

Steric and Electronic Effects Induced by Ancillary Ligand Substitutions on Cyclopentadienyl Osmium Complexes

Richard L. Jew

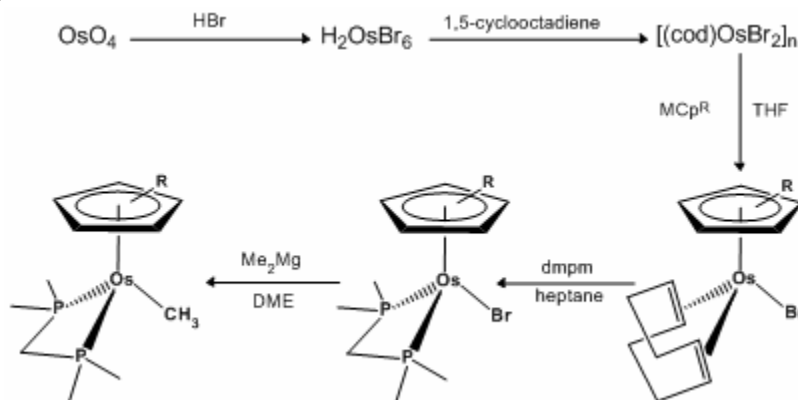
Final Seminar

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Selective chemical transformation of the hydrocarbon components of natural gas, such as methane, provides solutions to several problems: conversion of natural gas to a liquid would facilitate its transport to remote locations; transformation of methane deposits to benign forms would aid in environmental remediation of this greenhouse gas; and functionalizing inert hydrocarbons would allow natural gas to be harvested as a feedstock for the pharmaceutical and polymer industries.¹ Despite the abundance of recent reports of C-H bond activation processes, some of the mechanistic details – especially on solid catalyst surfaces – are still unknown, including what types of intermediates are formed.

Numerous studies have provided evidence that transition metal-coordinated alkanes are intermediates in these processes. Transient metal alkane species have been identified by UV-Vis spectroscopy² and time-resolved infrared spectroscopy.³⁻⁵ A number of isotopolog studies on alkyl hydride compounds report inverse kinetic isotope effects ($k_H/k_D < 1$) for the rates of reductive elimination of alkanes, which is consistent with a two-step mechanism involving an equilibrium between an alkyl hydride and a higher energy, alkane-bound tautomer intermediate prior to the rate-limiting reductive elimination step.⁶ IR^{7,8} and X-ray crystallographic studies^{9,10} have provided insight into the possible modes of binding by metal-bound alkanes, while recent work by Ball and coworkers¹¹⁻¹⁴ reports the observation of cyclopentane, pentane, and cyclohexane bound to photolytically generated Re fragments by NMR spectroscopy.

Scheme 1. Synthesis of $\text{Cp}^R\text{Os}(\text{dmpm})\text{CH}_3$ ($\text{MCp}^R = \text{NaC}_5\text{H}_4\text{Me}$, NaC_5H_5 , $\text{LiC}_5\text{H}_4\text{SiMe}_3$, $\text{KC}_5\text{H}_3(\text{SiMe}_3)_2$).



Gross and Girolami¹⁵ reported the low temperature protonation of $(\text{C}_5\text{Me}_5)\text{Os}(\text{dmpm})\text{Me}$ ($\text{dmpm} = \text{Me}_2\text{PCH}_2\text{PMe}_2$) with $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$ in CDFCl_2 at -120°C to form the *cisoid* methyl hydride complex $[(\text{C}_5\text{Me}_5)\text{Os}(\text{dmpm})\text{H}(\text{Me})][\text{HC}(\text{SO}_2\text{CF}_3)_2]$, which was characterized by ^1H NMR spectroscopy. A fluxional process involving exchange of hydrogen atoms at the methyl and hydride sites was indicated by temperature-dependent broadening of the methyl and hydride resonances and was confirmed by spin saturation transfer experiments performed between -125

and -95 °C. Spin saturation transfer data and simulations of the NMR line shapes were used to determine the free energy of activation for the hydrogen exchange process, ΔG^\ddagger , to be in the range of 8.07 to 8.19 kcal/mol, which are smaller values by ~8 kcal/mol than those reported for compounds that exhibit hydrogen scrambling, all of which occur at much higher temperatures. Reductive elimination of methane followed first order kinetics above -95 °C with $\Delta G^\ddagger = 13.5$ kcal/mol. These data suggest that the scrambling process occurs by formation of a transition metal methane complex.

