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The First Transition Metal η^2-SiH$_4$ Complexes, *cis*-Mo(η^2-SiH$_4$)(CO)(R$_2$PC$_2$H$_4$PR$_2$)$_2$, and Unprecedented Tautomeric Equilibrium between an η^2-Silane Complex and a Hydridosilyl Species: A Model for Methane Coordination and Activation

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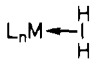
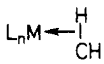
In recent years there has been great interest in the activation of methane by transition metal complexes in the hope of developing catalytic methane conversion.[1] Several organometallic systems are now known to cleave a C−H bond of methane to give hydridomethyl complexes.[2] However, the pathway by which the C−H bond cleavage occurs is less clear. There is a growing body of theoretical[3] and experimental data[4] in support of the intermediacy of a methane complex along the reaction coordinate for oxidative addition/reductive elimination of methane at transition metal centers, but the structure of such a methane complex is unknown. By analogy to the well-characterized η^2-H$_2$ complexes (**A**),[5] it seems likely that methane could coordinate to the metal in an η^2-fashion via a C−H σ bond (**B**). Although the isolation of a stable methane complex has been considered achievable,[6] the goal remains elusive. This prompted us to investigate the binding modes of SiH$_4$, a heavier congener of CH$_4$, toward transition metals in order to gain insight into methane coordination and activation. Here we describe the first examples of transition metal η^2-SiH$_4$ complexes (**C**), in which SiH$_4$ is coordinated to the metal in an η^2-fashion via a Si−H σ bond, and an unprecedented tautomeric equilibrium between an η^2-SiH$_4$ complex and a hydridosilyl species (eq 1), which serves as a model for methane coordination and subsequent activation.



A



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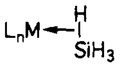
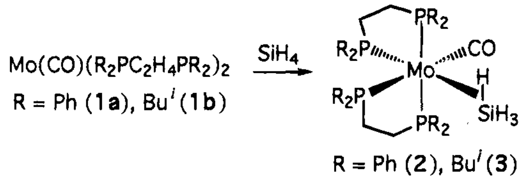


C

(1)

We recently reported that the agostic Mo···H−C interaction in Mo(CO)(R$_2$PC$_2$H$_4$PR$_2$)$_2$ is readily displaced by primary or secondary silanes to give η^2-silane complexes.[7] This is the first system in which Si−H, H−H, and agostic C−H σ bonds can be bound to the same metal fragment in an η^2-fashion. We have now found that reactions of Mo(CO)(R$_2$PC$_2$H$_4$PR$_2$)$_2$ (R = Ph (**1a**),[8] Bu^i (**1b**)[9]) with 1 equiv of SiH$_4$ in toluene give the first examples of η^2-SiH$_4$ complexes *cis*-Mo(η^2-SiH$_4$)(CO)(R$_2$PC$_2$H$_4$PR$_2$)$_2$ (R = Ph (**2**), Bu^i (**3**)) (eq 2), which are isolated as yellow solids.[10] The ^{31}P{^{1}H} NMR spectrum of **2** or **3** at room temperature shows four multiplet resonances each integrating for one phosphorus, indicating that all phosphorus nuclei are inequivalent. This is consistent with a six-coordinate octahedral structure, as shown in eq 2, with one Si−H σ bond of SiH$_4$ occupying a site cis to the CO. In contrast, if **2** and **3** were formulated as seven-coordinate hydridosilyl complexes, they would probably be fluxional at room temperature and give a single resonance in the ^{31}P{^{1}H} NMR spectra. Fluxionality has been a general observation for seven-coordinate complexes due to low-barrier intramolecular rearrangements.[11]



(2)

The η^2-coordination of SiH$_4$ in **2** and **3** is confirmed by the observation of J_{SiH} coupling constants (Table 1) for the η^2-bound Si−H bonds. The high-field region of the ^{1}H NMR spectrum of **2** or **3** shows a multiplet resonance assignable to the η^2-bound Si−H proton which is coupled to the four inequivalent phosphorus nuclei. Decoupling of the ^{31}P nuclei causes the multiplet resonance to collapse into a singlet flanked by ^{29}Si satellites. The J_{SiH} values of 50 and 31 Hz for **2** and **3**, respectively, fall within the range of values (20−70 Hz) found for the known η^2-silane complexes in which the silicon bears one or more substituents other than hydrogen.[7,12] These results suggest that **2** and **3** are better formulated as six-coordinate η^2-SiH$_4$ complexes than as seven-coordinate hydridosilyl species.

