Organometallics **2006**, *25*, 3791−3794 3791

Photochemical Reaction of $Mo(CO)_6$ with Et_2SiH_2: Spectroscopic Characterization and Crystal Structure of the Bis{(μ-η^2-hydridodiethylsilyl)tetracarbonylmolybdenum(I)} Complex [{$Mo(\mu\text{-}\eta^2\text{-}H{-}SiEt_2)(CO)_4$}$_2$]

Magdalena Stosur, Andrzej Kochel, Antoni Keller, and Teresa Szymańska-Buzar*

Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

Received April 3, 2006

Summary: Photolysis of $Mo(CO)_6$ *in n-heptane solution creates a coordinatively unsaturated* d^6 *species, which interacts with the Si−H bond of* Et_2SiH_2 *and leads to the formation of Mo−H and Mo−Si bonds. The formation of a Mo−H bond was corroborated by* ^1H *NMR spectroscopy due to the detection of a high-field resonance at* $\delta = -8.33$ *flanked by* ^{29}Si *satellites. The formation of Mo−Si bonds was confirmed by the detection of two sets of* ^{29}Si *satellites on the hydride signal, which provided* $J_{Si-H} = 57$ *and 33 Hz, and by the* $^{29}Si\{^1H\}$ *NMR spectrum, which revealed a resonance at* $\delta = 207.7$. *The latter signal in the* ^{29}Si *NMR spectrum was observed as a doublet of quintets with* $^1J_{Si-H} = 58$ *Hz and* $^2J_{Si-H} = 41$ *Hz. The* ^{95}Mo *NMR spectrum showed at high field a resonance at* $\delta = -3785$, *characteristic for seven-coordinate molybdenum compounds. The molecular structure of a novel bis{(*μ-η^2*-hydridodiethylsilyl)tetracarbonylmolybdenum(I)} complex, [{*$Mo(\mu\text{-}\eta^2\text{-}H{-}SiEt_2)(CO)_4$*}*$_2$*], was established by single-crystal X-ray diffraction studies. The molybdenum hydride observed in the* ^1H *NMR spectrum was located in the structure at a chemically reasonable position between the Mo and Si atoms of the Mo−Si bonds of the bridging silyl ligand with a Si−H bond length of 1.615(3) Å and that of the Mo−H bond amounting to 1.786(5) Å.*

Introduction

The activation of an Si−H bond by transition-metal complexes is central to catalytic processes known as hydrosilylation,[1] which is presumed to proceed through interaction of the Si−H bond of silane with the metal. Silanes can bind to a transition-metal center as σ-bond ligands in an η^2-fashion and then transform into a silyl-hydride complex, which is a key problem in the field of transition-metal-mediated Si−H bond activation, where silane and silyl complexes play an important role. A great amount of experimental and theoretical data for the binding and oxidative addition of silanes to coordinatively unsaturated transition-metal complexes has been accumulated recently.[2]

Research in our group has been focused on the applications of photochemistry to the synthesis of novel organometallic compounds, work being aimed primarily at the use of group 6 metal carbonyls. In recent studies we have found that photochemically activated $W(CO)_6$ reacts with the diphenylsilane Ph_2SiH_2 to yield the complex [(μ-$SiPh_2$){$W(CO)_5$}$_2$], which contains two $W(CO)_5$ moieties linked by a bridging silylene $SiPh_2$ ligand and a W−W bond.[3] This reaction most likely began with the oxidative addition of Ph_2SiH_2 to the coordinatively unsaturated intermediate $W(CO)_5$ and the formation of a seven-coordinate hydrido-silyl species, although no intermediates were observed and it is not clear at what point dimerization and H_2 loss occurred. In this paper we report Si−H bond activation of diethylsilane by photochemically activated $Mo(CO)_6$. The product of this reaction has been characterized by IR and NMR spectroscopy and has been shown by X-ray diffraction studies to be a silicon-bridged molybdenum dimer, which formally contains two molybdenum atoms in the first oxidation state bridged by two silyl ligands with an α-agostic Si−H bond. The X-ray crystal structure of an analogous tungsten complex, [{$W(\mu\text{-}\eta^2\text{-}H{-}SiEt_2)(CO)_4$}$_2$], was reported by Bennett and Simpson in 1971.[2b] Unfortunately, the hydrogen atoms were not located in the latter compound and no spectroscopic evidence for W−H or Si−H interaction was offered.

