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Late Transition Metal μ -Oxo and μ -Imido Complexes

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Abstract

The synthesis and reactions of late-transition-metal oxo and imido complexes was explored. The deprotonation of platinum(II) hydroxo complexes yielded new oxo complexes. Attempted deprotonation of Cp^{*}Rh(III) hydroxo complexes did not give oxo complexes but complex mixtures probably resulting from reduction of the Rh(III) center. The reaction of Na/Hg with [Cp^{*}RhCl₂]₂ gave the very reactive Rh(II) dimer, [Cp^{*}RhCl]₂. Rhodium(I) imido complexes with the bis(dimethylphosphino)methane ligand were prepared and found to be similar to the previously prepared bis(diphenylphosphino)methane complexes. Attempts to prepare bis(diphenylphosphino)methylamine, bis(diphenylphosphino)phenylamine, PMe₃ and NO⁺ analogues were not successful. Attempts to prepare Cp^{*}Rh(III) imido complexes resulted in amido complexes and reduction. Rhodium (III) tris(3,5-dimethylpyrazoyl)borate analogues are reduction resistant but have not yet yielded imido complexes. The first imido complexes of Au were prepared by treating a Au oxo complex with amines or isocyanates. Dimeric Cp^{*}Rh dioxygen and nitrosobenzene complexes were prepared by insertion into the Rh-Rh bond of [Cp^{*}RhCl]₂. The dioxygen complex activates a C-H bond of the Cp^{*} ligand on treatment with PMe₃. Imido and oxo complexes nitrene and oxygen atom transfer product in reactions with CO. A novel electrophilic ring addition was observed with sterically protected aryl imido complexes.

Introduction

This project is a study of the synthesis and reactivity of μ -oxo and μ -imido complexes of late-transition-metal (groups 9-11) of the second and third series.¹ Our interest in these complexes arises from 1) our desire to model surface species present in catalytic reactions (ethylene epoxidation on Ag,² NH_3 oxidation on Pt,³ NO reduction by CO on Rh,⁴ O_2 electroreduction on Pt⁵) and 2) the unique reactivity associated with complexes of "hard" ligands with "soft" metals.⁶

Major portions of the results from this project have been published in the open literature (reprints and preprints are appended). A summary of the project results follows and emphasizes unpublished, negative and preliminary results.

Syntheses

Oxo Complexes. Our successful deprotonation synthesis of the A-frame oxo complexes, $\text{M}_2(\mu\text{-O})(\text{CO})_2(\mu\text{-dppm})_2$ ($\text{M} = \text{Rh}$ and Ir , dppm = bis(diphenylphosphino)methane)⁷ lead to an exploration of the deprotonation of other late-transition-metal hydroxo complexes. Work had begun on the Maillis $[(\text{Cp}^*\text{M})_2(\mu\text{-OH})_3]^+$ ($\text{M} = \text{Ir}$ and Rh) system, as proposed, when it was brought to our attention that the Ir complex had already been successfully deprotonated/dehydrated by Bergman's group (eq 1). These results were subsequently published.⁸ Our efforts therefore focused on the Cp^*Rh system.

All efforts to deprotonated/dehydrate $[(\text{Cp}^*\text{Rh})_2(\mu\text{-OH})_3]^+$, $[(\text{Cp}^*\text{Rh})_2(\text{pz})_2(\mu\text{-OH})]^+$ and $[(\text{Cp}^*\text{Rhpy})_2(\mu\text{-OH})_2]^{2+}$ gave intractable mixtures. We believe that reduction of Rh(III) is the dominant reaction pathway in this system. Reoxidation of lower valent Cp^*Rh was therefore explored and $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})]_2$ was synthesized (eq 2). The Ir analogue could not be prepared nor

was further reduction of the Rh possible. $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})]_2$ is very reactive and treatment with N-methylmorpholine-N-oxide ($\text{R}_3\text{N-O}$) gives N-methylmorpholine and what we believe is a Rh oxo complex (eq 3). Unfortunately, pure samples or X-ray crystals could not be obtained.

Protonation gave X-ray crystals but the collected data set could not be solved.

Our attention turned to more reduction resistant systems and we discovered the facile deprotonation of $[\text{L}_2\text{Pt}(\mu\text{-OH})]_2^{2+}$ ($\text{L} = \text{PPh}_3$, py, eq 4).

