

Synthesis and Reactivity of Ruthenium(VI) and Osmium(VI) Nitrido and Imido Complexes

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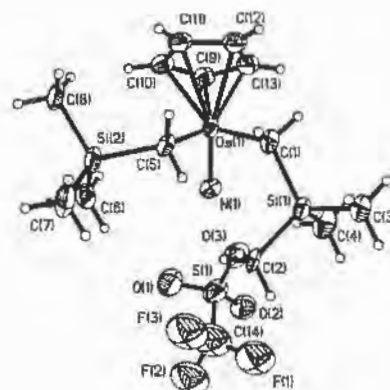
Final Seminar

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Transition metal complexes with metal nitrogen bonds are an important class of compounds.¹ Nitrido and imido ligands help stabilize high oxidation state metal complexes while only occupying one coordination site, making them attractive as ancillary ligands for catalytic systems.² They can also be the site of reaction. Nitrido ligands can be nucleophilic or electrophilic.^{3,4} Similarly, imido ligands can be either nucleophilic or electrophilic.^{5,6} Both types of ligands are important for their potential role in nitrogen fixation and their nitrogen group transfer reactivity.^{7,8}

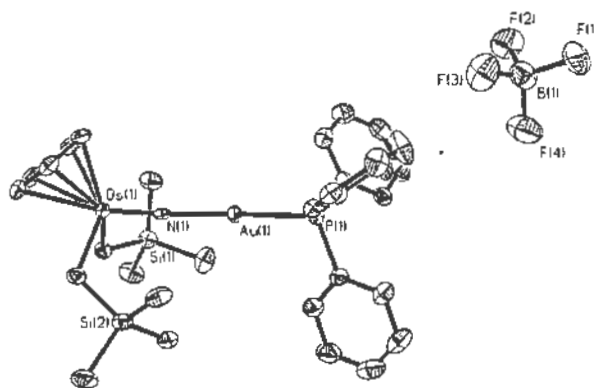
The reaction of $\text{Me}_3\text{SiOSO}_2\text{CF}_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2$ generates an unstable trimethylsilylimido complex by ^1H NMR and mass spectroscopy. In one reaction the parent imido complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{NH})(\text{CH}_2\text{SiMe}_3)_2][\text{OSO}_2\text{CF}_3]$ formed and the molecular structure was elucidated. (Figure 1) The imido proton could not be located in the electron difference map due to twinning of the crystals. The long Os-N bond distance (1.75 Å, Os-N double bond) and cationic nature show the formulation is correct. This complex also decomposes which lead me to synthesize the isolobal $^+\text{AuPPh}_3$ adduct, $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{NAuPPh}_3)(\text{CH}_2\text{SiMe}_3)_2][\text{BF}_4]$, as a model complex. X-ray crystallographic analysis also proved this structure. (Figure 2) This complex has an Os-N bond distance of 1.68 Å, an Os-N-Au bond angle of 176.6° , and a short N-Au bond (2.01 Å) suggesting an Os-N triple bond and a strong N-Au bond. Despite these data, reaction of this molecule with nucleophiles displaces the gold(I) moiety regenerating the osmium nitrido complex. (Scheme 1) Synthesis of $\text{Tp}^*\text{Ru}(\text{N})\text{Me}_2$ was achieved. (Tp^* = hydrotris(3,5-dimethylpyrazolyl)borate) Study of this compound's reactivity suggest it has a nucleophilic nitrido ligand.

Figure 1. Molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{NH})(\text{CH}_2\text{SiMe}_3)_2][\text{OSO}_2\text{CF}_3]$.



