitrogen analogue of this material having O replaced by NH).³⁴ This complex does not give an

epoxide on heating or ultraviolet irradiation, but it does undergo a unique photochemical fragmentation to acetone and carbene complex **30**.

The tetrakis(phosphine)ruthenium series also provided 2-oxametallacyclobutanes with equally interesting reactivity.³⁵ In this series protonation reactions converted benzyne complex **18**, via ring opening followed by cyclometallation, to oxametallacycle **31**. Once again we found no direct reductive elimination routes from this material to substituted epoxide. However, mild thermolysis of the oxametallacycle (45°C, 8 h) provided a good yield of complex **33**. The most reasonable route to this product involved β -methyl migration from carbon to the metal center—a very rare reaction—followed by cyclometallation of the phenyl ring. Other significant chemistry of **31** included hydrogenation to give L_4RuH_2 and 2-phenylpropan-2-ol, and several reactions (such as the transformation with benzaldehyde shown in Scheme 7) that extrude 2-phenylpropene. Despite the possibility that these



Scheme 7.

reactions proceed via the low-valent oxo complex $L_4Ru=O$, we were not able to obtain direct evidence that this intriguing intermediate is directly involved.

Two other related reactions that arose from this work, involving the chemistry of cyclic enolates, are illustrated at the bottom of Scheme 7. In one, **35** undergoes a reaction involving a sequential aldol condensation and (once again) β -methyl transfer to give the substituted "acac" complex **36**. The second example involves the preparation of 3-oxametallacyclobutane **37**. Ketone **37** is an example of a well-known class of complexes, but this particular example is unusual in its ability to lose a phosphine and undergo conversion to the oxatrimethylene-methane complex **38**.³⁵

LOW-VALENT HYDROXOMETAL COMPLEXES

Through the work described above, as well as important contributions from several other groups, low-valent electron-rich late transition metal alkoxo ($M-OR$) complexes are now better known than they were several years ago. Examples of low-valent monomeric $M-OH$ complexes, however, are still relatively rare, presumably because of their tendency to donate a proton to another $M-OH$ center and form μ -oxo complexes, which are often very stable.³⁶⁻³⁸ Recently, however, we have been able to use the stabilizing influence of the $Cp^*(L)Ir$ and L_4Ru fragments to obtain isolable (and, in two cases, structurally characterized) examples of late transition metal hydroxo complexes.

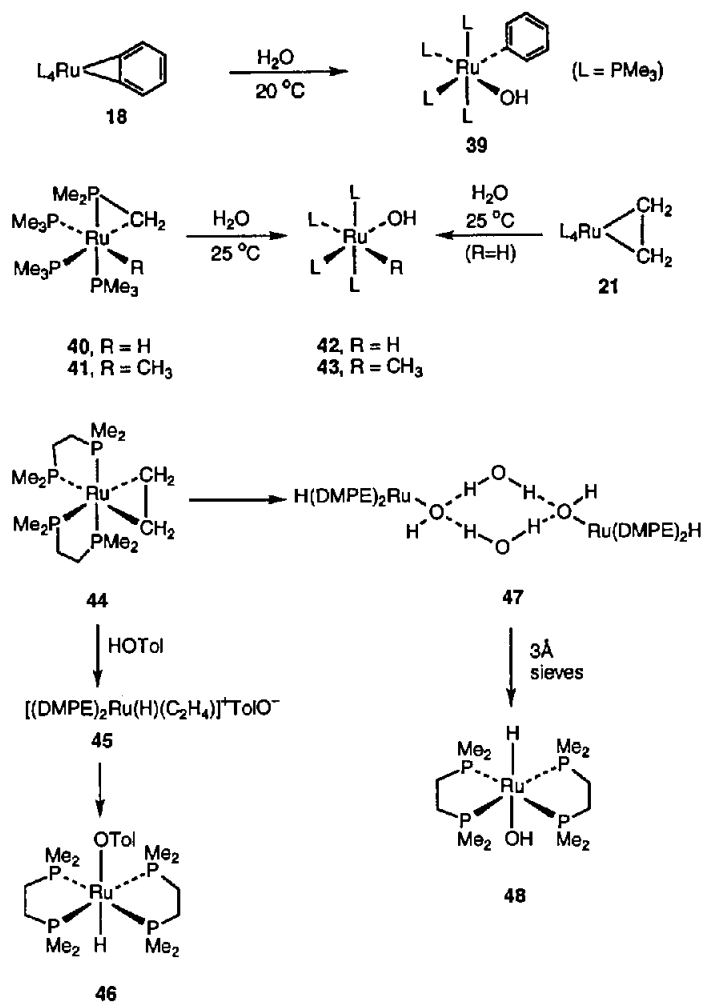
Our first example of this class of materials was a (phenyl)(hydroxo)ruthenium complex that was obtained from the addition of water to benzyne complex **18**. This led to (phenyl)(hydroxo)ruthenium complex **39** in 62% yield, which after isolation and crystallization was characterized by X-ray diffraction, establishing that it was neither aggregated nor hydrogen bound to water in the solid state.²⁷ More recently we have been able to prepare and isolate the (hydrido)(hydroxo)ruthenium complex **42** by addition of water to phosphine-cyclometallated complexes **40** or more conveniently by similar treatment of the ethylene complex **21**. The corresponding (methyl)(hydroxo) complex **43** has been obtained by treatment of **41** with water (Scheme 8).³⁹

