Selective H/D Exchange in Alkylsilanes Catalyzed by Osmium Phosphine Complexes: The First Evidence for β-Hydrogen Elimination from a Metal Silyl

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As a result of recent achievements in the synthesis and isolation of compounds containing multiple bonds to silicon, the search for silicon analogues of transition-metal olefin complexes has gained new impetus. Although metal silene (silaolefin) complexes have been previously proposed as reactive intermediates,[1] it was only recently that Wrighton and co-workers reported the first spectroscopic observations of metal silene complexes, formed by β-hydrogen elimination from unsaturated dimethylsilylmethyl (M-CH_2SiMe_2H) complexes.[2] The subsequent isolation and structural characterization by Tilley and co-workers[3] of ruthenium analogues provides conclusive evidence for the viability of silene complexes and for β-hydrogen elimination from silylmethyl complexes. We now report evidence for the previously unknown β-hydrogen elimination from trialkylsilyl (M-$Si(CH_2R)_3$) ligands and the intermediacy of osmium silene complexes in the selective H/D exchange between trialkylsilanes and benzene-d_6 catalyzed by $Os(PMe_3)_4(SiMe_2R)(H)$ (R = Me, Et; **1a**,**b**).

Thermolysis of $(CH_3)_3SiH$ in C_6D_6 in the presence of **1a**[4] proceeds according to eq 1, resulting in formation of $(CD_3)_3SiD$ (>90% D after approximately 4 days at 90 °C.) A concomitant increase in the C_6D_5H concentration is also observed.[5] Deuterium is also incorporated into the coordinated phosphine, silyl, and hydride ligands of **1a**. Compound **1a** is otherwise unchanged as determined from ^{31}P NMR spectra of the reaction mixture.[6]

$$(CH_3)_3Si\text{-}H \;+\; C_6D_6 \xrightarrow[90\ ^\circ C,\ 4\ days]{(PMe_3)_4Os(H)(SiMe_3)} (CD_3)_3Si\text{-}D \;+\; C_6D_5H \qquad (1)$$

Isotopic exchange between benzene-d_6 and metal hydrides has been observed in many instances and is generally attributable to oxidative addition of a benzene C-D bond to an unsaturated metal complex containing a hydride, followed by reductive elimination of a C-H bond leading to C_6D_5H and metal deuteride.[7,8] Following PMe_3 dissociation, such a process could easily lead to deuteration of the hydride position in **1a**, which coupled with facile Si-H(D) oxidative addition and reductive elimination cycles would lead to catalytic deuteration of the *Si-H* position in the free silane. Os(IV) species analogous to $(PMe_3)_3Os(H)(D)(C_6D_5)(SiMe_3)$ have been well established by Flood and co-workers as intermediates in intra- and intermolecular C-H activation processes involving $Os(PMe_3)_4(H)(R)$ (R = Ph, CH_3, $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$).[8]

The means by which deuterium is incorporated into the *C-H* positions of $(CH_3)_3SiH$, however, is a more complex issue. It is conceivable that the silane methyl groups undergo isotopic exchange independent of the Si-H bonds by an analogous mechanism involving silane C-H and C_6D_6 addition to the osmium center, yielding an Os(IV) intermediate such as $(PMe_3)_3Os(H)(D)(R)(CH_2SiMe_2H)$ (R = $SiMe_3$ or C_6D_5), which could then eliminate $(CH_2D)(CH_3)_2SiH$. However, the Si-CH_3/Si-H ratio as measured by NMR integrated intensities remains nearly constant (ca. 9:1) during the course of reaction 1, a rather surprising result if C-H and Si-H bonds react independently. Oxidative addition of Si-H bonds to unsaturated metal complexes is generally much more facile than the addition of C-H bonds, yet the invariance of the Si-CH_3/Si-H ratio implies that deuterium is incorporated into the methyl groups nearly an order of magnitude faster than into the Si-H positions. Allowing for the higher effective concentration of C-H bonds, this suggests that Si-H and C-H deuterations are equally facile, which is inconsistent with independent oxidative addition mechanisms.