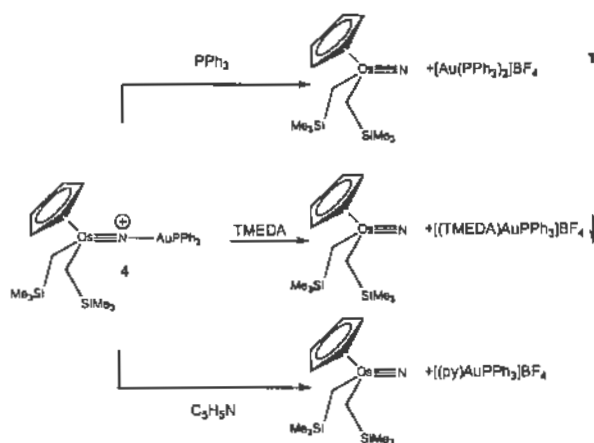
One possible reason for the instability of $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{NH})(\text{CH}_2\text{SiMe}_3)_2][\text{OSO}_2\text{CF}_3]$ is steric pressure at the metal. With this in mind, investigation of tetraalkylimido complexes began. Synthesis of $\text{M}(\text{NSiMe}_3)\text{Me}_4$ proceeds by the addition of one equivalent of $\text{Me}_3\text{SiOSO}_2\text{CF}_3$ to $[\text{N}(n\text{-Bu})_4][\text{M}(\text{N})\text{Me}_4]$. ($\text{M} = \text{Ru}$,

Figure 2. Molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{NAuPPh}_3)(\text{CH}_2\text{SiMe}_3)_2][\text{BF}_4]$.



Os) Although these complexes are also thermally unstable, their reactivity with small molecules was investigated. Both complexes react with water and carbon monoxide, but do not react with alkenes. Phosphines do not react with the complexes themselves, but trap some of the decomposition products yielding new complexes. Comparison of these results with the well-known alkyl imido complexes suggests there are significant differences in the steric and electronic properties of trimethylsilylimido complexes of ruthenium and osmium.⁹

Scheme 1



References

1. Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*, Wiley, New York, 1988.
2. Marshman, R. W. "Oxo, Imido, and Nitrido Compounds of Osmium(VI)," PhD Thesis, University of Illinois, Urbana-Champaign, 1990.
3. Marshman, R. W.; Shusta, J. M.; Wilson, S. R.; Shapley, P. A. "Synthesis and Reactivity of $(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2$, The First Cyclopentadienyl-Nitrido Transition-Metal Complex" *Organometallics*, 1991, 10, 1671-1676.

4. Crevier, T. J.; Mayer, J. M. "Direct Attack of Phenyl Anion at an Electrophilic Osmium-Nitrido Ligand," *J. Am. Chem. Soc.* **1998**, *120*, 5595-5596.
5. Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. "Monomeric (Pentamethylcyclopentadienyl)iridium Imido Compounds: Synthesis, Structure, and Reactivity," *J. Am. Chem. Soc.* **1991**, *113*, 2041-2054.
6. Leung, W.-H.; Hun, T. S. M.; Hou, H.-w.; Wong, K.-Y. "Arylimido Complexes of Ruthenium(IV) Porphyrins," *J. Chem. Soc., Dalt. Trans.*, **1997**, 237-243.
7. Yandulov, D. V.; Schrock, R. R. "Reduction of Dinitrogen to Ammonia at a Well-Protected Reaction Site in a Molybdenum Triamidoamine Complex," *J. Am. Chem. Soc.*, **2002**, *124*, 6252-6253.
8. Smieja, J. A.; Borneman, M.; Kittilstved, K.; Edwards, D.; Borda, E. "Reactivity of Os(TTP)(NC₆H₄NO₂)₂ (TTP = dianion of 5,10,15,20-tetra(p-tolyl)porphyrin) Including a Kinetic Study of Imido Ligand Transfer to Phosphines," *Polyhedron*, **2002**, *21*, 1889-1892.
9. Shapley, P. A.; Own Z.-Y.; Huffman, J. C. "Alkylation of Osmium(VI) Nitrido Complexes: Reaction of [Os(N)R₄][N-n-Bu₄] with [Me₃O][BF₄] and the X-ray Crystal Structures of [Os(N)(CH₂SiMe₃)₄][N-n-Bu₄] and [Os(NMe)(CH₂SiMe₃)₄]," *Organometallics*, **1986**, *5*, 1269-1271.