Results and Discussion

Photochemical Reaction of $Mo(CO)_6$ with Et_2SiH_2. When photochemical reaction of $Mo(CO)_6$ and Et_2SiH_2 in *n*-heptane solution was monitored by IR spectroscopy, the decay of the $\nu(C{\equiv}O)$ frequency at 1989 cm^{-1}, characteristic for $Mo(CO)_6$, and the appearance of new $\nu(C{\equiv}O)$ bands at 2042, 1982, and 1941 were observed. The ^1H NMR spectrum (500 MHz, −30 °C, toluene-d_8) of the residue obtained by the evaporation of *n*-heptane revealed a hydride resonance at $\delta = -8.33$ ppm, which appeared as a singlet (Figure 1). The high-field chemical shifts of this signal suggest a bridging character of the hydride ligand ($\delta = -4.0$ was found for terminal hydride in the $[MoH(CO)_5]^-$ anion, while for bridging hydride in the $[Mo_2(\mu\text{-}H)_2(CO)_8]^{2-}$ dianion, $\delta = -7.7$, and in the $[Mo_2(\mu\text{-}H)(CO)_{10}]^-$ anion, $\delta = -12.15$).[4] In addition, two sets of satellites

---

* Corresponding author. Fax: +48 71 328 23 48. Tel: +48 71 375 7221. E-mail: tsz@wchuwr.chem.uni.wroc.pl.

(1) (a) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1974**, *96*, 6235. (b) Abdelgader, W.; Chmielewski, D.; Grevels, F.-W.; Özkar, S.; Peynircioglu, N. B. *Organometallics* **1996**, *15*, 604. (c) Brunner, H.; Weber, M.; Zabel, M. *J. Organomet. Chem.* **2003**, *684*, 6. (d) Ganicz, T.; Mizerska, U.; Moszner, M.; O'Brien, M.; Perry, R.; Stańczyk, W. A. *Appl. Catal. Gen.* **2003**, *259*, 49. (e) Gustafsson, M.; Frejd, T. *J. Organomet. Chem.* **2004**, *689*, 438. (f) Arena, C. G.; Pattacini, R. *J. Mol. Catal. A: Chem.* **2004**, *222*, 47. (g) Paris, S. I. M.; Lemke, F. R. *Inorg. Chem. Commun.* **2005**, *8*, 425. (h) Imilinger, N.; Wurst, K.; Buchmeiser, M. R. *J. Organomet. Chem.* **2005**, *690*, 4433. (i) Barieille, L.; Becht, S.; Cui, J. L.; Gendre, P.; Moïse, C. *Organometallics* **2005**, *24*, 5802. (j) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374.

(2) (a) Elder, M. *Inorg. Chem.* **1970**, *9*, 762. (b) Bennett, M. J.; Simpson, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 7156. (c) Kawano, Y.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* **1992**, *428*, 125. (d) Luo, X.-L.; Kubas, G. J.; Bryan, J. C.; Burns, C. J.; Unkefer, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 10312. (e) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 1159. (f) Simons, R. S.; Tessier, C. A. *Organometallics* **1996**, *15*, 2604. (g) Butts, M. D.; Bryan, J. C. Luo, X.-L.; Kubas, G. J. *Inorg. Chem.* **1997**, *36*, 3341. (h) Corey, J. Y.; Braddock-Wiking, J. *Chem. Rev.* **1999**, *99*, 175. (i) Lin, Z. *Chem. Soc. Rev.* **2002**, *31*, 239. (j) Yu, X.; Morton, L. A.; Xue, Z.-L. *Organometallics* **2004**, *32*, 2210.

(3) Gądek, A.; Kochel, A.; Szymańska-Buzar, T. *Organometallics* **2003**, *22*, 4869.

