η^2-Coordination of Si–H σ Bonds to Transition-Metal Fragments That Also Bind η^2-Dihydrogen Ligands and Agostic C–H Bonds: Synthesis and Characterization of η^2-Silane Complexes *cis*-Mo(η^2-H-SiHR'$_2$)(CO)(R$_2$PC$_2$H$_4$PR$_2$)$_2$

Xiao-Liang Luo, Gregory J. Kubas,* Jeffrey C. Bryan,
Carol J. Burns, and Clifford J. Unkefer

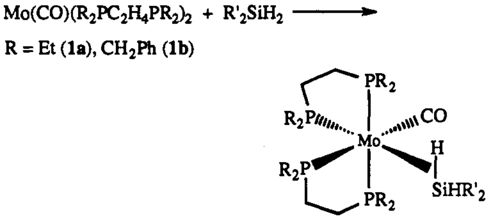
Inorganic, Structural, and
Applied Chemistry Group (CST-3)
Mail Stop C346, Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Received June 20, 1994

Recent developments in coordination chemistry have demonstrated that certain σ bonds can coordinate to transition metals in an η^2-fashion without bond cleavage by the formation of three-center two-electron bonds, giving rise to the so-called "σ complexes".[1] The η^2-coordination of σ bonds not only is of fundamental importance from a structural point of view but also has significant implications for the activation of σ bonds in transition-metal-catalyzed transformations. To date a substantial number of transition-metal σ complexes containing η^2-silane ligands,[1,2] η^2-H$_2$ ligands,[1,3] or agostic C–H bonds[1,4] have been sythesized and structurally characterized. However, no systems are known in which Si–H, H–H, and agostic C–H bonds can be bound to the same metal fragment in an η^2-fashion. In this communication, we report on the first example of such a system which provides a unique opportunity to study the differences between and/or common features among the three prototypes of σ complexes.

The formally 16-electron complexes Mo(CO)(R$_2$PC$_2$H$_4$PR$_2$)$_2$ (R = Et (**1a**), CH$_2$Ph (**1b**), Ph (**1c**)) have been shown to form adducts with a variety of small molecules.[5,6] In particular, the reaction of **1a**–**c** with H$_2$ affords either an η^2-H$_2$ complex or a dihydride species, depending on the basicity of the diphosphine ligand. The ^{1}H NMR spectroscopic data of **1b**[6] and the X-ray crystallographic data of **1c**[7] reveal that both compounds contain a weak agostic Mo···H–C interaction which occupies an otherwise vacant coordination site trans to the CO ligand.

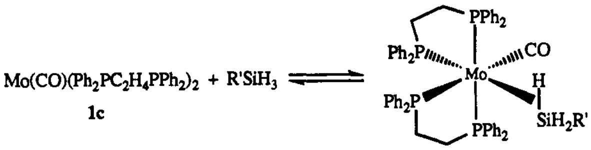
We have now found that compounds **1a**–**c** react with silanes to give η^2-silane complexes in which the Si–H σ bond of the silane is coordinated to the molybdenum center in an η^2-fashion. Thus, the addition of 1 equiv of a primary or secondary silane to dark-red solutions of **1a** or **1b** in toluene at room temperature resulted in the rapid formation of yellow solutions, from which the η^2-silane complexes *cis*-Mo(η^2-H-SiHR'$_2$)(CO)(R$_2$PC$_2$H$_4$PR$_2$)$_2$ (R = Et, SiHR'$_2$ = SiH$_2$Ph (**2a**), SiH$_2$(*n*-C$_6$H$_{13}$) (**2b**), SiHPh$_2$ (**2c**); R = CH$_2$Ph, SiHR'$_2$ = SiH$_2$Ph (**3a**), SiH$_2$(*n*-C$_6$H$_{13}$) (**3b**)) (eq 1) were isolated as yellow solids, except for **2b**, which was obtained as a pale-yellow oil.[8]



(1)

R = Et; SiHR'$_2$ = SiH$_2$Ph (**2a**), SiH$_2$(*n*-C$_6$H$_{13}$) (**2b**), SiHPh$_2$ (**2c**)
R = CH$_2$Ph; SiHR'$_2$ = SiH$_2$Ph (**3a**), SiH$_2$(*n*-C$_6$H$_{13}$) (**3b**)

The addition of 1 equiv of a primary silane R'SiH$_3$ (R' = Ph, *n*-C$_6$H$_{13}$) to a dark brown solution of Mo(CO)(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$ (**1c**) in C$_6$D$_6$ caused a lightening in color. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the resulting solutions reveal that the η^2-silane complexes *cis*-Mo(η^2-H-SiH$_2$R')(CO)(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$ (R' = Ph (**4a**), *n*-C$_6$H$_{13}$ (**4b**)) were formed in equilibrium with the agostic precursor **1c** (eq 2). Attempts to isolate complexes **4a** and **4b** have been unsuccessful even in the presence of an excess of the silane. The relatively weak binding of the silane in **4a** and **4b**, which contain the less basic diphosphine ligand Ph$_2$PC$_2$H$_4$PPh$_2$, is probably due to insufficient Mo(d$_\pi$) to Si–H(σ^*) back-donation.