Crystals from toluene ($L = PPh_3$) showed the interaction of a $LiBF_4$ contact ion pair with the oxo ligands.⁹ For $L = py$ the results are still preliminary. This system forms a primary focus for future work. Part of this work involves the coordinative ability of the oxo ligand. Preliminary results show that Ag^+ and $(COD)Rh^+$ coordinate to the oxo ligands of $[L_2Pt(\mu-O)]_2$ to produce new μ_3 -mixed-metal oxo complexes.

Imido Complexes. The imido ligand has a tremendous advantage over the oxo ligand in that it can be modified by changes in the nitrogen substituent. We took advantage of this in the A-frame imido/amido tautomeric system and prepared a range of aryl imido/amido complexes.¹⁰ This allowed a study of the properties and reactivity as a function of the basicity of the imido ligand (see below).

We also wished to study the properties and reactivities of both the imido and the oxo A-frame complexes as a function of the ancillary ligands. Modifications of the A-frame complexes was undertaken. We successfully prepared imido/amido A-frame complexes using the *dmpm* (bis(dimethylphosphino)methane) in place of *dppm*. Electronically, the complexes were very similar. However, steric differences are apparent in their reactivity (see below).

More extensive modifications of the phosphine ligand were attempted. In particular, we were interested in determining the importance of the tautomeric imido/amido equilibrium in the reaction chemistry. The ligands *dppma* (bis(diphenylphosphino)methylamine) and *dpppa* (bis(diphenylphosphino)phenylamine) were available and would eliminate the possibility of an imido/amido equilibrium. While we were able to prepare potential imido precursors (eg $[Rh_2(\mu-Cl)(CO)_2(\mu-dppma)_2]^+$) we were not able to obtain the imido (or oxo) complexes. NMR data indicated rearrangements to monomeric amido products. Facile bridging to chelating conversions are known for *dppm* complexes.

Replacement of the CO with NO^+ and PMe_3 was also explored (see appended preprint). For NO^+ , the imido and oxo precursor was successfully prepared but only inseparable mixtures could be obtained in reactions expected to give the imido or oxo complexes.

Concurrent with our work on the Cp^*Rh hydroxo systems was an investigation of the reactions of $[Cp^*RhCl_2]_2$ with $LiNHR$ ($R = t-Bu$, $p-MePh$, $p-FPh$ and o,o' -xylyl). Our goal was to produce an imido analogue of $[Cp^*Ir(\mu-O)]_2$. We did isolate the amido analogue of the hydroxo complex, $[(Cp^*Rh)_2(\mu-NHR)_3]^+$ ($R = p-MePh$ and $p-FPh$), but all attempts to deprotonate/deaminate this complex gave deeply colored solutions containing complex mixtures. Similar mixtures were obtained when the $Rh(II)$ complex, $[Cp^*RhCl]_2$ was treated with $LiNHR$ suggesting reduction of $Rh(III)$ in the former reactions. Dehydrohalogenation attempts on $Cp^*RhCl_2(NH_2R)$, $[Cp^*RhCl(NH_2R)_2]^+$ and $[Cp^*Rh(NH_2R)_3]^{2+}$ were similarly unsuccessful.

The apparent reduction in the above reactions indicated a need to stabilize $Rh(III)$. Tris(pyrazoyl)borate ligands, known to give complexes similar to the Cp ligands, were chosen

for this purpose. Our results are very promising and will feature prominently in future work. $\text{Tp}^*\text{RhCl}_2\text{py}$ ($\text{Tp}^* = \text{tris}(3,5\text{-dimethylpyrazoyl})$ borate) appeared to be a good starting point and treatment with $\text{LiNH}(\text{p-MePh})$ gave the bis-amido complex (eq 5, $\text{R} = \text{p-MePh}$).

Thermolysis of $\text{Tp}^*\text{Rh}(\text{NHR})_2\text{py}$, expected to lead to loss of py and elimination of amine to form the imido complex, gave a mixture of products which retained the pyridine. To increase lability we prepared the lutidine complex, $\text{Tp}^*\text{RhCl}_2(\text{lutidine})$, and treated it with LiNHR . Preliminary data indicates that the product is $[\text{Tp}^*\text{Rh}(\text{NHR})_3]^- \text{Li}^+$, a testament to the reduction stability of the $\text{Tp}^*\text{Rh}(\text{III})$ fragment but still not the desired product. Future work in this area is described in the renewal proposal.

