

Hydrogen Exchange between Hydride and Methyl Ligands in $[\text{Cp}^*\text{Os}(\text{dmpm})(\text{CH}_3)\text{H}^+]$

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Very recently Gross and Girolami¹ described the “first report of a transition metal methyl/hydride complex in which the hydrogens of the alkyl and hydride are exchanging at a rate sufficient to be dynamic on the NMR time scale.² The results suggest that an alkane complex $\text{L}_x\text{M}(\text{CH}_4)$ is formed reversibly from the methyl/hydride complex”.

In this communication I report density functional theory (DFT) calculations on a model of the Os(IV) methyl/hydride studied by Gross and Girolami. A bound methane complex is indeed found which lies ≈ 6 kcal/mol above the methyl/hydride. The theoretical barrier height connecting the two is in good agreement with the experimental kinetic data reported for hydrogen exchange. Once formed, the methane complex can scramble the hydrogen bound to the metal through a lower-lying transition state involving $\eta^2\text{-H}_2\text{H}$ coordination to the metal. The larger barrier measured for the reductive elimination of CH_4 may be a measure of the stability of the methyl/hydride.

The system studied by Gross and Girolami was the cationic Os(IV) complex $[\text{Cp}^*\text{Os}(\text{dmpm})(\text{CH}_3)\text{H}^+]$, where dmpm is bis(dimethylphosphino)methane and $\text{Cp}^* = \text{C}_5(\text{CH}_3)_5$. In the present work, I have studied a model complex in which the Cp^* ligand is replaced with $\text{Cp}(\text{C}_5\text{H}_5)$. The calculations employed the hybrid B3LYP³ DFT approximation,⁴ and a locally modified version⁶ of the Gaussian94 program⁷ capable of evaluating analytic second derivatives of the energy in applications involving effective core potentials. In addition to allowing computation of the zero-point energy corrections, the analytic second derivative capabilities are particularly helpful in locating transition states.

The zero-point corrected electronic energy of the various stationary points found is depicted schematically in Figure 1. Selected geometric parameters for these species are given in Table 1. The most stable point on the surface is the methyl/hydride (1).

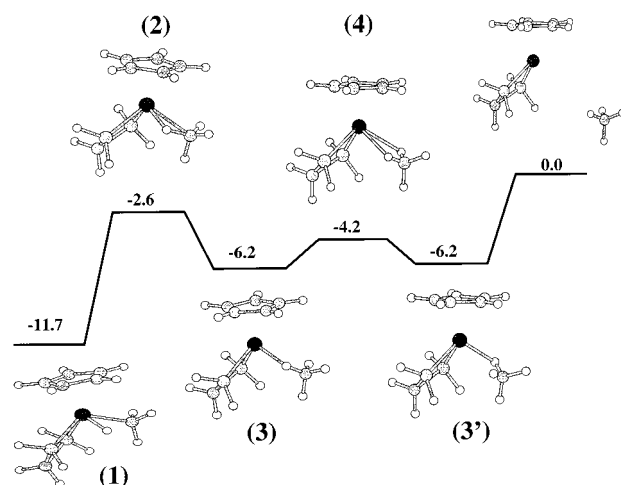


Figure 1. Schematic of the B3LYP energy surface for the reductive elimination of CH_4 from $[\text{CpOs}(\text{dmpm})(\text{CH}_3)\text{H}^+]$. The electronic energy plus zero-point correction (kcal/mol), relative to the ion plus free methane, is given above each structure. The methyl groups of the dmpm ligand are depicted here as hydrogens to simplify the graphic; the energies actually refer to the dmpm ligand.

Table 1. Selected Geometric Parameters(Å) for the Stationary Points in Figure 1

	$R_{\text{Os-H}}$	$R_{\text{H-C}}$	$R_{\text{Os-C}}$
$\text{CpOs}(\text{dmpm})(\text{CH}_3)\text{H}^+$ (1)	1.62	2.18	2.19
$\text{CpOs}(\text{dmpm})(\text{CH}_3\cdots\text{H})^+$ (2)	1.66	1.42	2.34
$\text{CpOs}(\text{dmpm})(\text{CH}_3\text{H})^+$ (3)	1.92	1.15	2.70
$\text{CpOs}(\text{dmpm})(\text{CH}_2\text{HH})^+$ (4)	2.27	1.11	2.69
$\text{CpOs}(\text{dmpm})^+ + \text{CH}_4$	—	1.09	—

It lies nearly 12 kcal/mol below the products of the reductive elimination, $\text{CpOs}(\text{dmpm})^+ + \text{CH}_4$. A stable methane complex (3) lies only ≈ 6 kcal/mol above the methyl/hydride. It is most fairly characterized as $\eta^1\text{-H}$ since the Os–H distance of 1.92 Å is much shorter than the 2.70 Å Os–C distance. The Os–H–C bond angle is 122° .

These two minima are connected through a transition state (2) that most closely resembles the methyl/hydride (Table 1). The frequency along the reaction coordinate at the transition state is $752i \text{ cm}^{-1}$. The theoretical barrier height for the formation of the methane complex from the methyl/hydride is $\Delta E = 9.2$ kcal/mol (Figure 1). This is in good agreement with the experimental enthalpy of activation for hydrogen exchange, $\Delta H = 7.1 \pm 0.9$ kcal/mol. The theoretical entropies of activation for this step are in qualitative agreement with those determined by Gross and Girolami. Experiment finds $\Delta S = -6.5 \pm 5$ eu, theory $\Delta S = -0.5$ eu. This difference is probably not especially significant, particularly given the omission of solvent effects in the theoretical treatment. It seems reasonable therefore to associate the experimental barrier with the formation of the methane complex.

