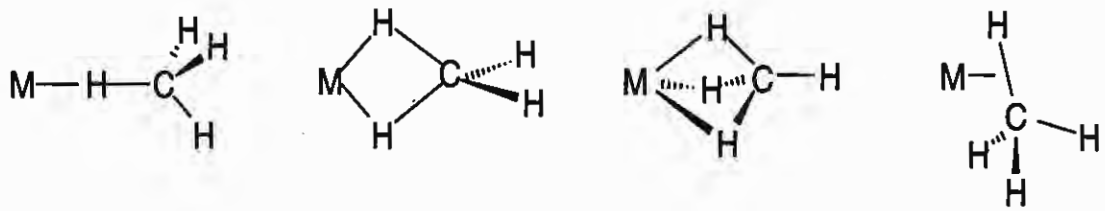
Pentamethylcyclopentadienyl Osmium Chemistry: An Approach To Transition Metal Alkane Complexes

Christopher L. Gross Final Seminar August 1, 1997

The activation of the C-H bonds of organic molecules is a goal of obvious economic and synthetic importance.[1] The majority of the known natural gas reserves (mostly methane) are located in remote locations and, thus, transportation is required for use. It is cost-prohibitive, however, to transport natural gas because the liquefaction of methane requires both pressure and refrigeration. Consequently, an inexpensive process to convert methane to a more readily transported material such as methanol would be highly desirable.

The C-H bonds of alkanes, however, are notoriously unreactive.[2,3] As a result, substantial effort has been devoted to develop effective ways to activate these bonds. While no generally effective catalyst has yet been devised, several transition metal complexes react stoichiometrically with alkanes by oxidative addition of the C-H bond. Studies of these systems have indicated that an intermediate in the oxidative addition (and reductive elimination) process is a metal alkane σ-complex.[4] Several possible alkane bonding modes are shown below:



Such σ-complexes are proposed to be analogous to transition metal dihydrogen compounds, but none has ever been prepared and studied in solution. We, therefore, were interested in whether the synthesis of such a compound might be possible. Our approach has been to protonate metal alkyl complexes with certain properties: strong metal-ligand bonds, highly basic metal center, and a small bite-angle chelating phosphine ligand. We identified the osmium complex $(C_5Me_5)Os(dmpm)Me$ as a suitable candidate.

Treatment of pentamethylcyclopentadiene with H_2OsBr_6 in *tert*-butanol affords the $(C_5Me_5)Os$ dimer $(C_5Me_5)_2Os_2Br_4$ (Figure 1).[5]

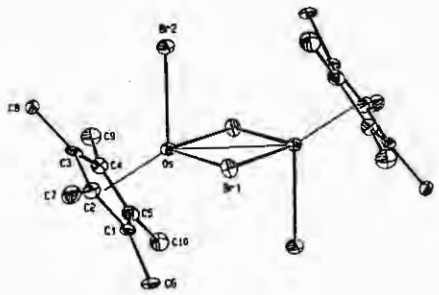


Figure 1. ORTEP diagram of $(C_5Me_5)_2Os_2Br_4$.

This compound provides a synthetic entry into a wide variety of $(C_5Me_5)Os$ complexes. As we have studied these compounds, it has become apparent that they exhibit many properties which are not found in the analogous ruthenium complexes. Foremost among these properties is the greater stability imparted to the osmium compounds as a result of the greater metal-ligand bond strengths. In a number of cases, we have been able to isolate osmium compounds for which the ruthenium analogues are either unstable or unknown.

The reaction producing $(C_5Me_5)_2Os_2Br_4$ also affords the Os^{IV} methallyl complex $(C_5Me_5)OsBr_2(\eta^3\text{-}H_2CC(Me)CH_2)$ as a side product; the 2-methallyl ligand presumably results from dehydration and C-H bond cleavage of the solvent *tert*-butanol. This complex has been synthesized independently.

Under the appropriate conditions, the reaction of pentamethylcyclopentadiene with H_2OsBr_6 also affords the unusual salt $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$.[6] The $Os_2Br_8^{2-}$ anion in this compound adopts a geometry in which the bromide ligands are eclipsed.

The dimer $(C_5Me_5)_2Os_2Br_4$ is readily cleaved by addition of Lewis bases to afford the corresponding paramagnetic 17-electron $(C_5Me_5)Os(L)Br_2$ complexes. Treatment of these compounds with sodium borohydride produces the trihydride complexes $(C_5Me_5)Os(L)H_3$ where L = PPh_3, $AsPh_3$, and $P(c\text{-}Hx)_3$. Protonation of the trihydrides with $HBF_4 \bullet Et_2O$ affords the Os^{IV} dihydride/dihydrogen complexes of stoichiometry $[(C_5Me_5)Os(L)H_2(H_2)][BF_4]$.[7] Neutron diffraction studies of the PPh_3 and $AsPh_3$ complexes show them to contain "stretched" dihydrogen ligands with H-H distances of 1.01 and 1.08 Å, respectively (Figure 2).