The synthesis of imido complexes from oxo complexes was explored in two systems. We were successful with $(\text{LAu})\text{O}^+$ and prepared a large range of imido analogues by treatment with amines or isocyanates. These results were recently published¹¹ and were followed by a letter from Professor H. Schmidbaur informing us he had also prepared the imido complexes by the amine route.

Our work in the L_2Pt system has not been as successful. The amine reactions give bis-amido complexes and the RNCO reactions are complex and we have not isolated any products. Reactions of L_2PtCl_2 with LiNHR gives chloro-amido and bis-amido complexes.

Dioxygen and RNO Complexes. As part of our modeling of the metal surface chemistry we are interested in the possibility of using dioxygen and RNO as oxo and imido sources. The existence of $[\text{Cp}^*\text{Ir}(\mu\text{-O})]_2$ and $[\text{L}_2\text{Pt}(\mu\text{-O})]_2$ ($\text{L} = \text{PPh}_3$) suggested to us that these complexes could be prepared by reductive splitting of dioxygen with Cp^*M and L_2Pt fragments. We began investigating the reactions of dioxygen and PhNO with $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})]_2$ and the reaction of $\text{L}_2\text{Pt}(\text{O}_2)$ with L_2Pt sources. Results from the Rh system have been partly published.¹² Unpublished results are given below.

Our first reaction of $\text{L}_2\text{Pt}(\text{O}_2)$ used L_3Pt as an L_2Pt source. The result was very interesting. The products are LO , L_xPt and Pt^0 . The products are not surprising given that L_3Pt dissociates in solution and $\text{L}_2\text{Pt}(\text{O}_2)$ is known to oxidize phosphine. What is remarkable is the rate. The reaction is much faster than the simple reaction of $\text{L}_2\text{Pt}(\text{O}_2)$ with free phosphine. This indicates a direct reaction of $\text{L}_2\text{Pt}(\text{O}_2)$ with L_2Pt or L_3Pt . We believe that insertion of L_2Pt into a

Pt-O bond of $\text{L}_2\text{Pt}(\text{O}_2)$ gives $\text{L}_2\text{Pt} \begin{array}{c} \text{O-O} \\ \diagup \quad \diagdown \\ \text{Pt} \end{array} \text{PtL}_2$ which then rapidly oxidizes the free phosphine. The insertion is discussed again in the renewal proposal.

Reactivity

In common with surface oxygen atoms,¹³ all of the oxo (except one) and imido complexes react with CO. The oxo complexes give CO_2 and the imido complexes give isocyanates and/or ureas. Work on the A-frame imido/amido complexes indicates that the urea is formed from the reaction of free isocyanate with complexed isocyanate and that the hydrogen source is at least partly from solvent abstraction. For both the Au and the A-frame systems the rate of the imido reactions depend on the electron donating properties of the imido substituent: Stronger donor groups (more basic imido groups) lead to faster rates.¹⁴ This most likely reflects nucleophilic attack on the carbonyl.

The Au product from the CO reactions of $(\text{LAu})_3\text{Y}^+$ is the cluster $[\text{Au}_6\text{L}_6]^{2+}$ (eq 6, $\text{L} = \text{PPh}_3$,

$\text{Y} = \text{O}$ or NR). These reactions represent the best synthesis of this cluster. The probable facile

synthesis of poly-imido complexes suggests the possibility of preparing, in a controlled fashion, larger clusters.

Other clusters are obtained in reactions of $(\text{LAu})_3\text{Y}^+$ with PPh_3 and with halides. A detailed investigation has shown that these reactions are initiated by the displacement of LAu^+ from $(\text{LAu})_3\text{Y}^+$ with the generation of highly basic $(\text{LAu})_2\text{Y}$ complexes. The following chemistry of $(\text{LAu})_2\text{Y}$ is complex and we still do not understand how the clusters are formed. Solvent (CH_2Cl_2) is involved and appears to be deprotonated at an early stage of the reaction. Cluster formation is not unique to the oxo and imido complexes: LAuOBU^t forms the same clusters on standing in CH_2Cl_2 . Results are still being analyzed.

Again, in common with surface oxygen atoms, the oxo and imido complexes are highly basic reacting readily with electrophiles. The aryl imido A-frame complexes display unique reactivity with carbon electrophiles where electrophilic addition to the aryl ring is observed (see appended reprint).¹⁵ Recent experiments show ring addition to be a kinetic product resulting from steric shielding of the imido nitrogen.