10.1021/om060290d CCC: $33.50

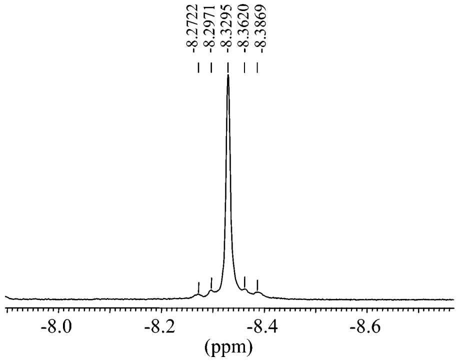


Figure 1. Hydride region of a ^{1}H NMR spectrum (500 MHz, toluene-d_8, −30 °C) of **1** showing two sets of ^{29}Si satellites for the agostic hydrogen atom (Si···H−Mo−Si).

of equal intensity were detected on the hydride signal, which provided a coupling constant value of 57 and 34 Hz. Integration of these satellite signals relative to the parent singlet supports their assignment as ^{29}Si (4.7% natural abundance) satellites. Two sets of ^{29}Si satellites of the Mo−H resonance point to the presence of two silicon ligands at the molybdenum center. The $J_{\mathrm{Si-H}}$ value of 57 Hz is typical of η^2-silane complexes[2] and strongly suggests a σ (Si−H) interaction with the molybdenum center. The second $J_{\mathrm{Si-H}}$ value of 33 Hz implies the presence of another silicon atom at the molybdenum center, coupled with a proton through two bonds. In addition to the ^{1}H NMR data, the ^{29}Si{^{1}H} NMR spectra (toluene-d_8) show a resonance at $\delta = 207.7$. In the ^{29}Si NMR spectrum the latter resonance was observed as a doublet of quintets with $^{1}J_{\mathrm{Si-H}} = 58$ Hz, typical for the Mo−η^2-(H−Si) bond,[2d] and with $^{2}J_{\mathrm{Si-H}} = 41$ Hz, due to coupling with four methylene protons of two ethyl groups. The large downfield chemical shift of the silicon resonance compared to that observed for the parent silane ($\delta = -22.62$ for Et_2SiH_2) suggests some degree of silylene character of the silicon ligand.[2c,h] A ^{29}Si NMR chemical shift very similar to that here ($\delta = 211.33$) has been observed for a tungsten dimer singly bridged by a silylene $SiPh_2$ ligand,[3] while for molybdenum compounds with nonbridging silyls ^{29}Si NMR resonances have been detected in the range from 19.9 to 108.3 ppm.[5a] For mononuclear molybdenum compounds containing nonbridging silylene ligands, [Cp*(dmpe)HMo═Si(Cl)Mes] and [Cp*(dmpe)HMo═Si(CH_2SiMe_3)Mes], ^{29}Si NMR resonances have been detected at $\delta = 182$ and 243 ppm, respectively.[5b]

The ^{13}C{^{1}H} NMR spectrum revealed three signals in the carbonyl region at δ 217.64, 212.29, and 203.10 in the intensity ratio 1:1:2, which suggests the presence of two mutually *trans* carbonyl ligands and two other carbonyl groups *cis* to the former but having in *trans* position two different ligands with a weaker π-accepting ability than the carbonyl ligands. The ^{95}Mo NMR spectrum (toluene-d_8) shows a resonance at $\delta = -3785$, considerably upfield from the molybdenum resonance for Mo(CO)$_6$ (observed at $\delta = -1856$) and for other six-coordinate molybdenum(0) compounds.[6] Similar upfield chemical shifts have recently been observed for seven-coordinate molybdenum(II) complexes ($\delta = -3798$ for [(μ-Cl)$_3$Mo$_2$(SnCl$_3$)(CO)$_7$], $\delta = -3792$ for [Mo(μ-Cl)(SnCl$_3$)(CO)$_3$(NCMe)$_2$], and $\delta = -3805$ for [Mo(μ-Cl)(SnCl$_3$)(CO)$_3$(η^4-C$_7$H$_8$)]).[7]

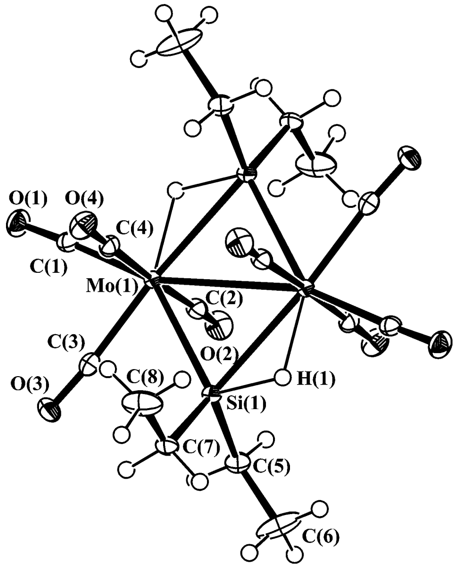


Figure 2. ORTEP diagram of [{Mo(μ-η^2-H−SiEt$_2$)(CO)$_4$}$_2$] (**1**).