Replacement of the four PMe_3 ligands with two bis-(dimethylphosphino)ethane (DMPE) ligands provides additional information about this general class of addition reactions. First, we found that weak acids such as phenols, thiols, etc. add across the $Ru-C$ bond in the bis(DMPE)ethylene com-

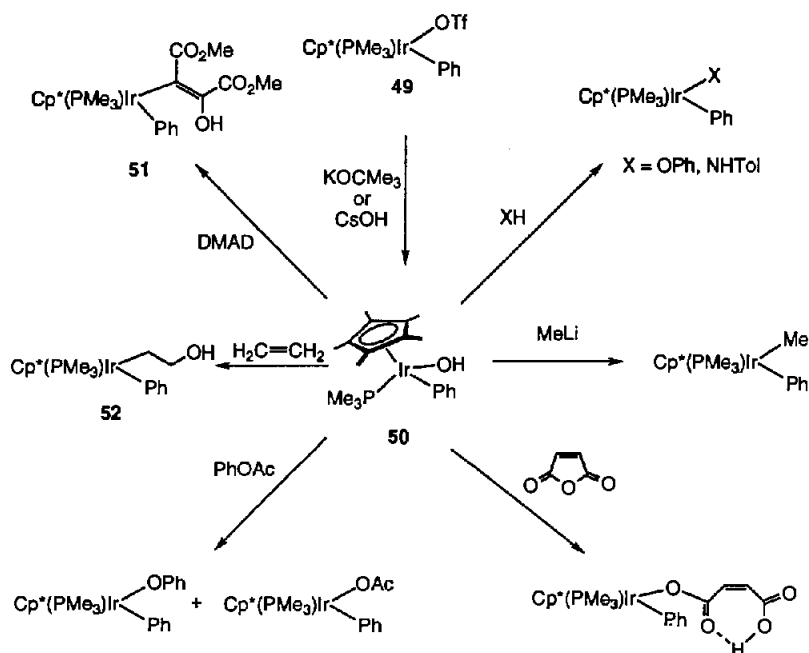
plex **44** to give products analogous to those obtained from **21**, as described earlier. However, in the addition of *p*-cresol a new species, spectroscopically characterized as the cationic ethylene hydride **45**, could be detected as an intermediate in the conversion of **44** to the final addition product **46**. Presumably a similar intermediate intervenes in the reaction of **21** with *p*-cresol (Scheme 5), but it is not stable enough to accumulate and be detected in that system. Perhaps most interesting is the (hydrido)(hydroxo)ruthenium complex that is formed by addition of water to bis(DMPE) complex **44**. An X-ray diffraction study demonstrated that this molecule (**47**) is a dimer in which two hydroxoruthenium moieties are held together by two water bridges, as shown in Scheme 8. An unusual aspect of the hydrogen-bonding bridge is that neither hydroxoruthenium proton is involved; only the hydrogens of the water molecules form the hydrogen bonds between water and the $Ru-OH$ ligands.^{29,39}

Recently the $Cp^*Ir(PMe_3)$ system has also provided us with an isolable hydroxometal complex. Treatment of the reactive triflate complex $Cp^*(L)Ir(Ph)(OSO_2CF_3)$ (**49**) with either $KOtBu$ or $CsOH$ leads to a high yield of the hydroxo (iridium) complex **50**.⁴⁰ Studies on this complex have revealed a reaction chemistry much more extensive than that of the corresponding alkyl complexes; some of the transformations observed with **50** are summarized in Scheme 9. Several of these are reflective of the (alkoxo)(hydrido)iridium complex **4** discussed earlier. Unique to this system, however, are the apparent insertion reactions with dimethylacetylenedicarboxylate (DMAD) to give substituted vinyl complex **51** and with ethylene to give the hydroxyethyl complex **52**.

