

ORGANOOSMIUM (VI) HYDROXO COMPLEXES AND THE SYNTHESIS OF HETEROBIMETALLIC CATALYSTS FOR AEROBIC ALCOHOL OXIDATION

Adam M. Kiefer

Final Seminar

June 27, 2008

Organometallic hydroxo complexes are a small, but growing class of compounds.¹ With the increasing use of water as a benign, non-polluting solvent, a fundamental understanding of the synthesis and reactivity of hydroxo complexes will be of great importance.² Organometallic complexes containing terminal hydroxo ligands react with electrophiles and acid to produce a variety of interesting complexes. The synthesis, reactivity and structure of osmium (VI) hydroxo complexes will be discussed, as well as applications and possible applications of these relatively rare complexes.

Organometallic osmium(VI) hydroxo compounds *cis* and *trans* $[\text{N}(n\text{-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{OH})_2]$ result from the substitution of chloride for hydroxide ligands in precursor compounds. Depending on the molecular structure, these compounds behave as nucleophiles, Bronsted bases, or Lewis bases in their reactions. The *cis* analog $[\text{N}(n\text{-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{OH})_2]$ reacts readily with CO_2 to produce a carbonate compound $[\text{N}(n\text{-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{CO}_3)]$. The *trans* isomer $[\text{N}(n\text{-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{OH})_2]$ (Figure 1) reacts with CO_2 to slowly form the same carbonate compound. It is protonated by other acids to give a neutral hydroxo dimer $\{\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-OH})\}_2$. The *trans* isomer also reacts with K_2CrO_4 and acid to generate the heterobimetallic oxidation catalyst $[\text{NBu}_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-O})_2\text{CrO}_2]$. The *anti* isomer of $\{\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-OH})\}_2$ reacts with $\text{Pd}(\text{bpy})(\text{OSiMe}_3)_2$ to produce a coordinatively unsaturated, heterometallic complex $\{\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2\}_2(\mu_3\text{-O})_2\text{Pd}(\text{bpy})$.³

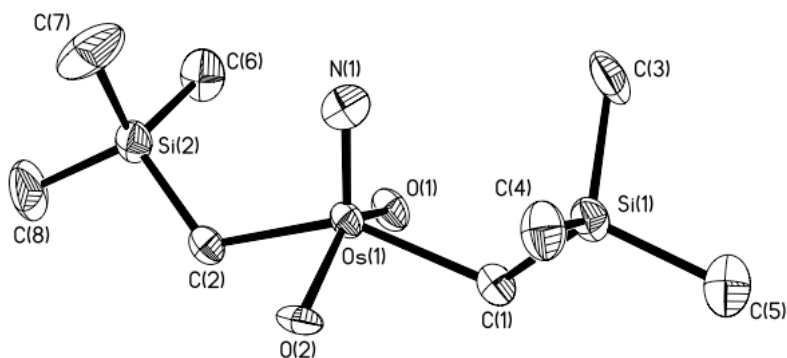
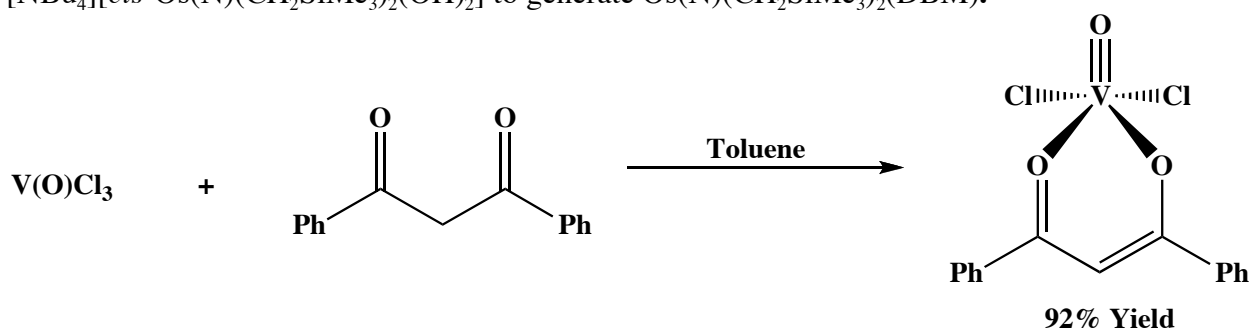


Figure 1: An ORTEP diagram of the anion $[\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2]$