These spectroscopic data provide evidence for the assignment of the new Mo−Si complex as seven-coordinate with four carbonyl ligands, hydride, and two silicon ligands in the coordination sphere. To achieve a more complete bonding picture, a novel molybdenum complex was examined by X-ray crystallography. Yellow single crystals suitable for X-ray diffraction analysis were grown as a result of crystallization from a saturated *n*-heptane solution at −10 °C, and their analysis showed the presence of a dinuclear molybdenum species bridged by two silicon ligands (see below).

X-ray Crystal Structure of [{Mo(μ-η^2-H−SiEt$_2$)(CO)$_4$}$_2$] (1). An ORTEP diagram of **1** is shown in Figure 2. Table 1 contains crystal and data collection parameters, whereas selected bond lengths and bond angles can be found in Table 2. The most significant aspect of the structure of **1** is that it shows unambiguously that the hydrogen atom is bound to the molybdenum atom (H−Mo = 1.786(5) Å) as well as to the silicon atom (H−Si = 1.615(3) Å), to bridge one of the Mo−Si bonds of the bridging silyl ligands. Thus, the bridged Mo−Si bond is substantially longer (Mo(1)−Si(1)^{i} = 2.7093(6) Å) than the other one (Mo(1)−Si(1) = 2.6152(6) Å) and much longer than observed in other molybdenum complexes with nonbridging silyls. The Mo−Si bond lengths in the silyl hydride metallocene complexes fall in the range 2.513(1)−2.604(1) Å.[5a] The Mo−H bond in **1** is only slightly longer than terminal Mo−H bonds found in a trihydride complex formed in reaction of [MoH$_4$(dppe)$_2$] with Ph$_2$SiH$_2$ (Mo−H = 1.70(6), 1.72(6), and 1.76(6) Å)[8a] but a little shorter than for the terminal hydride ligand in *trans*-[Mo(H)(NBEt$_3$)(depe)$_2$], where a Mo−H distance of 1.85(2) Å has been detected.[8b] However, for the molybdenum-silane compound *cis*-[Mo(η^2-H−SiH$_2$Ph)(CO)(depe)$_2$], containing a Mo−η^2-(H−Si) bond, a Mo−H distance of 1.70(5) Å has been found,[2d] and for the [Mo$_2$(μ-H)(CO)$_{10}$]$^-$ anion, with a

---

(4) (a) Darensbourg, M. Y.; Slater, S. *J. Am. Chem. Soc.* **1981**, *103*, 5914. (b) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2296. (c) Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 4376. (d) Petersen, J. L.; Masino, A.; Stewart, R. P. *J. Organomet. Chem.* **1981**, *208*, 55. (e) Lin, T. J.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 6252.

(5) (a) Koloski, T. S.; Pestana, D. C.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 489. (b) Mork, B. V.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 357.

(6) (a) Jaitner, P.; Wohlgenannt, W. *Montash. Chem.* **1982**, *113*, 699. (b) Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169. (c) Mason, J. *Chem. Rev.* **1987**, *87*, 1299.

(7) (a) Szymańska-Buzar, T. *Coord. Chem. Rev.* **2005**, *249*, 2195. (b) Stosur, M.; Górski, M.; Szymańska-Buzar, T. Unpublished results.

(8) (a) Minato, M.; Yang, Z. D.; Zhang, L.-B.; Hirabayashi, R.; Kakeya, M.; Matsumoto, T.; Harakawa, A.; Kikutsuji, G.; Ito, T. *Organometallics* **2005**, *24*, 3434. (b) Cugny, J.; Schmalle, H. W.; Fox, T.; Blacque, O.; Alfonso, M.; Berke, H. *Eur. J. Inorg. Chem.* **2006**, 540.

