Metal−Alkane Complexes. Rapid Exchange of Hydrogen Atoms between Hydride and Methyl Ligands in [$(C_5Me_5)Os(dmpm)(CH_3)H^+$]

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We wish to describe the first example of a transition metal methyl/hydride complex in which the hydrogen atoms of the alkyl and hydride are exchanging at a rate sufficient to be dynamic on the NMR time scale. The results suggest that an alkane complex $L_xM(CH_4)$ is formed reversibly from the methyl/hydride complex over 100 times per s at −100 °C.[1]

Protonation of the osmium(II) alkyl $(C_5Me_5)Os(dmpm)(CH_3)$, where dmpm is bis(dimethylphosphino)methane,[2] with ~1 equiv of the carbon acid $H_2C(SO_2CF_3)_2$ in $CDFCl_2$[3] at −120 °C yields the osmium(IV) methyl/hydride complex [$(C_5Me_5)Os(dmpm)(CH_3)H^+$] (**1**).[4,5] The ^1H NMR spectrum of **1** at this temperature features a resonance at δ −13.03 for the Os−H group and a resonance at δ 0.54 for the Os−Me group; a HMQC experiment showed that the latter peak is correlated with the Os−Me resonance at δ −37.9 in the $^{13}C\{^1H\}$ NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows that the two ends of the dmpm ligand are inequivalent, as expected for a structure in which the methyl and hydride resonances are mutually "cisoid". There is no evidence of the formation of the "transoid" isomer under any conditions.

Remarkably, when the temperature is raised, the Os−H and Os−Me peaks broaden due to onset of coalescence (Figure 1); this process also exchanges the two ends of the dmpm ligand. Simulations of the line shapes are consistent with an exchange process that permutes the four hydrogen atoms in the Os−H and Os−Me sites. The exchange rates deduced from the simulations are 10, 22, 45, 85, and 170 s^{-1} at −120, −115, −110, −105, and −100 °C, respectively.[6]

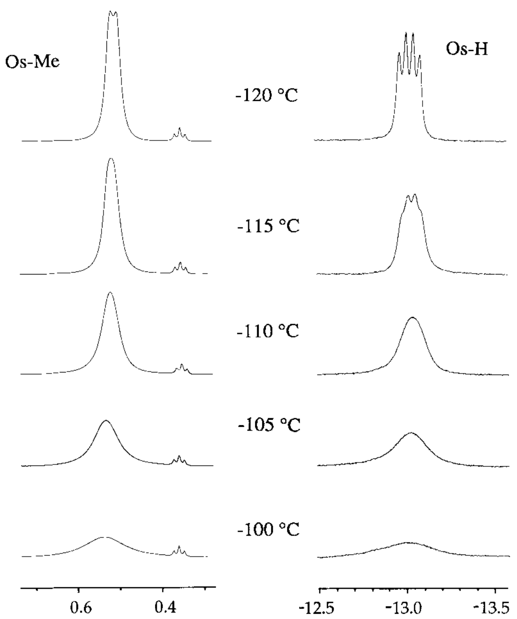

Figure 1. Temperature dependence of the methyl (left) and hydride (right) resonances seen in the 500 MHz ^1H NMR spectrum of **1**. Simulations of these line shapes are given in the Supporting Information.

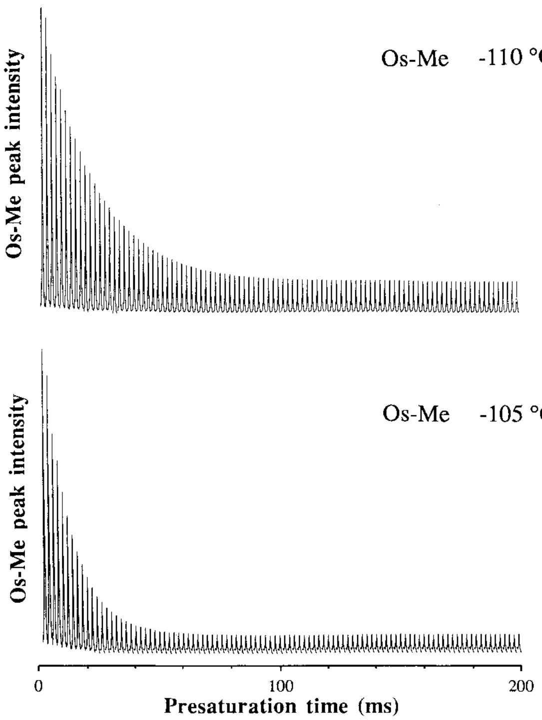

Figure 2. Spin saturation transfer results showing decay of the methyl resonance upon irradiating the hydride resonance in **1** at −110 and −105 °C for different lengths of time. The Os−Me peak intensity is plotted as a function of presaturation time, which increases from 0 to 200 ms (left to right) in increments of 2 ms.