The X-ray crystal structure of **3** is shown in Figure 1.[13] The four hydrogen atoms on the Si were not located due to a positional disorder between the η^2-SiH$_4$ and CO ligands. If the molybdenum-bound Si−H hydrogen is disregarded, the coordination geometry about the molybdenum is that of a distorted octahedron, with the CO and Si being cis to each other. In addition, the geometry of the MoP$_4$CSi core is very similar to that in the related compound *cis*-Mo(η^2-H-SiH$_2$Ph)(CO)(Et$_2$C$_2$H$_4$-

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(10) Data for **2**: ^{1}H{^{31}P} NMR (C$_6$D$_6$, 298 K) δ 6.2−8.0 (m, Ph, 40 H), 4.46 (s, $^1J_{\mathrm{SiH}}$ = 181 Hz, 3 H, Si*H*$_3$), 1.7−2.4 (m, 8 H, C*H*$_2$), −6.87 (s, J_{SiH} = 50 Hz, 1 H, Mo(η^2-*H*-*Si*)); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 298 K) δ 72.1 (m, 1 P), 66.9 (m, 1 P), 56.9 (m, 1 P), 44.9 (m, 1 P); IR (Nujol, cm^{-1}) ν(Si−H) 2081, 2028, 2000, ν(CO) 1783, ν(Mo−H−Si) 1743. Anal. Calcd for C$_{53}$H$_{52}$MoOP$_4$Si: C, 66.80; H, 5.50. Found: C, 66.09; H, 5.34. Data for **3**: ^{1}H{^{31}P} NMR (C$_6$D$_6$, 298 K) δ 4.34 (s, $^1J_{\mathrm{SiH}}$ = 163 Hz, 3 H, Si*H*$_3$), 0.9−2.8 (m, 80 H, Bu$^i_2$PC$_2$H$_4$PBu$^i_2$), −7.98 (s, J_{SiH} = 31 Hz, 1 H, Mo(η^2-*H*-Si)); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 298 K) δ 67.3 (m, 1 P), 52.9 (m, 1 P), 46.9 (m, 1 P), 37.2 (m, 1 P); IR (Nujol, cm^{-1}) ν(Si−H) 2059, 2028, 1967, ν(CO) 1788, ν(Mo−H−Si) 1752. Anal. Calcd for C$_{37}$H$_{84}$MoOP$_4$Si: C, 56.04; H, 10.68. Found: C, 55.72; H, 10.51.

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(13) Crystal data for **3**: light yellow prism, 0.16 × 0.18 × 0.35 mm^3; M_r = 793.0; triclinic, space group $P\bar{1}$; a = 10.362(2) Å, b = 10.455(2) Å, c = 24.034(5) Å, α = 77.76(3)°, β = 77.62(3)°, γ = 63.27(3)°, V = 2251 Å^3, Z = 2; D_{calcd} = 1.164 g/cm^3; Enraf-Nonius CAD4 diffractometer; 193 K; Mo Kα radiation (λ = 0.710 73 Å); scan method ω; data collection range 4.0−50.0°; total number of reflections measured, 8379; number of independent reflections, 7898 (R_{int} = 2.0%); number of observed reflections, 5282 ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by a full matrix least-squares procedure to give final residuals of R = 0.050 and R_w = 0.061; GOF = 1.20.