Table 1. Crystal Data and Structure Refinement Parameters for 1

empirical formula	$C_{16}H_{22}Mo_2O_8Si_2$
fw	590.40
cryst size (mm)	0.10 × 0.10 × 0.07
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	9.1424(8)
b (Å)	10.0636(9)
c (Å)	14.1503(13)
β (deg)	120.638(6)
V (Å^3)	1120.16(17)
Z	2
D_{calcd} (g/cm^3)	1.750
diffractometer	Kuma KM4CCD
radiation	Mo Kα (λ = 0.71073), graphite monochromated
temp (K)	100(2)
μ, mm^{-1}	1.264
F(000)	588
data collected, θ min./max. (deg)	3.03/28.45
index ranges	$-11 \leq h \leq 12$, $-13 \leq k \leq 13$, $-18 \leq l \leq 17$
no. of reflns collected	8669
R_{int}	0.0261
abs coeff, min./max.	0.897/0.789
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	2628/0/138
final residuals: R_1, wR_2($I > 2\sigma(I)$)	0.0243, 0.0552
R_1, wR_2 (all data)	0.0301, 0.0570
GOF	1.100

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1[a]

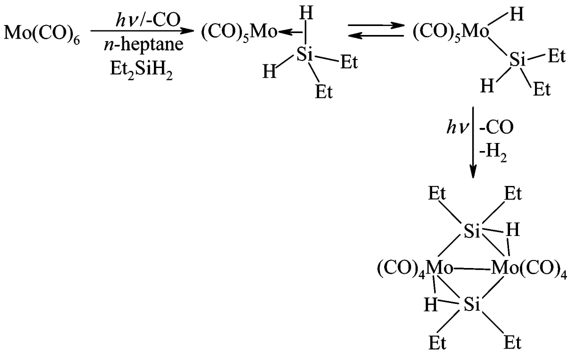
atoms	distance	atoms	angle
Mo(1)−C(3)	1.998(2)	C(3)−Mo(1)−C(1)	78.94(8)
Mo(1)−C(1)	2.013(2)	C(3)−Mo(1)−C(2)	91.56(8)
Mo(1)−C(2)	2.056(2)	C(1)−Mo(1)−C(2)	89.10(8)
Mo(1)−C(4)	2.061(2)	C(3)−Mo(1)−C(4)	90.50(8)
Mo(1)−Si(1)	2.6152(6)	C(1)−Mo(1)−C(4)	90.08(8)
Mo(1)−Si(1)^i	2.7093(6)	C(2)−Mo(1)−C(4)	177.60(8)
Mo(1)−Mo(1)^i	3.2026(4)	C(3)−Mo(1)−Si(1)	65.74(6)
Si(1)−C(5)	1.886(2)	C(1)−Mo(1)−Si(1)	144.09(6)
Si(1)−C(7)	1.889(2)	C(2)−Mo(1)−Si(1)	85.70(6)
Si(1)−Mo(1)^i	2.7093(6)	C(4)−Mo(1)−Si(1)	96.28(6)
Si(1)−H(1)	1.6150	C(3)−Mo(1)−Si(1)^i	169.56(6)
O(1)−C(1)	1.140(3)	C(1)−Mo(1)−Si(1)^i	109.75(6)
O(2)−C(2)	1.139(3)	C(2)−Mo(1)−Si(1)^i	94.32(6)
O(3)−C(3)	1.150(3)	C(4)−Mo(1)−Si(1)^i	83.84(6)
O(4)−C(4)	1.130(3)	Si(1)−Mo(1)−Si(1)^i	106.07(1)
C(5)−C(6)	1.528(3)	C(3)−Mo(1)−Mo(1)^i	119.77(6)
C(7)−C(8)	1.521(3)	C(1)−Mo(1)−Mo(1)^i	161.29(6)
		C(2)−Mo(1)−Mo(1)^i	90.14(6)
		C(4)−Mo(1)−Mo(1)^i	89.92(6)
		Si(1)−Mo(1)−Mo(1)^i	54.38(1)
		Si(1)^i−Mo(1)−Mo(1)^i	51.69(1)
		C(5)−Si(1)−C(7)	105.4(1)
		C(5)−Si(1)−Mo(1)^i	116.50(7)
		C(7)−Si(1)−Mo(1)^i	123.63(7)
		Mo(1)−Si(1)−Mo(1)^i	73.93(1)

[a] Symmetry transformations used to generate equivalent atoms: i ($-x-1$, $-y-1$, $-z-1$).

