Formation of Molybdenum Silyl Complexes from Hydrides by Net Silylene Transfer: Evidence for a Radical Chain Mechanism

Donald H. Berry* and Jack H. Mitstifer

*Department of Chemistry and Laboratory for
Research on the Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104*

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Carbenes and carbene precursors are known to react with transition-metal complexes to produce alkyl[1] and alkylidene[2,3] complexes, as well as a host of compounds in which the intact precursor molecule is coordinated to the metal center.[4] Our interest in the synthetic and mechanistic chemistry of transition-metal complexes of silicon ligands led us to consider the analogous reactions of silylenes. Unfortunately, silylene sources comparable to diazomethane or methylenetrimethylphosphorane are not known; silylene generation is usually accomplished under photolytic[5] or pyrolytic[6] conditions which only the hardest of organotransition-metal products could withstand. It was therefore with great interest that we noted Seyferth and co-workers' reports of net dimethylsilylene transfer at 65–75 °C from hexamethylsilacyclopropane (HMS) to a variety of substrates.[7-10] A substantial body of evidence has been presented which indicates that thermal extrusion of dimethylsilylene can occur from HMS.[7] We now report the silylation of molybdenum hydride bonds by using HMS under mild conditions via a radical chain mechanism.

Treatment of hydrocarbon solutions of CpMo(CO)$_2$(L)H (L = CO, PMe$_3$; **1a,b**) with an equimolar quantity of HMS results in formation of CpMo(CO)$_2$(L)SiMe$_2$H (**2a,b**) at 25 °C, as shown in eq 1. The silyl compounds are formed with >95% selectivity

1a,b   **2a,b**
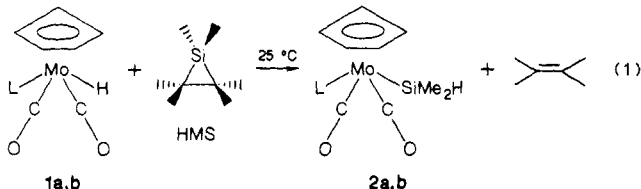
as determined by ^{1}H NMR (ca. 70% isolated yields[11,12]). A quantitative yield of 2,3-dimethyl-2-butene (tetramethylethylene)
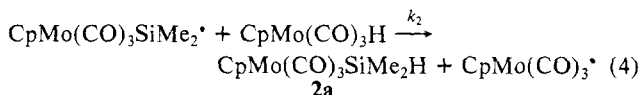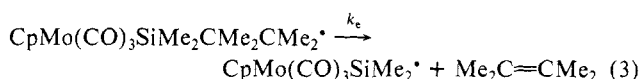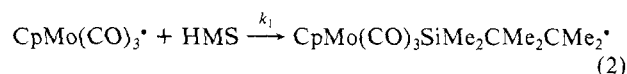
is detected, along with a small amount of [CpMo(CO)$_2$(L)]$_2$ (2–5%).

Spectroscopic data for **2a** are virtually identical with those reported by Malisch and Kuhn, who prepared **2a** by the reaction of Na[CpMo(CO)$_3$] with Me$_2$SiHCl.[13] Attempts to prepare **2b** by thermal or photolytic substitution of **2a** with PMe$_3$ led to extensive decomposition.

Although the formation of **2a** and **2b** corresponds to the desired net silylene transfer, the nature of this transformation is not immediately obvious. In addition to the extrusion of dimethylsilylene at temperatures >65 °C, HMS has been shown to undergo a wide range of reactions at lower temperatures,[14-17] including free radical chain reactions with tin and germanium hydrides.[18] Therefore a more detailed study seemed in order.

Although kinetic studies seem to indicate that reaction 1 is first order in both [**1a**] and [HMS], rates were found to vary significantly with different batches of **1a**, suggesting initiation or catalysis by trace impurities.[19,20] HMS has previously been shown to react by radical pathways with certain reagents.[14,17,21] In the case of the heavier group 14 hydrides, the CMe$_2$CMe$_2$ moiety is retained as a "thexyl" group in the products, R$_3$M–SiMe$_2$CMe$_2$CMe$_2$H (M = Sn, Ge).[18,22] Seyferth has proposed a radical chain mechanism for these reactions.

Given the well-established role of chain and nonchain free radical mechanisms in reactions of transition-metal hydrides (including **1a**),[23] it is plausible to extend Seyferth's mechanism to the molybdenum hydrides. To account for the formation of olefin and the dimethylsilyl complex in this instance requires an additional step involving elimination of tetramethylethylene, yielding a molybdenum-substituted silyl radical (eq 2–4).

$$CpMo(CO)_3{}^{\bullet} + HMS \xrightarrow{k_i} CpMo(CO)_3SiMe_2CMe_2CMe_2{}^{\bullet} \quad (2)$$

$$CpMo(CO)_3SiMe_2CMe_2CMe_2{}^{\bullet} \xrightarrow{k_e}$$
$$CpMo(CO)_3SiMe_2{}^{\bullet} + Me_2C{=}CMe_2 \quad (3)$$

$$CpMo(CO)_3SiMe_2{}^{\bullet} + CpMo(CO)_3H \xrightarrow{k_2}$$
$$CpMo(CO)_3SiMe_2H + CpMo(CO)_3{}^{\bullet} \quad (4)$$
$$\textbf{2a}$$

Addition of silyl radicals to olefins is usually quite exothermic, and the reverse, silyl elimination, has only been observed at elevated temperatures.[24] However, interaction of the unpaired electron on silicon with the molybdenum center could provide sufficient stabilization of the silyl radical to favor the elimination shown in (3) at lower temperatures.