Direct evidence against intermolecular addition of silane C-H bonds as part of the deuteration mechanism is found in the total absence of isotopic exchange found for $(CH_3)_4Si$ in the presence of **1a** or **1b** at 90 °C;[9] i.e., silane methyl groups are not labeled in the absence of an Si-H group. The possibility that steric differences account for the lack of reactivity of $(CH_3)_4Si$ compared with $(CH_3)_3SiH$ seems remote, given that H/D exchange is observed for a significantly more hindered substrate (vidi infra).

$$(CH_3)_4Si \;+\; C_6D_6 \xrightarrow[90\ ^\circ C,\ weeks]{\mathbf{1a,b}} \text{No Exchange} \qquad (2)$$

Significantly, the catalytic deuterium exchange reaction is highly regioselective. Treatment of a 5-fold excess of $(CH_3)_2(CH_3CH_2)SiH$ with $(PMe_3)_4Os(H)(SiMe_2Et)$ (**1b**) in C_6D_6 at 90 °C catalytically yields $(CD_3)_2(CH_3CD_2)SiD$ (eq 3); no deuterium incorporation into the ethyl CH_3 position is detected by ^1H or ^2H NMR. Although silicon is known to activate adjacent C-H bonds toward oxidative addition, it is extremely unlikely that preferential H/D exchange in the *secondary* ethyl positions would arise from an intermolecular C-H addition when the *primary* positions of $SiMe_4$ are unreactive.[9]

$$(CH_3)_2(CH_3CH_2)Si\text{-}H \xrightarrow[90\ ^\circ C,\ C_6D_6]{(PMe_3)_4Os(H)(SiMe_2Et)} (CD_3)_2(CH_3CD_2)Si\text{-}D \qquad (3)$$

In summary, any proposed mechanism must reconcile the observations that (1) at least one Si-H bond is required for deuterium exchange into silane alkyl groups, (2) deuteration of C-H and Si-H positions occurs at comparable rates, and (3) deuterium is only incorporated into C-H bonds immediately adjacent to the silicon atom. We believe the simplest and most consistent mechanism which addresses these observations is as follows: deuterium is introduced into the cycle by the exchange of **1b** with C_6D_6 producing $(PMe_3)_3Os(D)(Si(CH_3)_2CH_2CH_3)$ as described above. Exchange with free silane at this point yields only Si-D labeled silane.[10] Alternatively, β-hydrogen elimination occurs

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(1) (a) Pannell, K. H. *J. Organomet. Chem.* **1970**, *21*, P17-18. (b) Bulkowski, J. E.; Miro, N. D.; Sepelak, D.; Van Dyke, C. H. *J. Organomet. Chem.* **1975**, *101*, 267-277. (c) Tamao, K.; Yoshida, J.-I.; Okazaki, S.; Kumada, M. *Isr. J. Chem.* **1976/1977**, *15*, 265-270.

(2) (a) Randolf, C. L.; Wrighton, M. S. *Organometallics* **1987**, *6*, 365. (b) Lewis, C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 7768.

(3) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 7558-7560.

(4) Compound **1a** can be prepared by the reaction of excess Me_3SiH with either $(PMe_3)_4Os(H)(CH_2CMe_3)$ (12 h at 90 °C) or $(PMe_3)_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ (350 nm $h\nu$, 4 days), followed by recrystallization from hexanes: ^1H NMR (C_6D_6) δ 1.49 (t, J_{PH} = 2.6 Hz, two mutually trans PMe_3), 1.30 (m, two cis PMe_3), 0.79 (s, $SiMe_3$), -12.00 (ddt, J_{PH} = 16, 27, 51 Hz, Os-H); $^{31}P\{^1H\}$ NMR δ -52.1 (t, J_{PP} = 21 Hz), -58.2 (q, $J_{PP} \sim$ 20 Hz), -60.3 (q, $J_{PP} \sim$ 20 Hz).

(5) Reactions were carried out as follows: Solutions containing ca. 5 mg (0.010 mmol) of **1**, 0.050 mmol of alkylsilane, ca. 2 mg of hexamethylbenzene (internal standard), and 0.5 mL (5.65 mmol) of benzene-d_6 were sealed in an NMR tube. The tubes were submerged in a 90 °C oil bath and removed periodically for observation of the ^1H, ^2H, and ^{31}P NMR spectra. Volatile products were subsequently analyzed by ^1H and ^2H NMR. No deuterium incorporation into hexamethylbenzene was observed.