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Table 1. J_{SiH} Coupling Constants[a] for *cis*-Mo(η^2-SiH_4)(CO)($R_2PC_2H_4PR_2$)$_2$

complex	R	J_{SiMoH} (Hz)[b]	$^1J_{SiH}$ (Hz)[c]
2	Ph	50	181
3	Bu^i	31	163
4a	Et	35	164

[a] Measured by $^1H\{^{31}P\}$ NMR. [b] Si–H coupling constants for η^2-bound Si–H bonds. [c] Si–H coupling constants for uncoordinated Si–H bonds.

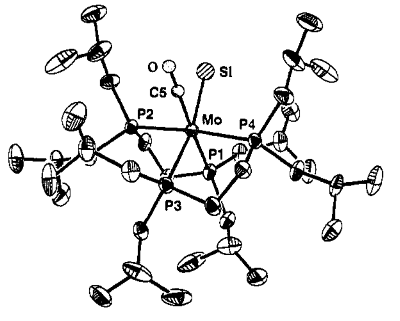


Figure 1. ORTEP drawing with 50% probability ellipsoids (one of each pair of disordered atoms is omitted for clarity) of *cis*-Mo(η^2-SiH_4)(CO)($Bu^i_2PC_2H_4PBu^i_2$)$_2$ (**3**). Selected bond lengths (Å) and angles (deg): Mo–P(1), 2.525(2); Mo–P(2), 2.479(2); Mo–P(3), 2.531(2); Mo–P(4), 2.454(2); Mo–C(5), 1.927(11); Mo–Si, 2.556(4); P(2)–Mo–P(4), 174.5(1); Si–Mo–C(5), 82.2(3); P(1)–Mo–Si, 92.3(1); P(2)–Mo–Si, 79.0(1); P(3)–Mo–Si, 168.7(1); P(4)–Mo–Si, 106.1(1).

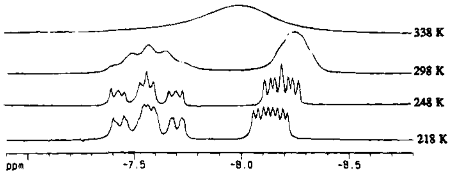
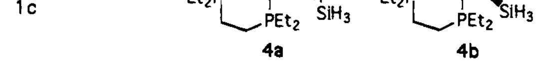


Figure 2. High-field region of variable-temperature ^1H NMR spectra (500.13 MHZ) of an equilibrium mixture of **4a** and **4b** in $C_6D_5CD_3$.

$PEt_2)_2$,[7] in which the three hydrogen atoms on the Si were located, confirming the η^2-coordination of a Si–H σ bond. The Mo–Si distances in the two compounds (2.556 and 2.501 Å) are also similar. Thus, the crystal structure of **3** is consistent with the η^2-SiH_4 coordination observed in solution by NMR.

Reaction of Mo(CO)($Et_2PC_2H_4PEt_2$)$_2$ (**1c**)[9] with 1 equiv of SiH_4 in toluene gives *cis*-Mo(η^2-SiH_4)(CO)($Et_2PC_2H_4PEt_2$)$_2$ (**4a**) (eq 3), which is isolated as a pale yellow solid.[14] Remarkably,



1c

4a

4b

(3)

in solution the η^2-SiH_4 complex **4a** is in equilibrium with its seven-coordinate hydridosilyl tautomer MoH(SiH_3)(CO)($Et_2PC_2H_4PEt_2$)$_2$ (**4b**) (eq 3). Thus, the high-field region of the ^1H NMR spectrum (Figure 2) at 298 K shows two resonances, with the broad multiplet at δ −8.27 assigned to the η^2-bound Si–H proton of **4a** and the broad quintet at δ −7.58 assigned to the terminal hydride ligand of **4b**. The broadness of the two resonances is due to the exchange between **4a** and **4b**. Accordingly, upon cooling of the sample the two resonances become sharp, whereas upon heating they broaden and then coalesce into a broad feature. Similar temperature-dependent behavior is observed for the two resonances arising from the uncoordinated SiH_3 protons of **4a** and **4b**. The η^2-SiH_4 coordination in **4a** is confirmed by the J_{SiH} coupling constant of 35 Hz (Table 1) observed for the η^2-bound Si–H bond by $^1H\{^{31}P\}$ NMR.