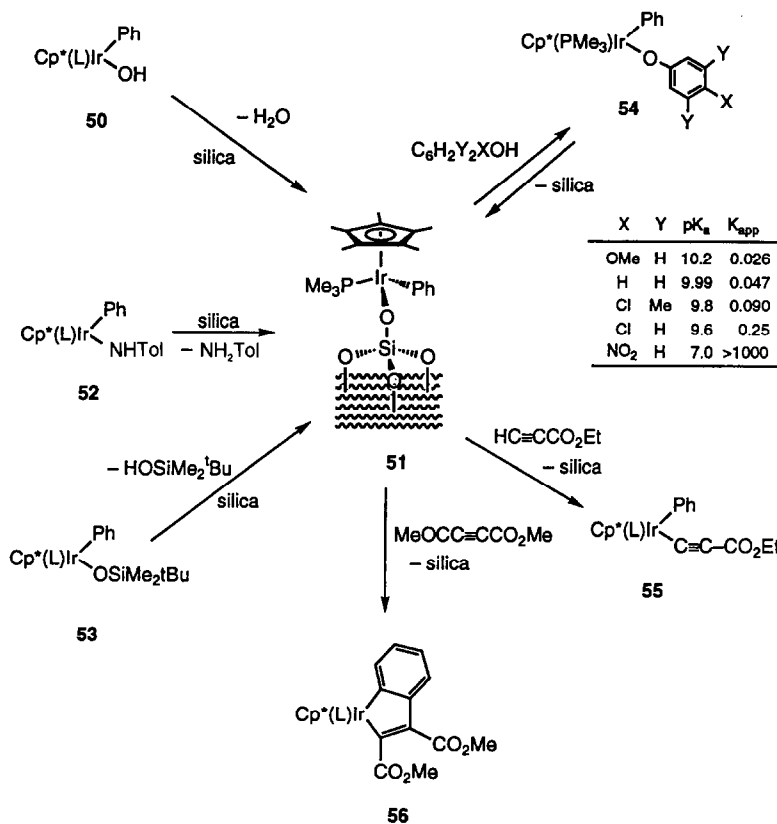
Finally, in very recent work we have found that the hydroxoiridium complex **50** is a convenient substrate for carrying out attachment of metal complexes to silica supports.⁴¹ As shown in Scheme 10, treatment of silica with **50** at room temperature results in smooth attachment of iridium to the silica surface, presumably via $Ir-O-Si$ bonds. The same supported material can be obtained by treatment of silica with the amido complex **52** and the siloxido complex **53**. Persuasive evidence that the product **51** is formed without structural rearrangement is provided by treatment of the supported complex with phenols, which quantitatively returns the organometallic species as the corresponding phenoxo complexes **54**. Exchange of the silica "ligand" with phenols is a reversible process, and concentration dependence studies have allowed us to measure apparent equilibrium constants for the interchange. In an analogous proton transfer reac-



Scheme 8.



Scheme 9.



Scheme 10.

tion that leads to new metal-carbon bonds, **51** reacts with ethyl propiolate to give (alkynyl) (phenyl)iridium complex **55**. Finally, using other organic reagents it is possible to induce more deep-seated changes at the iridium center. Perhaps the most interesting example involves the reaction of **51** with dimethylacetylenedicarboxylate, which induces a cyclization reaction leading to the metallacycle **56**. Ongoing studies are directed at expanding the scope of these reactions and obtaining a mechanistic understanding of transformations such as the conversion of **51** to **56**.

SUMMARY AND CONCLUSIONS

During the past ten years the work described here has contributed to a growing literature which demonstrates that relatively low-valent, electron-rich "late" transition metal complexes with metal-oxygen single bonds can be prepared. The chemical properties of these materials so far uncovered distinguish them in many ways from their alkylmetal analogues. We look forward to the synthesis of additional examples of currently rare members of this class of complexes, such as electron-rich monomeric metal hydroxides. We also anticipate more

extensive mechanistic studies on their reactions, which should help to illuminate the role played by alkoxy and hydroxy complexes in metal-catalyzed organic oxygenation reactions.

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