hydride bridge between the two molybdenum atoms, Mo−H distances of 1.76(5) and 1.93(5) Å have been observed.[4d] The length of the molybdenum-bound Si−H bond, 1.615(3) Å, is significantly lengthened relative to the typical terminal Si−H distance (1.4−1.5 Å) in free silanes or in nonbridging silyl ligands, which suggests substantial Mo(d_π)-to-Si−H (σ*) back-donation. A slightly greater Si−H bond lengthening was found for η^2-coordinated silane in *cis*-[Mo(η^2-H−SiH$_2$Ph)(CO)(depe)$_2$] (η^2-Si−H = 1.77(6) Å, σ-Si−H = 1.42(6) and 1.41(6) Å).[2d]

The two molybdenum atoms in complex **1** are separated by 3.2026(4) Å, a distance that is consistent with a Mo−Mo bond. An only slightly shorter metal−metal bond length (3.183(1) Å)[2b] has been observed in an analogous structurally characterized dinuclear carbonyl complex of tungsten containing a bridging diethylsilyl ligand, but a slightly longer metal−metal bond distance (W−W = 3.2256(8) Å) has been detected in a dinuclear compound containing a bridging diphenylsilyl ligand [{W(μ-η^2-H−SiPh$_2$)(CO)$_3$(PiPr$_3$)}$_2$].[2g] Mo−Mo distances shorter than in **1**, in the range 3.066(1)−3.126(1) Å, have been observed in the tetrahedral [MoH(CO)$_3$]$_4^{4-}$ unit.[4e] The (Mo−Si)$_2$ core is planar, with the angle Mo(1)−Si(1)−Mo(1)^i = 73.93(1)°, similar to those in analogous tungsten compounds.[2b,g]

Scheme 1. A Possible Mechanistic Pathway for the Conversion of Mo(CO)$_6$ to 1



1

The Mo−CO bond lengths fall in the range 1.998(2)−2.061(2) Å. The shortest Mo−CO bond distance is observed for CO in the position nearly *trans* to the silicon atom (C(3)−Mo(1)−Si(1)^i = 169.56(6)°). The latter Mo−CO distance is only a little shorter than the other Mo−CO bond, 2.013(2) Å, which is almost *trans* to the next molybdenum atom (C(1)−Mo(1)−Mo(1)^i = 161.29(6)°). The two mutually *trans* carbonyl ligands (C(2)−Mo(1)−C(4) = 177.60(8)°) are at very similar distances from the molybdenum atom, 2.056(2) and 2.061(2) Å. These data are in very good agreement with the ^{13}C NMR spectra of compound **1**, in which three signals were observed in the carbonyl carbon region with the intensity ratio 1:1:2.

The angle subtended at the silicon atom by the two ethyl groups is close to tetrahedral, while the Mo(1)−Si(1)−Mo(1)^i angle is considerably more acute at 73.93(1)°.

In summary, the crystal structure of **1** is very similar to that of an analogous tungsten complex, [{W(μ-η^2-H−SiEt$_2$)(CO)$_4$}$_2$], reported by Bennett and Simpson in 1971.[2b] It is not surprising for compounds of two elements with nearly identical covalent radii.

Consideration of the Formation Mechanism of the Mo−Si Complex 1. A reasonable mechanism accounting for the high-yield formation of **1** is shown in Scheme 1. The initial reaction sequence involves CO dissociation, η^2-silane coordination, and oxidative addition of the Si−H bond of Et$_2$SiH$_2$ to give a very unstable silyl-hydride complex of molybdenum, formally in the second oxidation state. Such intermediate compounds were recently detected by ^{1}H NMR spectroscopy in photochemical reaction of group 6 metal carbonyls and triethylsilane.[9] Continuing photolysis results in the release of another CO molecule and leads to the dimerization of the molybdenum species, followed by reductive elimination of the dihydrogen molecule and formation of complex **1**, which contains two molybdenum atoms formally in the first oxidation state.

---

[9] (a) Matthews, S. L.; Pons, V.; Heinekey, D. M. *Inorg. Chem.* DOI, 10.1021/ic052134p. (b) Gądek, A.; Szymańska-Buzar, T. *Polyhedron* **2006**, *25*, 1441.

An alternative mechanism proposed by Bennett and Simpson,[2a] which includes the intermediacy of the silylene complex $[W(CO)_5(SiEt_2)]$ and its photochemical reaction with an additional molecule of silane, cannot be completely ruled out.