Theoretical studies^{16,17} of $[(C_5Me_5)Os(dmpm)H(Me)^+]$ confirm that the hydrogen exchange process likely occurs through a coordinated methane ligand, and suggest that decreasing the electron richness of the metal center could favor the coordinated methane complex over the methyl hydride form; this effect can be rationalized through a Dewar-Chatt-Duncanson type of bonding model, where less metal-to-ligand backbonding will disfavor the methyl hydride oxidative addition adduct. To effect this electronic change, Dickinson synthesized the tetramethyl-cyclopentadienyl analogue $[(C_5Me_4H)Os(dmpm)H(Me)^+]$, but found that instead of decreasing the activation barrier, ΔG^\ddagger actually increased to ~8.7 kcal/mol, which is ~0.5 kcal/mol higher than that of the (C_5Me_5) compound.

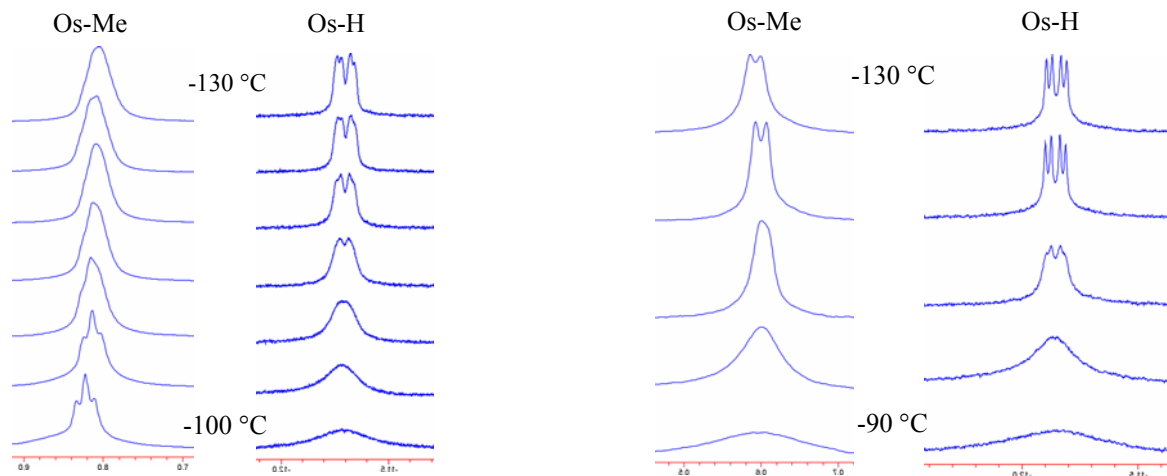


Figure 1. Temperature dependent line broadening of $[(C_5H_5)Os(dmpm)H(CH_3)^+]$ (left) and $[(C_5H_4Me)Os(dmpm)H(CH_3)^+]$ (right).

To further investigate this result, the osmium(II) methyl compounds $(C_5H_4Me)Os(dmpm)Me$ and $(C_5H_5)Os(dmpm)Me$ were synthesized according to Scheme 1 and protonated with $H_2C(SO_2CF_3)_2$ in $CDCl_2$ at -130 °C. 1H NMR spectroscopy was used to identify the *cisoid* methyl hydride protonation products in solution. Spin saturation transfer experiments were used to abstract a ΔG^\ddagger value for hydrogen exchange of 8.47 kcal/mol at -110 °C for $[(C_5H_4Me)Os(dmpm)H(Me)^+]$, which was lower than that of C_5Me_4H , but higher than that of C_5Me_5 . Spin saturation transfer data were obscured for the C_5H_5 compound due to the presence of a triplet underneath the methyl resonance, but coalescence rate data from the broadening of the phosphine ligand P-Me resonances, along with NMR line shape simulations, were used to determine $\Delta G^\ddagger = 7.93$ kcal/mol at -110 °C, which was lower than that of the C_5Me_5 compound. Despite the consistent decrease in the electron donating nature of the C_5R_5 ligand across the series $C_5Me_5 \rightarrow C_5Me_4H \rightarrow C_5H_4Me \rightarrow C_5H_5$, the lack of a linear trend in the ΔG^\ddagger values indicated that electronic changes were not solely responsible for the variations in barrier heights.