Definitive evidence that the hydrogen atoms in the Os−H and Os−Me sites are exchanging with one another has been obtained from spin saturation transfer experiments.[7] Presaturation of the Os−H resonance leads to selective loss of intensity of the Os−Me peak. No other peak in the spectrum (besides the Os−H resonance itself) changes in intensity; this includes the resonance due to the $HC(SO_2CF_3)_2^-$ anion. Rate constants for the exchange process can be obtained by measuring the intensity of the Os−Me resonance as a function of the presaturation time (Figure 2). We find that k equals 9.4, 20, 42, 81, and 160 s^{-1} at temperatures of −120, −115, −110, −105, and −100 °C, respectively.[6] These rate constants agree very closely with those deduced above from the simulations of the line shapes. From these values, we calculate that $\Delta H^‡ = 7.1 \pm 0.9$ kcal/mol and $\Delta S^‡ = -6.5 \pm 5$ eu for the hydrogen scrambling process.[8] At

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(1) For a review of transition metal alkane complexes, see: Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125−3146.

(2) This osmium(II) alkyl can be prepared from $(C_5Me_5)Os(dmpm)Br$, which has been recently described. See: Gross, C. L.; Girolami, G. S. *Organometallics* **1996**, *15*, 5359−5367.

(3) Siegel, J.; Anet, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629−2630.

(4) NMR data for **1** in $CDFCl_2$ at −120 °C. ^1H NMR: δ 4.79 (4-line pattern, $\Sigma = 37.8$ Hz, PCH_2), 4.06 (s, $(SO_2CF_3)_2CH^-$), 3.56 (4-line pattern, $\Sigma = 40.3$ Hz, PCH_2), 1.94 (s, C_5Me_5), 1.89 (br s, PMe_2), 1.78 (m, 2 PMe_2), 1.35 ("d", $^2J_{PH} = 8.7$ Hz, PMe_2), 0.55 ("d", $^2J_{PH} = 7.2$ Hz, Os−Me), −13.03 (dd, $^2J_{PH}$ =18.2, 39.6 Hz, Os−H). $^{13}C\{^1H\}$ NMR: δ 120.6 (q, $^1J_{CF} = 322.7$ Hz, $(SO_2\mathit{C}F_3)_2CH^-$), 96.1 (s, C_5Me_5), 52.4 (s, $(SO_2CF_3)_2\mathit{C}H^-$), 51.0 (t, $^1J_{PC} = 32.0$ Hz, $P\mathit{C}H_2$), 26.6 ("d", $^1J_{PC} = 44.4$ Hz, PMe), 16.4 ("d", $^1J_{PC} = 31.1$ Hz, 2 PMe_2), 10.0 (s, $C_5\mathit{Me}_5$), 9.0 (m, PMe_2), −37.9 (m, Os−Me). $^{31}P\{^1H\}$ NMR: δ −69.6 (d, $^2J_{PP} = 114.1$ Hz), −77.0 (d, $^2J_{PP} = 114.1$ Hz).

(5) For protonation of the similar osmium and ruthenium hydrides Cp^*ML_2H and characterization of the resulting molecular dihydrogen complexes, see: Bullock, R. M.; Song. J.-S.; Szalda, D. J. *Organometallics* **1996**, *15*, 2504−2526. Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166−5175.

(6) The rates given are for hydrogen atoms leaving the methyl site.

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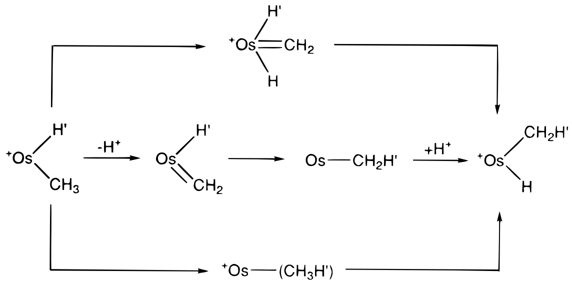
−100 °C, this corresponds to a free energy of activation of 8.1 kcal/mol.