Reactivity of a Molybdenum Dimer with a Bridging Silyl Ligand. In the solid state, compound **1** is stable indefinitely under an inert atmosphere. In toluene-d_8 solution it is also stable in the absence of air, and no changes in its ^1H NMR spectra were observed over a period of days. However, over a prolonged time decomposition of **1** due to diffusion of water to the NMR tube and the formation of several products was identified by ^1H NMR spectroscopy. Monitoring of this behavior by ^1H NMR spectroscopy showed the decay of the hydride signal at −8.33 ppm and the appearance of two new signals in an intensity ratio 1:1 at $\delta = 4.84$ (quintet, $^3J_{H-H} = 2.15$ Hz, $^1J_{Si-H} = 199$ Hz, Si−H) and at $\delta = 4.10$ (s, O−H), assigned to diethylhydridosilanol, Et_2SiHOH.[2f,10] Another signal, with an intensity different from sample to sample, at $\delta = 4.87$ (quintet, $^3J_{H-H} = 2.15$ Hz, $^1J_{Si-H} = 199$ Hz, Si−H), can originate from disiloxane, present as an impurity.

Summary and Conclusions

We have shown that photochemically generated coordinatively unsaturated molybdenum carbonyls activate the Si−H bond of diethylsilane with the formation of an η^2-H−Si−Mo bond. The molecular structure of the novel bis{(μ-η^2-hydridodiethylsilyl)tetracarbonylmolybdenum(I)} complex, $[\{Mo(\mu\text{-}\eta^2\text{-}H{-}SiEt_2)(CO)_4\}_2]$ (**1**), was established by single-crystal X-ray diffraction studies. The molybdenum hydride observed in the ^1H NMR spectrum was located in the structure at a chemically reasonable position (Mo−H = 1.786(5) Å). The spectroscopic data are consistent with the solid-state structure of a silicon-bridged molybdenum dimer, which formally contains two molybdenum atoms in the first oxidation state bridged by two silyl ligands with an α-agostic Si−H bond. It is very probable that the initial Si−H bond activation involves oxidative addition of the Si−H bond to form a Mo(II) hydrido-silyl intermediate followed by reductive elimination of the dihydrogen molecule and dimerization to give a dimolybdenum moiety doubly bridged by two silyl ligands, with an η^2-H−Si−Mo bond.

To the best of our knowledge, this paper represents a rare study that simultaneously resolves both the spectroscopic properties and the X-ray molecular single-crystal structure of a molybdenum complex containing an η^2-Si−H bond.

Experimental Section

General Considerations. The synthesis and all operations were conducted under an atmosphere of nitrogen using standard Schlenk techniques. Solvents and liquid reagents were predried with CaH_2 and vacuum transferred into small storage flasks prior to use. IR spectra were measured with a Nicolet 400 FT-IR instrument. ^1H, $^{13}C\{^1H\}$, ^{95}Mo, and $^{29}Si\{^1H\}$ NMR spectra were recorded with a Bruker AMX 500 MHz instrument at 500.13 MHz for ^1H, 125.76 MHz for ^{13}C, 99.36 MHz for ^{29}Si, and 32.00 MHz for ^{95}Mo. ^{13}C NMR experiments were performed using the DEPT and gated coupled spectra to obtain coupling constants. All proton and carbon chemical shifts are referenced to either the residual proton signal of toluene-d_8 at δ 2.10 for ^1H NMR or the natural abundant carbon signal of the deuterated solvent at δ 20.4 for ^{13}C NMR spectra. ^{95}Mo NMR chemical shifts were calibrated relative to $Mo(CO)_6$ ($\delta_{Mo} = -1856$), and ^{29}Si NMR chemical shifts were referenced relative to Ph_2SiH_2 ($\delta_{Si} = -37.08$) used as external standards. The photolysis source was an HBO 200 W high-pressure Hg lamp.

