

Trispyrazolylborate and Tetramethylcyclopentadienyl Complexes of Osmium

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Final Seminar

December 13, 2005

Transition metal alkane complexes have been observed in low temperature matrices,^{1,2} in the solid state,^{3,4} in the gas phase,^{2,5} and in solution.^{6,7} They are also implicated as unobserved intermediates in the oxidative addition reactions of alkanes by transition metals.^{2,5} Previous NMR studies in our group showed that the hydrogen atoms in the methyl and hydride ligands of $[(C_5Me_5)Os(dmpm)Me(H)^+]$ exchange rapidly; the free energy of activation for the process is 8.1 kcal/mol.⁸ Martin⁹ and Morokuma and co-workers¹⁰ have carried out density functional calculations on this system, and their studies indicate the intermediacy of a methane complex. The objective of our current research is to prepare and investigate new methyl/hydride complexes in order to understand, and ultimately to prepare, stable alkane complexes.

Treatment of H_2OsBr_6 with excess 1,5-cyclooctadiene (cod) in refluxing *tert*-butanol affords the new polymer $[OsBr_2(cod)]_x$ in high yield (90 %), as a yellow-brown precipitate. This polymer, which is the bromo analogue of the previously described chloro compound $[OsCl_2(cod)]_x$,^{11,12} provides an entry into a variety of trispyrazolylborate (Tp) and tetramethylcyclopentadienyl (C_5Me_4H) complexes of osmium. The goal of this research has been to prepare osmium alkyls with these ligands for protonation studies.

Treatment of $[OsBr_2(cod)]_x$ with KTp in refluxing ethanol affords the compounds $TpOs(cod)H$ and $TpOs(cod)Br$. Reaction of $TpOs(cod)Br$ with NaOMe yields the structurally characterized complex $TpOs(cod)OMe$. Treatment of $TpOs(cod)H$ with MeOTf gives $TpOs(cod)OTf$, and this latter compound can be treated with $MgMe_2$ to yield $TpOs(cod)Me$. $TpOs(cod)Me$ is remarkably inert towards many acids, including the carbon acid $H_2C(SO_2CF_3)_2$ and HBF_4 .

Treatment of $[OsBr_2(cod)]_x$ with either the new compound $Mg(C_5Me_4H)_2$ or the new compound $K(C_5Me_4H) \cdot dme$ affords $(C_5Me_4H)Os(cod)H$ and $(C_5Me_4H)Os(cod)Br$. The cod ligand of $(C_5Me_4H)Os(cod)Br$ can be replaced with dmpm to give $(C_5Me_4H)Os(dmpm)Br$. The reaction of $(C_5Me_4H)Os(dmpm)Br$ with NaOMe affords the monohydride $(C_5Me_4H)Os(dmpm)H$ which can be protonated to give the classical dihydride complex $(C_5Me_4H)Os(dmpm)H_2^+$. Treatment of $(C_5Me_4H)Os(dmpm)Br$ with $MgMe_2$ affords $(C_5Me_4H)Os(dmpm)Me$.

Protonation of $(C_5Me_4H)Os(dmpm)Me$ at $-135^\circ C$ with $H_2C(SO_2CF_3)_2$ in $CDFCl_2$ generates the *cis* methyl hydride compound $[(C_5Me_4H)Os(dmpm)Me(H)^+]$ (Figure 1). This is the tetramethylcyclopentadienyl analogue of the previously reported pentamethylcyclopentadienyl complex $[(C_5Me_5)Os(dmpm)Me(H)^+]$.

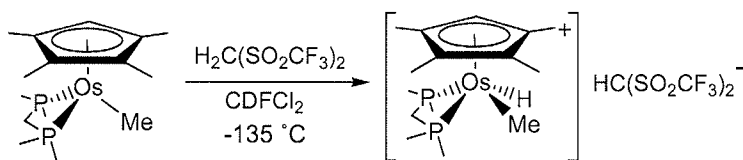


Figure 1: Structure of $[(C_5Me_4H)Os(dmpm)Me(H)^+][HC(SO_2CF_3)_2^-]$.

As was previously observed in the C_5Me_5 compound, the hydrogen atoms between the methyl and hydride ligands in $[(C_5Me_4H)Os(dmpm)Me(H)^+]$ undergo rapid exchange. This exchange is detectable by changes in the line widths of the 1H NMR resonances and from spin saturation transfer experiments. The free energy of activation for the exchange, ~ 8.6 kcal/mol, is 0.5 kcal/mol larger than observed for the C_5Me_5 compound. The activation enthalpy and entropy for the hydrogen exchange in $[(C_5Me_4H)Os(dmpm)Me(H)^+]$ are $\Delta H^\ddagger = 7.5 \pm 0.7$ kcal/mol and $\Delta S^\ddagger = -6 \pm 4$ eu, respectively. As in the C_5Me_5 compound, we propose that the exchange is occurring through a coordinated methane intermediate. $[(C_5Me_4H)Os(dmpm)Me(H)^+]$ liberates methane at temperatures at or above -85 °C.

We have prepared two unusual osmium containing salts in the course of this research. Treatment of H_2OsBr_6 with 4 equiv. of $C_5Me_4H_2$ in *tert*-butanol affords $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$. The brown color of the salt suggests that the anion adopts an eclipsed conformation (D_{4h} symmetry) and this conclusion has been confirmed by a single-crystal X-ray diffraction experiment. Treatment of $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$ with cod in refluxing ethanol gives $(C_5Me_4H)_2Os$ and the unusual salt $[(C_5Me_4H)_2OsBr][Os_2HBr_4(cod)_2]$. A single crystal X-ray crystallographic study of the latter compound indicates that the anion adopts a confacial bioctahedral structure in which the hydride and two bromide ligands bridge between the two osmium centers (see Figure 2). This anion is the first example of an anionic diosmium complex containing a bridging hydride.

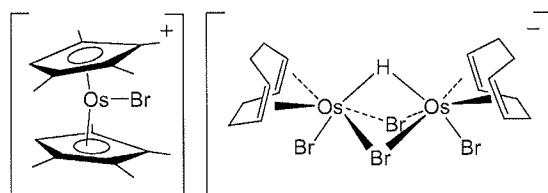


Figure 2: Structure of $[(C_5Me_4H)_2OsBr^+][Os_2HBr_4(cod)_2^-]$.

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