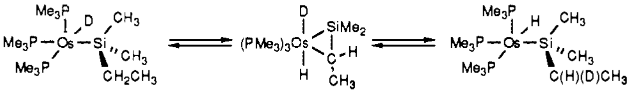
(6) The ^{31}P resonances of **1** do, however, shift by up to 1 ppm with deuteration of the PMe_3 ligands. The sensitivity of ^{31}P chemical shifts to deuterium substitution has been noted previously: Hansen, P. E. *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1983; Vol. 15, pp 105-233.

(7) For example: (a) Hodges, R. J.; Garnett, L. *J. Phys. Chem.* **1969**, *73*, 1525. (b) Barefield, E. K.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* **1970**, *92*, 5234-5235. (c) Jones, W. D.; Maguire, J. A. *Organometallics* **1986**, *5*, 590-591.

(8) (a) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 7964-7970. (b) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1346-1347. (c) Harper, T. G. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915-7916.

(9) At 90 °C in the absence of excess Me_3SiH in benzene-d_6, **1a** slowly reacts to form $(PMe_3)_4Os(D)(C_6D_5)$. During this process, added $SiMe_4$ is not deuterated. Thermolysis of a mixture of Me_4Si and Me_2EtSiH with **1b** in benzene-d_6 leads only to deuteration of $HSiMe_2Et$ as described in the text; no deuteration of Me_4Si is detected by NMR or GC-MS.

from the silyl ligand to yield $Os(PMe_3)_3(H)(D)(\eta^2\text{-}Me_2SiCHCH_3)$, a silene complex or silametallacycle. Subsequent migration of deuteride onto the silene ligand would effect isotopic exchange of an alkyl C–H position, as shown in eq 4. Further



reaction with C_6D_6 could result in incorporation of additional deuterium into the silane, eventually followed by exchange with free silane. Thus both Si–H and C–H deuteration would be initiated by a single intermolecular Si–H addition, and only those C–H positions adjacent to silicon (β to the metal) will be susceptible to exchange.

The β-hydrogen migration process is well-documented in the chemistry of transition-metal alkyls. This work provides the first evidence for β-hydrogen migration in metal silyls. Furthermore, the formation of transient silene complexes such as $(PMe_3)_3Os(H)_2(\eta^2\text{-}Me_2SiCH_2)$ formally represents the dehydrogenation of the silane within the osmium coordination sphere. In conjunction with subsequent reaction chemistry, this process could form the basis for other, more useful, catalytic transformations of organosilanes as well as synthetic routes to stable silene complexes. We are currently exploring this new mode of reactivity with such goals in mind.

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(10) Exchange between free silane and $(PMe_3)_3Os(D)(SiMe_3)$ could proceed through either Os(IV) or Os(0) intermediates (e.g., $P_3Os(H)(D)(SiMe_3)_2$ or P_3Os). On the basis of the extensive studies of Flood and co-workers, the former would appear most likely.[8]

Gas-Phase Water and Hydroxyl Binding Energies for Monopositive First-Row Transition-Metal Ions[1]

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We report the binding energies of a single water molecule and a single hydroxyl group to singly charged cations of the first-row transition metals, obtained with use of collision-induced dissociation in a triple-quadrupole mass spectrometer.[2] For Fe^+, Co^+, and Ni^+, the second hydration energies have been determined as well. As found recently[2] for Cu^+, they are larger than the first hydration energies.

Data of this type were previously available for covalent bonds in metal ion hydrides.[3] Successive gas-phase hydration energies of some main group metal ions are known,[4] but the only results published for bonds between transition-metal ions and simple ligands such as water are those for $Cu^{+\,2,5}$ and Ag^+.[5] A few monopositive transition-metal ion hydroxyl bond strengths were previously determined by standard gas-phase methods.[6-9]

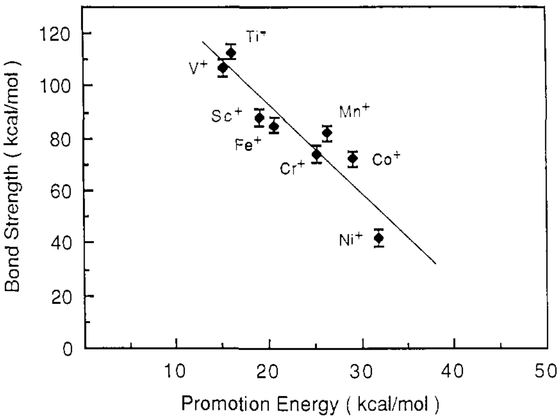

Figure 1. Transition-metal ion hydroxide bond strengths vs promotion energy.[13]

