

Oxo, Imido, and Nitrido Compounds of Osmium(VI):  
Comparative Reactivity and Ligand Effects

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Final Seminar

September 10, 1990

There has been a great deal of activity in recent years in the organometallic chemistry of transition metals in high oxidation states. The interest in these compounds stems from their similarity to intermediates in catalytic reactions, including olefin polymerizations [1], olefin metathesis [2], oxidation reaction [3], and ammoxidation of unsaturated organic molecules. [4]. High oxidation state organometallic complexes can also model the reactive sites of certain metalloenzymes [5]. Oxo, imido, and nitrido complexes of transition metals are of particular interest due to their role in oxidation, ammoxidation, and nitrogen fixation reactions [6].

The reactions of some nitrido, imido, and oxo complexes have been studied. Reactions were observed with carbon monoxide [7], olefins and acetylenes [8], acids and other electrophiles [9]. Imido ligands have been reported to be more reactive or less reactive than oxo ligands in different oxo-imido metal complexes [10], however, oxo, imido and nitrido ligands have not previously been directly compared, either in the same complex, or in isostructural complexes.

Three five-coordinate alkyl complexes,  $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_4]$ ,  $Os(NMe)(CH_2SiMe_3)_4$  [11], and  $Os(O)CH_2SeMe_3$  [12] were prepared and characterized by IR, NMR, and UV-visible spectroscopy, electrochemical techniques and by single crystal X-ray diffraction. For  $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_4]$  and  $Os(NMe)(CH_2SiMe_3)_4$ , isotopic labeling studies were used to identify bands associated with the heteroatoms. The infrared band assigned to the imido ligand of  $Os(NCH_3)R_4$ , ( $R = Me, CH_2SeMe_3$ ) was due not to an independent nitrogen-carbon stretching vibration but instead a combination band of coupled osmium-nitrogen and nitrogen-carbon vibrations. Proton and carbon NMR studies showed a significant downfield shift for the  $\alpha$ -carbon protons for the oxo and imido compounds as compared with the nitrido compound. A fluxional process was observed in the low temperature proton NMR of  $Os(NMe)(CH_2SiMe_3)_4$  and  $Os(O)(CH_2SeMe_3)_4$ . All have a square pyramidal structure in the solid state, with the imido and oxo complexes showing a slight distortion towards trigonal bipyramidal. The bond distances in the oxo and imido complexes are consistent with the heteroatom acting as a four electron donor.

The nitrido complex,  $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_4]$ , did not react with carbon monoxide while both  $Os(NMe)(CH_2SiMe_3)_4$  and  $Os(O)(CH_2SiMe_3)_4$  were reductively carbonylated under CO pressure to produce  $Os(CO)_5$ ,  $(Me_3SiCH_2)_2CO$ , and either  $MeNCO$  or  $CO_2$ . The methylimido complex is much more reactive than the oxo complex and the acyl species: the addition of one and two equivalents of carbon monoxide produced  $Os(NMe)(C(O)CH_2SeMe_3)(CH_2SiMe_3)_3$  and  $Os(NMe)(C(O)CH_2SiMe_3)_2(CH_2SiMe_3)_2$ , respectively.

An insertion product,  $Os(NMe)(C(NHMe_3)CH_2SiMe_3)(CH_2SiMe_3)_3$ , was formed in the reaction between  $Os(NMe)(CH_2SiMe_3)_4$  and *tert*-butylisocyanide. The order of reactivity towards electrophilic attack is  $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_4] > Os(NMe)(CH_2SiMe_3)_4 \gg Os(O)(CH_2SiMe_3)_4$ . The nitrido complex formed 1:1 adducts with Lewis acids, was alkylated at nitrogen upon reaction with organic electrophiles, and reacted with mineral acids by cleavage one or two of the metal-carbon bonds [13]. Electrophilic cleavage of one metal-carbon bond occurred more slowly with the methylimido complex upon reaction with  $HBF_4$  or  $HCl$ . The oxo complex is stable towards electrophiles. The rather dramatic difference in reaction chemistry between  $Os(NMe)R_4$  and  $Os(O)R_4$  may be due to the possibility of isomerization of the ligand in the imido complex. This would greatly change the reactivity of the complex towards electrophiles and nucleophiles.

Modifications in the ligand environment surrounding the metal influences the chemical behavior of the heteroatoms. The cyclopentadienyl osmium compounds, CpOs(N)-(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> and (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Os(N)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>, were made by the reaction of NaCp or LiC<sub>5</sub>Me<sub>5</sub> with [N-*n*-Bu<sub>4</sub>][Os(N)Cl<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>]. These compounds behave as Lewis bases. The addition of AgBF<sub>4</sub> to CpOs(N)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> formed a dimeric compound, {[CpOs(μ-N)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Ag}(BF<sub>4</sub>). A reversible reaction was observed with BF<sub>3</sub>·OEt<sub>2</sub>. The equilibrium was detected by a downfield shift of the methylene proton resonances as more BF<sub>3</sub> was added. At low temperature the reaction could be slowed down enough so that both species could be observed on the NMR time scale. This behavior is in contrast to that seen in Os(N)-(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub><sup>-</sup>, where BF<sub>3</sub> coordinates strongly enough so that a discrete complex can be isolated [13]. A slow reaction is observed with methyl triflate resulting in the formation of the cationic methylimide complex, [CpOs(NMe)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>](OTf). Again this is in direct contrast to the rapid reaction observed between Os(N)R<sub>4</sub><sup>-</sup> and alkyl triflates.

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