Reductive elimination of methane occurs following first-order kinetics at measurable rates above −95 °C, but this process involves a different transition state because the activation energy, $\Delta G^{\ddagger} = 13.5$ kcal/mol, is higher than that for hydrogen scrambling.

Previous studies of $L_xM(R)D$ complexes suggest that, in a few cases, the deuterium label can scramble into hydrogen positions on the alkyl ligand R at temperatures near that at which the compound decomposes.[9−16] When referenced to a common temperature, however, the methyl/hydride scrambling rate we observe for **1** is millions of times faster than the scrambling rates seen in these other complexes. The exchange process in **1** is the only one that is detectable by changes in the line widths of the ^1H NMR resonances or by a spin saturation transfer experiment.

Although exchange of the Os−CH_3 and Os−H hydrogen atoms could take place by means of α-hydrogen elimination to form an osmium methylene dihydride intermediate (see Scheme 1), this mechanism is unlikely because a 20-electron intermediate would be generated. Processes that might reduce the electron count, such as $\eta^5 \rightarrow \eta^3$ slippage of the C_5Me_5 ring and dissociation of one arm of the phosphine ligand, have very high activation barriers (>30 kcal/mol) as shown by studies of related (C_5Me_5)Os(dmpm)X compounds.[17] Exchange via reversible deprotonation of the Os−CH_3 group by the $HC(SO_2CF_3)_2^-$ anion is also ruled out by the NMR results.

Scheme 1. Possible Methyl/Hydride Exchange Mechanisms



Instead, exchange of the Os−CH_3 and Os−H hydrogen atoms in **1** most likely takes place by formation of a coordinated methane ligand. If the methane complex responsible for hydrogen scrambling is a transition state, its energy is 8 kcal/mol higher than that of the methyl/hydride tautomer. Alternatively, if the methane complex is a true intermediate (as has been proposed in other systems that exhibit alkyl/hydride exchange), its energy is only 2−8 kcal/mol higher than that of the methyl/hydride tautomer.[18] By changing the ancillary ligands attached to the osmium center, it may prove possible to reverse the relative energies of the two tautomers so that the methane complex is the ground state.[19] We are directing our current efforts along these lines.

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Supporting Information Available: Figures of simulations of the NMR line shapes shown in Figure 1, an Eyring plot of $\ln(kh/k_BT)$ vs $1/T$ for the methyl/hydride scrambling process in **1**, and a plot of $\ln(I)$ vs time for the reductive elimination of methane from **1** at −90 and −95 °C (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(7) For a description of spin saturation transfer experiments, see: Faller, J. W. In *Determination of Organic Structure by Physical Methods*; Nachod, F. C., Zuckerman, J. J., Eds.; Academic: New York, 1973; Chapter 2. Although the diminution of the methyl resonance could be caused by a negative nuclear Overhauser enhancement, this possibility can be ruled out because negative NOEs are not expected for small molecules such as **1**, and because the diminution of the Os−Me resonance at long saturation times becomes significantly more pronounced (not less pronounced) as the temperature is raised.

(8) Errors in the activation parameters have been calculated by propagation of error formulas given in Morse, P. M.; Spencer, M. D.; Wilson. S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646−1655.

(9) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537−1550.

(10) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332−7346.

(11) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc*. **1986**, *108*, 4814−4819.

(12) Gould, G.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502−5504.

(13) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172−1179.

(14) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897−3908.

(15) Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647−1648.

(16) In only one other case have the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ been measured for an alkyl/hydride hydrogen scrambling process. In a study of $[Cp_2Re(CH_3)D^+]$, Heinekey showed that $\Delta H^{\ddagger} = 22.3 \pm 1.9$ kcal/mol and $\Delta S^{\ddagger} = 24 \pm 9$ eu for the reaction which scrambles deuterium into the methyl hydrogen sites.[12]

(17) Gross, C. L.; Girolami, G. S. Unpublished observations.

(18) The lower limit is set by the observation that no resonances due to the methane tautomer are observed at −120 °C, so that its equilibrium concentration must be less than ∼1%.

(19) For a recent discovery of an alkane complex that is stable in the solid state at room temperature, see: Evans, D. R.; Drovetskaya, T.; Bau, R.; Reed, C. A.; Boyd, P. D. W. *J. Am. Chem. Soc.* **1997**, *119*, 3633−3634.