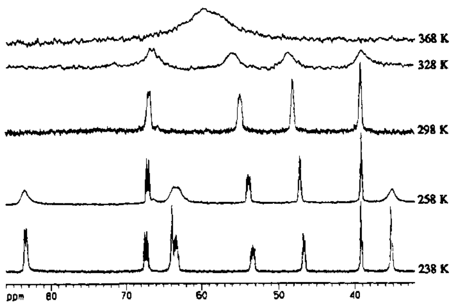


Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra (202.46 MHz) of an equilibrium mixture of **4a** and **4b** in $C_6D_5CD_3$.

The coexistence of **4a** and **4b** is also demonstrated by $^{31}P\{^1H\}$ NMR (Figure 3). At 298 K, four resonances are observed for **4a**, as in the case of **2** and **3**, which is consistent with the six-coordinate octahedral structure, whereas no resonances are observed for **4b** due to the fluxionality of the seven-coordinate structure.[11] Cooling the sample below 298 K leads to the gradual appearance of four new resonances assignable to **4b**. Heating the sample above 298 K causes exchange of **4a** with **4b**, and only an averaged resonance is observed at 368 K.

Although several examples of tautomeric equilibria between an η^2-H_2 complex and a dihydride species are known,[15] eq 3 represents the first example of tautomeric equilibrium between an η^2-silane complex and a hydridosilyl species. The ratio of **4a** to **4b** is temperature-dependent, and ^1H NMR integration yields thermodynamic parameters for conversion of **4a** to **4b**: $\Delta H = -0.61 \pm 0.2$ kcal/mol and $\Delta S = -2.1 \pm 0.7$ eu.

It is of interest to note that both the NMR data of **2**, **3**, and **4a** and the crystal structure of **3** indicate that the η^2-SiH_4 and CO ligands are cis to each other in an octahedral structure, which is in contrast to the related η^2-H_2 complexes *trans*-Mo(η^2-H_2)(CO)($PR_2PC_2H_4PR_2$)$_2$ (R = Ph,[9] CH_2Ar[16]), in which the η^2-H_2 and CO ligands are trans to each other. This structural difference is likely to have electronic origin, since the η^2-SiH_4 ligand is sterically not very demanding. It is conceivable that the higher π-accepting ability of SiH_4 as compared to H_2 favors SiH_4 being cis to the strongly π-accepting CO ligand.

In summary, we have synthesized the first examples of transition metal η^2-SiH_4 complexes and obtained spectroscopic evidence for an unprecedented tautomeric equilibrium between an η^2-SiH_4 complex and a hydridosilyl species. The η^2-coordination of SiH_4 in **4a** followed by Si–H bond cleavage to give the hydridosilyl species **4b** serves as a model for methane coordination and subsequent activation.

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Supplementary Material Available: X-ray diffraction data for **3** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) Data for **4a** and **4b**: $^1H\{^{31}P\}$ NMR ($C_6D_5CD_3$, 268 K) δ 4.56 (s, $^1J_{SiH} = 164$ Hz, SiH_3, **4a**), 3.48 (s, $^1J_{SiH} = 143$ Hz, SiH_3, **4b**), 0.5–2.0 (m, PC_2H_4P, C_2H_5), −7.57 (s, Mo*H*, **4b**), −8.23 (s, $J_{SiH} = 35$ Hz, Mo(η^2-*H*-Si), **4a**); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 238 K) δ 83.3 (m, 1 P, **4b**), 67.4 (m, 1 P, **4a**), 63.9 (m, 1 P, **4b**), 63.4 (m, 1 P, **4b**), 53.1 (m, 1 P, **4a**), 46.4 (m, 1 P, **4a**), 39.1 (m, 1 P, **4a**), 35.2 (m, 1 P, **4b**); IR (Nujol, cm^{-1}) ν(Si–H) 2047, 1995, 1972, ν(CO) 1775, ν(Mo–H–Si) 1732. Anal. Calcd for $C_{21}H_{52}MoOP_4Si$: C, 44.36; H, 9.22. Found: C, 44.24; H, 9.14.

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