$M^+(H_2O)_2$ and $M^+OH(H_2O)$ ions were generated[2] by 6–10 keV Ar atom impact on cold frosted metal plates or hydrated metal salts under conditions where negligible quantities of protonated water clusters are formed, velocity selected in a retarding-stop analyzer, mass selected by a quadrupole mass filter, and after acceleration permitted to undergo a single collision with Ar or Xe (10^{-5}–10^{-4} Torr) in a second quadrupole which functioned as an ion guide. The product ions were analyzed in a third quadrupole. The excitation curves obtained by variation of the accelerating voltage were analyzed as described elsewhere.[2] The curve for the parent ion $M^+(H_2O)_n$ defines its velocity distribution, used to deconvolute the curves for the daughter ions $M^+(H_2O)_{n-1}$ and $M^+(H_2O)_{n-2}$. The differences of their thresholds define the successive binding energies of water molecules. A similar procedure starting with $M^+OH(H_2O)$ ions yields the hydroxyl binding energies (Table I). The accuracy of the results is believed[2] to be ±3 kcal/mol.

For three of the new values a comparison with literature data is possible. The agreement is excellent for $D(Cr^+\text{–}OH)$[8] and $D(Co^+\text{–}OH)$,[7,9] but our value for $D(Fe^+\text{–}OH)$[7,9] is 8–12 kcal/mol higher. Considering the combined error bars, a possible explanation of the difference might be that the Fe^+ product of collision-induced dissociation of $FeOH(H_2O)^+$ is produced in its quartet state, about 5 kcal/mol above the ground sextet state.[10] This would be a likely outcome if the ground state of $FeOH(H_2O)^+$ is a triplet.

Two obvious structures are possible for the ions: $H—M^+{=}O$ or $M^+—OH$ and $H—M^+—OH$ or $M^+—OH_2$. Assuming that bond energies are additive in a first rough approximation,[11] the energy $E(H—M^+{=}O)$ needed for removal of OH from $H—M^+{=}O$ can be estimated from known values of $D(M^+—H)$[3] and $D(M^+{=}O)$.[8] The results are listed in Table I and differ greatly from our measured OH binding energies, except in the case of Ti^+. We take this as evidence that our ions have the structure $M^+—OH$, with the possible exception of $H—Ti^+{=}O$.

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(1) Initial work was performed at the Chemistry Department of the University of Utah.

(2) Magnera, T. F.; David, D. E.; Stulik, D.; Orth, R. G.; Jonkman, H. T.; Michl, J. *J. Am. Chem. Soc.*, in press.

(3) Elkind, J. L.; Armentrout, P. B. *Inorg. Chem.* **1986**, *25*, 1078.

(4) (a) Dzidić, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466. (b) Kochanski, E.; Constantin, E. *J. Chem. Phys.* **1987**, *87*, 1661. (c) Tang, I. N.; Lian, M. S.; Castleman, A. W., Jr. *J. Chem. Phys.* **1976**, *65*, 4022. Tang, I. N.; Castleman, A. W., Jr. *J. Chem. Phys.* **1974**, *60*, 3981. Tang, I. N.; Castleman, A. W., Jr. *J. Chem. Phys.* **1972**, *57*, 3638.

(5) Holland, P. M.; Castleman, A. W., Jr. *J. Chem. Phys.* **1982**, *76*, 4195.

(6) (a) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (b) Stevens, A. E.; Beauchamp, J. L. *Chem. Phys. Lett.* **1981**, *78*, 291. Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501. Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 8117.

(7) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 6176.

(8) Kang, H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5663. Kang, H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 7502.

(9) Murad, E. *J. Chem. Phys.* **1980**, *73*, 1381.

(10) Moore, C. E. *Atomic Energy Levels*; NSRDS-NBS 35; National Bureau of Standards: Washington, DC, 1971; Vol. II.

(11) The large difference between the first and second hydration energies of Fe^+ calls for caution in assuming bond energy additivity. We have relied only on large energy differences in drawing structural conclusions.

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