An additional effect of altering the C_5R_5 ligand in the above series is decreasing the steric demand of the ligand. One possible consequence of this change is that the dmpm ligand can migrate closer to the C_5R_5 ring as the number of methyl groups decreases, which may also allow the H-Os-Me angle to open up and increase the distance between the hydride and methyl groups, resulting in an increased exchange barrier. To counter this effect, the synthesis in Scheme 1 was repeated with the sterically bulkier but less electron-donating¹⁸ $C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2$, and C_9H_7 (indenyl) ligands in place of C_5H_5 . Although the indenyl analogue was not synthetically accessible through this synthesis, methyl compounds of both silylcyclopentadienyl ligands were synthesized in good yields. Protonation reactions with these compounds, however, were unsuccessful, but we expect that ΔG^\ddagger for these corresponding methyl hydride complexes will be lower than the other observed values.

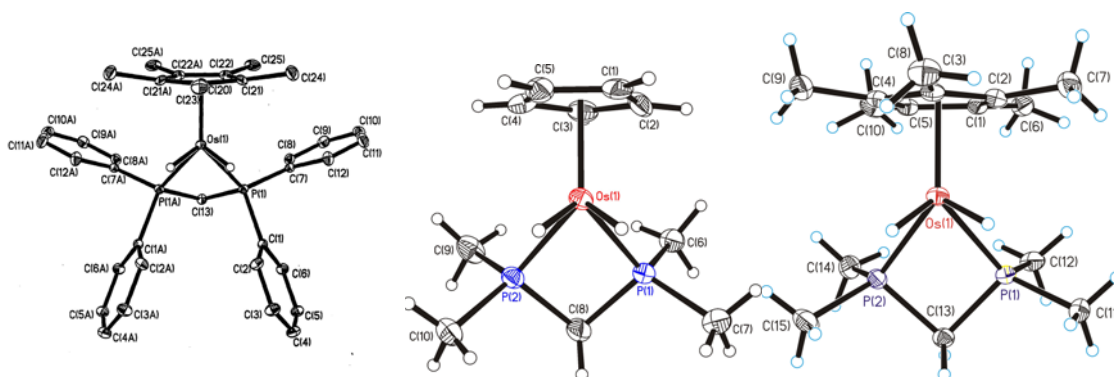


Figure 2. Single crystal X-ray structures of $[(C_5Me_5)Os(dppm)H_2]^+$, $[(C_5H_5)Os(dmpm)H_2]^+$, and $[(C_5Me_5)Os(dmpm)H_2]^+$.

Structural studies were also conducted to gauge the effect of ancillary ligand substitutions on the steric demands of these systems. Reaction of $(C_5H_5)Os(dmpm)Br$ with NaOMe in refluxing methanol afforded $(C_5H_5)Os(dmpm)H$, which was crystallized in pentane. The X-ray crystal structure of this compound was compared to the previously reported $(C_5Me_5)Os(dmpm)H$ structure, but relevant angles – especially the dihedral angle between the C_5 ring plane and the P-Os-P plane – were extremely similar, and offered little insight. Better structural analogues of the seven-coordinate, osmium(IV) methyl hydride complexes were the osmium(IV) dihydride cations, which were synthesized by reaction of $(C_5R_5)Os(P-P)H$ with $HBF_4 \cdot Et_2O$ ($C_5R_5 = C_5Me_5$, C_5H_5 ; P-P = dmpm, dppm). Structures of $[(C_5H_5)Os(dmpm)H_2][BF_4]$ and $[(C_5Me_5)Os(dmpm)H_2][BF_4]$ were compared to the benchmark compound $[(C_5Me_5)Os(dppm)H_2][BF_4]$; crystallization of $[(C_5H_5)Os(dppm)H_2][BF_4]$ yielded only the *transoid* complex, which was unfit for comparison. Although the H-Os-H angle in the C_5H_5 compound was significantly smaller than those of the C_5Me_5 compounds, the C_5/P -Os-P dihedral angle of 48.9° for the C_5H_5 compound was smaller than the 57.1° and 56.0° angles for the respective dmpm and dppm complexes of C_5Me_5 , suggesting that the phosphine ligand is indeed migrating toward the C_5 ring. T_1 measurements also indicate that the $H \cdots H$ distance in the C_5H_5 compound is longer than those of the C_5Me_5 compounds.

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