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(11) A solution of CpMo(CO)$_3$H (302 mg, 1.23 mmol) and HMS (240 μL, 1.32 mmol) in 6 mL of petroleum ether was stirred in the dark under argon for 7 h, filtered to remove the red crystals of [CpMo(CO)$_3$]$_2$ (12 mg, 4%), and recrystallized from petroleum ether at −80 °C to yield **2a** as pale pink crystals (250 mg, 67%). ^{1}H NMR δ 4.97 (septet, ^3J = 3.7 Hz, SiMe$_2$*H*), 4.45 (s, Cp), 0.59 (d, ^3J = 3.7 Hz, Si*Me*$_2$H).

(12) **2b** prepared in 70% yield by a similar procedure,[11] but with a 48-h reaction time. ^{1}H NMR δ 5.29 (septet, ^3J = 3.7 Hz, SiMe$_2$*H*), 4.58 (d, $^3J_{PH}$ = 0.8 Hz, Cp), 0.99 (d, $^2J_{PH}$ = 8.9 Hz, PMe$_3$), 0.87 (d, ^3J = 3.7 Hz, Si*Me*$_2$H); IR ν(CO) = 1914 (s), 1844 (s) cm^{-1}; ν(Si–H) = 2061 (w) cm^{-1}; mass spectrum, *m/z*, calcd for C$_{12}$H$_{21}$MoPSi, 354.01025; found, 354.00644.

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(19) The reaction was followed by ^{1}H NMR in benzene-d_6 under nitrogen except where noted. Rates described as equivalent in the text are the same within the estimated standard deviation, ca. 5%.

(20) In all cases **1a** was sublimed twice and stored at −40 °C in the drybox freezer. No impurities were evident in the ^{1}H NMR spectrum.
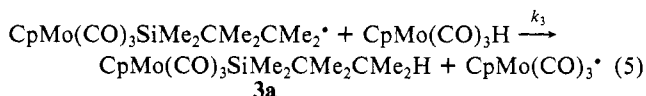
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It was not expected that such similar radical chain mechanisms would selectively yield thexyl products for tin and germanium vs. the dimethylsilyl products in the case of molybdenum hydrides. However, analysis employing the steady-state approximation for the radical species in (2)–(5) predicts that, irrespective of initiation,

$$CpMo(CO)_3SiMe_2CMe_2CMe_2{}^{\bullet} + CpMo(CO)_3H \xrightarrow{k_3}$$
$$CpMo(CO)_3SiMe_2CMe_2CMe_2H + CpMo(CO)_3{}^{\bullet} \quad (5)$$
$$\mathbf{3a}$$

the product ratio for this mechanism is given by [3a]/[2a] = k_3[1a]/k_e, where **3a** is the thexylsilyl product in analogy to the group 14 derivatives.[25] In other words, formation of the thexyl product should be favored by high concentrations of **1a**.

As no substantial quantity of any other product was observed at hydride concentrations up to ca. 0.9 M in benzene, a finely ground sample of **1a** was treated with neat HMS. Analysis of this reaction mixture by ^{1}H NMR showed the formation of **2a** and ca. 13% of **3a**, the thexyldimethylsilyl molybdenum complex,[26] as predicted by the proposed radical chain mechanism.

The trace amounts of molybdenum dimers [CpMo(CO)$_2$(L)]$_2$ formed in eq 1 are consistent with chain termination during the reaction.

A ca. 10-fold increase in the initial rate is observed upon addition of a few mole percent of triphenylmethyl radical (as the dimer).[27] In a separate experiment, stoichiometric reaction of trityl dimer with **1a** in the absence of HMS produced triphenylmethane and [CpMo(CO)$_3$]$_2$, presumably from the coupling of CpMo(CO)$_3$ radicals.

Attempts to establish the intermolecularity of (1) by means of a cross-over experiment using CpMo(CO)$_3$D and (MeCp)-Mo(CO)$_3$H were thwarted by the extremely rapid isotopic scrambling observed between these complexes in the absence of HMS.

Comparison of initial rates measured by using a single batch of **1a** shows no effect on eq 1 by carbon monoxide (1.5 atm) or tetramethylethylene (0.317 M).[19] These facts, in conjunction with a negative activation entropy ($\Delta S^{\ddagger} = -25 \pm 3$ eu),[28] preclude reversible dissociation of these species in the rate-controlling step. Changing solvent from benzene to THF also leaves the rate unchanged.