The heterocyclic compound 2,5-diformylfuran (DFF) is a ligand and a starting material in the synthesis of nematocides and natural products, but is relatively expensive (\$30-\$65 / 100 mg).⁴⁵ The heterobimetallic complex $[\text{NBu}_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-O})_2\text{CrO}_2]$ ^{3,6} catalyzes the aerobic oxidation of 5-hydroxymethyl-furfural (HMF) to 2,5-diformylfuran (DFF). The oxidation is temperature dependent. At 65 °C and 20 psi O₂, 5 mol % $[\text{NBu}_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-O})_2\text{CrO}_2]$ catalyzes the oxidation of HMF to DFF in as high as 76 % yield. Currently we are exploring new methods of immobilizing $[\text{NBu}_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-O})_2\text{CrO}_2]$ on silica supports.

Although oxovanadium(V) chloride is inexpensive and easily purified, it is a very strong oxidant, reacts with trace amounts of water, and is difficult to use as a starting material for the synthesis of oxovanadium (V) complexes.⁷ The ligands dibenzoyl methane and N-phenyl salicylaldehyde react with VOCl_3 in toluene to generate the complex $\text{V}(\text{O})\text{Cl}_2(\text{DBM})$ ($\text{DBM}=\text{C}_6\text{H}_5\text{C}(\text{O})\text{CHC}(\text{O})\text{C}_6\text{H}_5$) and a complex of the general formula $\text{C}_{13}\text{H}_{11}\text{Cl}_3\text{NO}_2\text{V}$. The square pyramidal complex $\text{V}(\text{O})\text{Cl}_2(\text{DBM})$ (Scheme 1) is a black solid that is stable in solution, but reacts with trace water. The complex $\text{C}_{13}\text{H}_{11}\text{Cl}_3\text{NO}_2\text{V}$ is unstable in the solution phase. In a solution of ether/hexane, $\text{V}(\text{O})\text{Cl}_2(\text{DBM})$ reacts with NaOSiMe_3 to yield the uncharacterized intermediate $\text{V}(\text{O})(\text{DBM})(\text{OSiMe}_3)_2$, which reacts with the organometallic dihydroxo complex $[\text{NBu}_4][\text{cis-Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{OH})_2]$ to generate $\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{DBM})$.



Scheme 1: Synthesis of $\text{V}(\text{O})\text{Cl}_2\text{DBM}$ from VOCl_3

References

1. Roesky, Herbert W.; Singh, Sanjay; Yusuff, K.K.M.; Maguire, John A.; Hosmane, Narayan S.; *Chem Rev.*, **2006**, *106*, 3813-3843.
2. (a) Balahura, R. J.; Sorokin, A.; Bernadou, J.; Meunier, B. *Inorg. Chem.*, **1997**, *36*, 3488-3492. (b) Kervinen, K.; Korpi, H.; Mesu, J. G.; Soulimani, F.; Repo, T.; Rieger, B.; Leskela, M.; Weckhuysen, B. M. *Eur. J. Inorg. Chem.*, **2005**, 2591-2599.
3. Kiefer, A. M.; Giles, J. A.; Shapley, P. A., Synthesis, structure, and reactivity of organometallic osmium(VI) hydroxo compounds. *Organometallics* **2007**, *26*, (8), 1881-1887.
4. Lewkowski, J., Synthesis, chemistry and applications of 5-hydroxymethyl-furfural and its derivatives. *Arkivoc* **2001**, *2*, (part i), 17-54.

-
5. Halliday, G. A.; Young, R. J.; Grushin, V. V., One-pot, two-step, practical catalytic synthesis of 2,5-diformylfuran from fructose. *Organic Letters* **2003**, 5, (11), 2003-2005.
 6. Shapley, P. A.; Zhang, N.; Allen, J. L.; Pool, D. H.; Liang, H. C. *J. Am. Chem. Soc.*, **2000**, 122, 1079-1091.
 7. a) Beard, C. D.; Barrie, R. J.; Evans, J.; Levason, W.; Reid, G.; Spicer, M. D., Synthesis and properties of complexes of vanadium(V) oxide trichloride with nitrogen- and oxygen-donor ligands. *European Journal of Inorganic Chemistry* **2006**, (21), 4391-4398.
b) Makhaev, V. D.; Borisov, A. P.; Matkovskii, P. E., Synthesis of cyclopentadienylvanadium oxydichloride from vanadium oxotrichloride. *Russian Journal of General Chemistry* **2004**, 74, (3), 465-466.