Summary

Good synthetic methods have greatly increased the number and variety of oxo and imido complexes and promise to produce more. Deprotonations of hydroxo complexes has proved to be an excellent synthetic method for the oxo complexes. Imido complexes are proving more difficult to synthesize but can be prepared in some cases from the oxo complexes by reactions with amines or isocyanates. Considerable progress has also been made in the elucidation of the chemistry of late-transition-metal oxo and imido complexes. Oxygen atom and nitrene transfers to CO, tautomeric equilibria involving imido and amido complexes, aryl-imido ring activation, and many reactions demonstrating the high basicity of late-transition-metal oxo and imido complexes have been observed. Much of this is novel chemistry and in line with what is known about oxygen adatoms on late-transition-metal surfaces.

References

- (1) New IUPAC/ACS periodic group notations.
- (2) Grant, R. B.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1983**, 662-663.
- (3) Asscher, M.; Guthrie, W. L.; Lin, T.-H.; Somorjai, G. A. *J. Phys. Chem.* **1984**, *88*, 3233-3238.
- (4) Lorimer, P.; Bell, A. T. *J. Catal.* **1979**, *59*, 223. Hecker, W. L.; Bell, A. T. *J. Catal.* **1983**, *84*, 200.
- (5) Hoare, J. P. *The Electrochemistry of Oxygen*; Wiley-Interscience: New York, 1968; pp 143-151.
- (6) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533 and *J. Chem. Ed.* **1968**, *54*, 643.
- (7) Sharp, P. R.; Flynn, J. R. *Inorg. Chem.* **1987**, *26*, 3231-3234.
- (8) McGhee, W. D.; Foo, T.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8543-8545.
- (9) Li, W.; Barnes, C. L.; Sharp, P. R. *J. Chem. Soc., Chem. Commun.* In press.
- (10) Ge, Y.-W.; Peng, F.; Sharp, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 2632-2640. Sharp, P. R.; Ge,

Y.-W. *J. Am. Chem. Soc.* **1987**, 109, 3796-3797.

(11) Ramamoorthy, V.; Sharp, P. *Inorg. Chem.* **1990**, 29, 3336-3338.

(12) Sharp, P.R.; Hoard, D.; Barnes, C. L. *J. Am. Chem. Soc.* **1990**, 112, 2024-2026.

(13) Madix, R. J.; Jorgensen, S. W. *Surf. Sci.* **1987**, 183, 27-43. (b) Akhter, S.; White, J. M. *Surf. Sci.* **1986**, 167, 101-126. (c) Berlowitz, P.; Yang, B. L.; Butt, J. B.; Kung, H. H. *Surf. Sci.* **1986**, 171, 69-82. (d) Outka, D. A.; Madix, R. J. *J. Am. Chem. Soc.* **1987**, 109, 1708-1714 and references cited therein.

(14) Ge, Y.-W.; Sharp, P. R. *Organometallics* **1988**, 7, 2234-2236.

(15) Ge, Y.-W.; Sharp, P.R. *J. Am. Chem. Soc.* **1990**, 112, 3667-3668.

Publications During Grant Period (Copies attached)

Ge, Y.-W.; Sharp, P.R. *Inorg. Chem.*, submitted.

Li, W.; Barnes, C. L.; Sharp, P.R. *J. Chem. Soc., Chem. Commun.* in press.

Roth, S.; Ramamoorthy, V.; Sharp, P. R. *Inorg. Chem.* **1990**, 29, 3345-3348.

Ramamoorthy, V.; Sharp, P. *Inorg. Chem.* **1990**, 29, 3336-3338.

Ge, Y.-W.; Sharp, P.R. *J. Am. Chem. Soc.* **1990**, 112, 3667-3668.

Ge, Y.-W.; Peng, F.; Sharp, P.R. *J. Am. Chem. Soc.* **1990**, 112, 2632-2640.

Sharp, P.R.; Hoard, D.; Barnes, C. L. *J. Am. Chem. Soc.* **1990**, 112, 2024-2026.

Ge, Y.-W.; Sharp, P. R. *Organometallics* **1988**, 7, 2234-2236.

Estimate of Unobligated Balance

No balance is expected at the end of this Budget Period (May, 14, 1991).

*Preprint and reprints
removed and cycled
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