In summary, silylene transfer from HMS to molybdenum hydrides is quantitative, and appears to proceed by radical chain ring opening and olefin elimination to yield a transient silyl radical. The apparent stabilization of the silyl radical by metal substitution suggests that radical paths may be more common with metal complexes of silicon ligands than is generally observed in organosilicon chemistry.[29]

(25) The product ratio is determined from the following rate expressions for formation of products: d[2a]/dt = $k_1 k_e$[Mp$^{\bullet}$][HMS]/(k_3[1a] + k_e) and d[3a]/dt = $k_1 k_3$ [Mp$^{\bullet}$] [HMS] [1a]/(k_3 [1a] + k_e), where Mp designates the CpMo(CO)$_3$ group.

(26) The residue from a subsequent fractional sublimation was enriched in this product (60%), although we have been unable to isolate **3a** completely free of **1a** and **2a**. Compound **3a**: ^{1}H NMR δ 4.59 (s, Cp), 1.98 (septet, J = 6.7 Hz, C*Me*$_2$*H*), 1.07 (s, SiC*Me*$_2$), 0.94 (d, J = 6.7 Hz, C*Me*$_2$H), 0.63 (s, Si*Me*$_2$); mass spectrum, m/z calcd 390.0549; found 390.0604.

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(28) Activation parameters were determined from an Eyring plot of rates at four temperatures (16.7–50.5 °C): $\Delta H^{\ddagger} = 13.3 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger}$ = −25 ± 3 eu.

(29) The facile radical chain halogenation of silicon hydrides in M(R$_2$SiH) complexes also appears to be a result of the stability of M(R$_2$Si$^{\bullet}$).[13]

Reversible Long-Range Electron Transfer in Ruthenium-Modified Sperm Whale Myoglobin

Charles M. Lieber, Jennifer L. Karas, and Harry B. Gray*

Contribution No. 7488, Arthur Amos Noyes Laboratory
California Institute of Technology
Pasadena, California 91125
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The kinetics and thermodynamics of long-range (>10 Å) electron transfer (ET) for several ruthenium-modified metalloproteins have been reported recently.[1-5] Electron transfer in these systems has been measured from a reduced surface ruthenium(II) (a$_5$Ru, a = NH$_3$) to an oxidized-protein center (either Fe^{III} or Cu^{II}). Measurement of ET in the reverse direction, however, requires formation of a mixed-valence ruthenium(III)–reduced-protein complex, a species that was inaccessible by methods previously employed.[2-4] We have now developed a technique utilizing flash photolysis to generate this key intermediate, thereby enabling us to measure ET rates from the iron(II)–heme to different ruthenium(III) histidine-48 acceptors in sperm whale myoglobin (Mb). In this system the closest donor–acceptor edge–edge distance is 13 Å.[1,2]

Our methodology for studying ET from a reduced-protein center to a covalently bound ruthenium acceptor is summarized in Scheme I; the kinetics are followed using flash spectroscopic techniques. Flash photolysis generates electronically excited tris(2,2′-bipyridine)ruthenium(II) (Ru(bpy)$_3^{2+}$*), a powerful oxidant, which is quenched via electron transfer from the reduced (Ru^{II}) metalloprotein complex (Ru^{II}–PFe^{II}, Fe^{II} = iron(II)–heme or other reduced-protein center) in a rapid bimolecular step to yield Ru^{III}–PFe^{II}. In order to observe the desired intramolecular ET process, Ru^{III}–PFe^{II} → Ru^{II}–PFe^{III}, it is essential that Ru(bpy)$_3^+$ be efficiently removed from the system; otherwise, the exergonic ($\Delta E^{\circ} = 1.1$ V) back reaction (k_b, Scheme I) will rapidly regenerate Ru^{II}–PFe^{II}. We have found that a suitable scavenger system for aqueous solution experiments consists of nickel(II) hexamethyltetraazacyclodecane (Ni^{II}Me$_6$ane) and 3-bromopropionic acid (RBr). In this system Ni^{II}Me$_6$ane is reduced by Ru(bpy)$_3^+$ to the Ni^I species, which then reacts irreversibly with RBr.[6]

With this technique, we have measured the Fe^{II} to Ru^{III} ET kinetics in a$_5$Ru(histidine-48)-modified myoglobin (a$_5$Ru(48)-MbFe), a system in which the reduction potentials of the heme and the pentaammineruthenium are closely matched ($\Delta E^{\circ} = 20$ mV).[1,2] The change in the heme absorption at 556 nm following flash photolysis of a solution containing a$_5$Ru^{II}(48)MbFe^{II} is shown in Figure 1. Immediately after the flash, a small net bleaching is observed (the direct oxidation of the heme by Ru(bpy)$_3^{2+}$*), followed by a relatively slow further oxidation that can be assigned

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