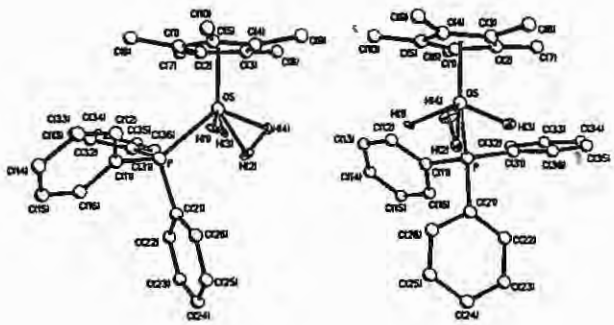


Figure 2. ORTEP diagrams of $[(C_5Me_5)Os(PPh_3)H_2(H_2)^+]$ from the neutron study.

$(C_5Me_5)_2Os_2Br_4$ can be used to synthesize other polyhydride complexes as well. Treatment of $(C_5Me_5)_2Os_2Br_4$ with $LiAlH_4$ followed by addition of methanol affords the osmium polyhydride complexes $(C_5Me_5)OsH_5$ and $(C_5Me_5)_2Os_2H_4$ (Figure 3).[5] Protonation of $(C_5Me_5)OsH_5$ with $HBF_4 \bullet Et_2O$ produces the Os^{VIII} hexahydride complex $[(C_5Me_5)\text{-}OsH_6][BF_4]$. In the presence of *tert*-butyllithium and N,N,N',N",N"-pentamethyldiethylene-triamine (pmdeta), $(C_5Me_5)OsH_5$ is deprotonated to form $[Li(pmdeta)][(C_5Me_5)OsH_4]$.

In addition to high-valent osmium complexes, $(C_5Me_5)_2Os_2Br_4$ is also useful in the preparation of low-valent osmium complexes. The compounds of stoichiometry $(C_5Me_5)Os(L)_2X$ (X = Br, H) have been prepared where L is PPh_3, PMe_3, PEt_3, 1/2-dmpm, 1/2-dmpe, 1/2-dppm, and 1/2-cod.[8] Similarly, the alkyl complexes $(C_5Me_5)Os(PMe_3)_2Me$, $(C_5Me_5)Os(PMe_3)_2Et$, $(C_5Me_5)Os(PEt_3)_2Me$, $(C_5Me_5)Os(dmpe)Me$, and $(C_5Me_5)Os(dmpm)Me$ have also been prepared.

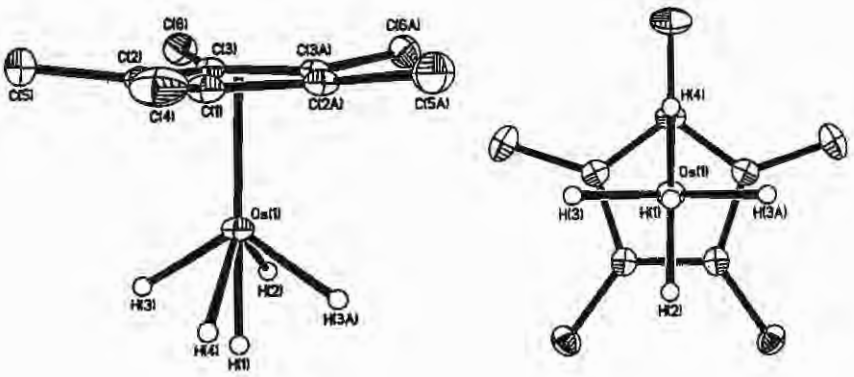


Figure 3. ORTEP diagrams of $(C_5Me_5)OsH_5$.

Protonation of the hydride complexes $(C_5Me_5)Os(L)_2H$ where L is PPh_3, PMe_3, PEt_3, 1/2-dmpm, 1/2-dmpe, and 1/2-dppm with $HBF_4 \bullet Et_2O$ produces the dihydride cations of stoichiometry $[(C_5Me_5)Os(L)_2H_2][BF_4]$. For the PPh_3, PMe_3, PEt_3, and dmpe compounds, only the *trans* dihydride isomer is observed. For the dmpm and dppm complexes, however, a mixture of the *cis* and *trans* isomers is observed in solution.

Protonation of $(C_5Me_5)Os(PMe_3)_2Me$ with $HBF_4 \bullet Et_2O$ at room temperature affords the Os^{IV} alkyl hydride complex $[(C_5Me_5)Os(PMe_3)_2Me(H)][BF_4]$. This complex adopts a geometry in which the methyl and hydride ligands occupy mutually "*trans*" positions in a four-legged piano stool structure.

Protonation of $(C_5Me_5)Os(dmpm)Me$ at -120 °C with $H_2C(SO_2CF_3)_2$ in $CDFCl_2$ generates the *cis* methyl/hydride compound $[(C_5Me_5)Os(dmpm)Me(H)^+]$. As the temperature is raised, the ^1H NMR resonances of the methyl and hydride ligands broaden owing to a scrambling process that exchanges hydrogen atoms among the methyl and hydride sites. This exchange is proposed to occur by formation of an osmium-methane intermediate. Spin saturation transfer experiments support this proposal, and show that the exchange rate is 180 sec^{-1} at -100 °C (Figure 2). The free energy of activation for the exchange is calculated to be 8.1 kcal/mol, and the activation enthalpy and entropy are 7.1 ± 0.9 kcal/mol and -6 ± 5 eu, respectively. At temperatures above -95 °C the compound loses methane with first order kinetics; the free energy of activation for the loss of methane is 13.5 kcal/mol. We conclude that the methane tautomer is only 1.4 to 8.1 kcal/mol higher in energy than the methyl/hydride tautomer, and strategies will be discussed that could lead to a complex in which the methane tautomer is the ground state.

References

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