If the rate-limiting step for hydrogen scrambling is determined by the $[\text{Os}]\text{H}^+(\text{CH}_3) \rightarrow [\text{Os}](\text{CH}_3)\text{H}^+$ conversion, then there must exist a lower-lying path from the methane complex that exchanges the hydrogen bound to the metal center with one of the hydrogens of the methyl group. Such a path was found and is also shown in Figure 1. The methane complex 3 passes through a transition state of $\eta^2\text{-H}_2\text{H}$ character 4 to the analogous methane complex 3'. The barrier is quite low, only 2 kcal/mol according to the calculations.⁸

(8) Another transition state was found, nearly degenerate with the one in Figure 1, which is not pictured. It also involves $\eta^2\text{-H}_2\text{H}$ coordination to the metal, but in this case the plane containing the two hydrogens and the metal is perpendicular to the one discussed in the text.

- (1) Gross, C. L.; Girolami, G. S. *J. Am. Chem. Soc.* **1998**, *120*, 6605.
 (2) Earlier examples of $\text{L}_x\text{M}(\text{CH}_3)\text{H}$ complexes which exchange hydrogens, albeit much more slowly, include the following: Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. Gould, G.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502. Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172. Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897. Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647.
 (3) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
 (4) The osmium center was described with the LANL2 relativistic effective core potential⁵ and a modification of the LANL2DZ basis set in which the primitive functions are completely uncontracted. Two nearly linearly dependent p functions result from this procedure, $\alpha = (0.4923, 0.51)$; only the former was retained in the final basis set. A polarization function of f character ($\alpha = 0.6$), optimized in preliminary studies, completes the Os basis set. The ligands were described with the 6-31G* basis set.
 (5) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
 (6) Russo, T. V.; Martin, R. L.; Hay, P. J.; Rappé, A. K. *J. Phys. Chem.* **1995**, *102*, 9315.
 (7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94 (Revision E.1)*; Gaussian, Inc.: Pittsburgh, PA, 1995.

A simple estimate of the kinetic isotope effect for the process $[\text{Os}]\text{H}(\text{CH}_3) \rightarrow [\text{Os}](\text{CH}_3\text{H}')$ is provided by the difference in zero-point energies at transition state **2** when H' is replaced by deuterium. This estimate gives $k_{\text{H}}/k_{\text{D}} = 1.6$. Experimental verification of this ratio would further support the assertion that formation of the methane complex is the bottleneck in the hydrogen exchange.

Might the substitution of Cp for Cp* in the model complex alter these conclusions? An estimate⁹ finds it to be of little consequence (~ 1 kcal/mol) as far as the relative stabilities of the methyl/hydride, the methane adduct, and the barriers pictured in Figure 1 are concerned. The Cp* does, however, reduce the binding energies of these species relative to the asymptote by ~ 3 kcal/mol.

Gross and Girolami also reported a free energy of activation for reductive elimination of methane from the methyl/hydride of $\Delta G = 13.5$ kcal/mol at -100 °C. No barrier is anticipated (nor was one found in the calculations) for the elimination of CH₄ from the methane complex. The 13.5 kcal/mol may simply be a measure of the stability of the methyl/hydride.¹⁰ The energy calculated for the methyl/hydride is not incompatible with this conclusion, but remember it is not a free energy, and the entropic contribution would tend to decrease its stability by roughly 6 kcal/mol at this temperature.

(9) This question was addressed by explicit calculations on the reaction of CH₄ with the model ions $\text{CpOs}(\text{H}_2\text{PCH}_2\text{PH}_2)^+$ and $\text{Cp}^*\text{Os}(\text{H}_2\text{PCH}_2\text{PH}_2)^+$, where the dmpm ligand has been replaced by a simpler phosphine. The more polarizable Cp* ligand uniformly reduces the binding energies of the minima and transition states relative to the free ion plus methane by ~ 3 – 4 kcal/mol. The differences in energy associated with the scrambling process are therefore largely unaffected. This correction should transfer to the dmpm ligand.

(10) Only slight changes are observed if the methyl groups of the dmpm ligand are replaced by hydrogens. The zero-point corrected energies (kcal/mol) analogous to those in the figure are the following: **1** (-11.9), **2** (-4.7), **3** (-9.1), and **4** (-7.3).

If the surface in Figure 1 is read right to left, it describes the activation of methane by the cationic Os(II) complex $[\text{Cp}^*\text{Os}(\text{dmpm})^+]$. Low-temperature C–H activation by the isoelectronic Ir(III) cation, $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{CH}_3)^+]$, was reported earlier by Arndtsen and Bergman.¹¹ In this case, the σ -bond metathesis



can be followed. Theoretical calculations by Strout et al.¹² and Su and Chu¹³ found that this reaction also proceeds via intermediate methane and alkyl/hydride complexes. As opposed to the Os(II) complex, in the Ir(III) case the methyl/hydride is calculated to be bound only slightly relative to free methane,¹³ if at all.¹² The barrier for formation of the methyl/hydride from the methane complex is also significantly larger (≈ 12 kcal/mol vs 4 kcal/mol). The qualitative aspects of the surfaces are similar, however. Evidence seems to be accumulating for an analogous energy landscape in the activation of alkanes by Pt(II) complexes.¹⁴

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