Synthesis of 1. A solution of $Mo(CO)_6$ (0.10 g, 0.38 mmol) and Et_2SiH_2 (0.3 mL, 2.32 mmol) in freshly distilled *n*-heptane (30 mL) was irradiated through Pyrex at room temperature. The course of the reaction was monitored by IR measurements in solution, and photolysis was stopped when the IR band of $Mo(CO)_6$ at ca. 1990 cm^{-1} reached its minimum intensity (about 2 h). The volatile materials (solvent and unreacted $Mo(CO)_6$) were then stripped off the reaction mixture under reduced pressure at room temperature, yielding 0.11 g of a brown product (ca. 98% yield). The residue was analyzed by IR and NMR spectroscopy. At this stage of the synthesis, the ^1H NMR method showed ca. 96% of a hydride compound characterized by a signal at δ −8.33 and other hydride complexes with signals at δ −4.47, −5.53, −7.74, −7.82, and −9.34. Two proton signals in an intensity ratio 1:1 at $\delta = 4.84$ (quintet, $^3J_{H-H} = 2.15$ Hz, $^1J_{Si-H} = 199$ Hz, Si−H) and at $\delta = 4.10$ (s, O−H) were assigned to Et_2SiHOH. The resonance at $\delta = 4.87$ (q, $^3J_{H-H} = 2.15$, $^1J_{Si-H} = 199$ Hz, Si−H) was assigned to disiloxane.[2f,9] Pure crystalline **1** was obtained during a slow crystallization process from a saturated *n*-heptane solution at −10 °C.

Spectral Data for 1. IR (ν, cm^{-1}): (*n*-heptane) ν (C≡O) 2046 (s), 1983 (vs), 1941 (s); (Nujol) ν (C≡O) 2045 (s), 1982 (vs), 1939 (s), δ (MoCO) 587 (w), 574 (w). ^1H NMR (toluene-d_8, −30 °C): δ 1.10 (t, $^3J_{H-H} = 8.1$ Hz; 6H, CH_2Me), 0.69 (q, $^3J_{H-H} = 8.1$ Hz; 4H, CH_2Me), −8.33 (s, 1H; $^1J_{Si-H} = 57$ Hz, $^2J_{Si-H} = 33$ Hz). ^{13}C NMR (toluene-d_8, −30 °C): δ 217.64 (1CO), 212.29 (1CO), 203.10 (2CO), 7.23 (t, $^1J_{C-H} = 117$ Hz, $^1J_{Si-C} = 60$ Hz, CH_2Me), 6.92 (q, $^1J_{C-H} = 125$ Hz, CH_2Me). ^{29}Si NMR (toluene-d_8): δ 207.7 (dq, $^1J_{Si-H} = 58$ Hz, $^2J_{Si-H} = 41$ Hz. ^{95}Mo NMR (toluene-d_8): δ −3785.

X-ray Crystallography. General Considerations. Yellow single crystals of **1** for X-ray diffraction studies were grown from the concentrated *n*-heptane solution at −10 °C. Crystal data were collected at −173 °C on a Kuma KM4-CCD diffractometer with graphite-monochromated Mo Kα radiation, generated from a X-ray tube operated at 50 kV and 35 mA. A yellow crystal with the approximate dimensions of 0.10 × 0.10 × 0.07 mm was used for data collection. The images were indexed, integrated, and scaled using the Oxford Diffraction data reduction package.[11a] The experimental details together with crystal data are given in Table 1. The structure was solved by the heavy atom method using SHELXS-97[11b] and refined by the full-matrix least-squares method on all F^2 data using SHELXL-97.[11c] Non-hydrogen atoms were included in the refinement with anisotropic displacement parameters. The hydrogen atoms bound to carbon atoms were included from ideal geometry of molecules and not refined. The hydrogen atom bound to Si and Mo atoms was located in the difference Fourier electron-density map and refined isotropically. The data were corrected for absorption[11a] (min./max. absorption coefficients 0.789 and 0.897). Crystallographic data for compound **1** have been deposited at the Cambridge Crystallographic Data Centre with deposition no. CCDC-299304. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1123-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information Available: Crystallographic data for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060290D

---

[10] (a) Greene, J.; Curtis, M. D. *Inorg. Chem.* **1978**, *17*, 2324. (b) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732. (c) Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, *8*, 1885.

[11] (a) Oxford Diffraction Poland Sp., CCD data collection and reduction GUI, Version 1.173.13 beta (release 14.11.2003), 1995−2003. (b) Sheldrick, G. M. *SHELXS-97*, Program for Crystal Structure Solution; University of Göettingen: Germany, 1997. (c) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement, University of Göettingen: Germany, 1997.