(2)

R' = Ph (**4a**), *n*-C$_6$H$_{13}$ (**4b**)

The ^{31}P{^{1}H} NMR spectra of **2**–**4** at room temperature show four multiplet resonances, each integrating for one phosphorus, indicating that all four phosphorus nuclei are chemically inequivalent. This is consistent with an octahedral structure, as shown in eqs 1 and 2, in which the silane is regarded as *one* ligand with the midpoint of one Si–H σ bond taking up a coordination site cis to the CO ligand. In contrast, if **2**–**4** were formulated as seven-coordinate hydrido silyl complexes, they would probably be fluxional at room temperature and accordingly would show a single resonance in their ^{31}P{^{1}H} NMR spectra, because stereochemical nonrigidity (at least at room temperature) is a common phenomenon for seven-coordinate complexes due to facile intramolecular exchange processes.[9]

The η^2-silane coordination in **2**–**4** is established by the observation of J_{SiH} coupling constants for the η^2-bound Si–H bonds. The upfield region of the ^{1}H NMR spectra of **2**–**4** shows a multiplet resonance assignable to the η^2-bound Si–H proton which is coupled to the four inequivalent phosphorus nuclei as well as the uncoordinated Si–H protons. Upon decoupling of ^{31}P nuclei, the upfield resonance collapses into a pattern which still shows the coupling to the uncoordinated Si–H protons (J_{HH} = 2–8 Hz), but is now clearly flanked by ^{29}Si satellites. As indicated in Table 1, the magnitude of J_{SiH} depends upon the nature of both the diphosphine substituents and the substituents on silicon. By

---

(1) (a) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

(2) (a) Schubert, H. *Adv. Organomet. Chem.* **1990**, *30*, 151. (b) Hart-Davis, A. J.; Graham, W. A. G. *J. Am. Chem. Soc.* **1971**, *93*, 4388. (c) Rabaa, H.; Saillard, J.-Y.; Schubert, U. *J. Organomet. Chem.* **1987**, *330*, 397. (d) Colomer, E.; Corriu, R. J. P.; Marzin, C.; Vioux, A. *Inorg. Chem.* **1982**, *21*, 368.

(3) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Henderson, R. A. *Transition Met. Chem.* **1988**, *13*, 474. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (d) Crabtree, R. H.; Luo, X.-L.; Michos, D. *Chemtracts: Inorg. Chem.* **1991**, *3*, 245. (e) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (f) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

(4) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(5) Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569.

(6) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Eckert, J. *Inorg. Chem.*, in press.

(7) Sato, M.; Tatsumi, T.; Kodama, T.; Hidai, M.; Uchida, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 4447.

(8) Spectroscopic and microanalytical data for the representative compound **2a** are as follows. ^{1}H{^{31}P} NMR (C$_6$D$_6$, 298 K): δ 8.16 (d, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 2 H, Ph), 7.30 (t, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 2 H, Ph), 7.19 (t, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 1 H, Ph), 5.86 (dd, J_{HH} = 5.7 and 3.9 Hz, $^1J_{\mathrm{SiH}}$ = 169 Hz, 1 H, Si*H*), 5.75 (d, J_{HH} = 5.7 Hz, $^1J_{\mathrm{SiH}}$ = 164 Hz, 1 H, Si*H*), 0.5–2.0 (m, 48 H, PC$_2$*H*$_4$P, C$_2$*H*$_5$), –8.11 (d, J_{HH} = 3.9 Hz, J_{SiH} = 39 Hz, 1 H, Mo(η^2-*H*-Si)). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 298 K): δ 63.4 (m, 1 P), 53.7 (m, 1 P), 47.7 (m, 1 P), 36.9 (m, 1 P). IR (Nujol, cm^{-1}): ν(Si–H) 2004, 1960; ν(CO) 1777; ν(Mo–H–Si) 1742. Anal. Calcd for C$_{27}$H$_{56}$MoOP$_4$Si: C, 50.31: H, 8.76. Found: C, 50.64; H, 9.01.

(9) Luo, X.-L.; Schulte, G. K.; Demou, P.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 4268 and references therein.

0002-7863/94/1516-10312$04.50/0

Table 1. J_{SiH} Coupling Constants[a] for *cis*-$Mo(\eta^2\text{-}H\text{-}SiHR'_2)(CO)(R_2PC_2H_4PR_2)_2$

complex	R	$SiHR'_2$	J_{SiMoH} (Hz)[b]	$^1J_{SiH}$ (Hz)[c]
2a	Et	SiH_2Ph	39	164, 170
2b	Et	$SiH_2(n\text{-}C_6H_{13})$	42	155, 168
2c	Et	$SiHPh_2$	50	172
3a	CH_2Ph	SiH_2Ph	41	164, 165
3b	CH_2Ph	$SiH_2(n\text{-}C_6H_{13})$	42	160, 166
4a	Ph	SiH_2Ph	57	187, 194
4b	Ph	$SiH_2(n\text{-}C_6H_{13})$	61	180, 181

[a] Determined 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.

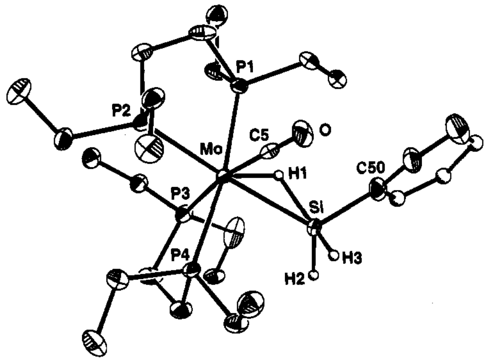


Figure 1. ORTEP drawing with 50% probability ellipsoids (isotropically refined atoms are represented by shaded (carbon) or open (hydrogen) circles; one of each pair of disordered atoms is omitted for clarity) of *cis*-$Mo(\eta^2\text{-}H\text{-}SiH_2Ph)(CO)(Et_2PC_2H_4PEt_2)_2$ (**2a**). Selected bond lengths (Å) and angles (deg) are as follows: Mo–P(1), 2.446(2); Mo–P(2), 2.548(2); Mo–P(3), 2.549(2); Mo–P(4), 2.491(2); Mo–C(5), 1.932(6); C(5)–O, 1.189(7); Mo–Si, 2.501(2); Mo–H(1), 1.70(5); Si–H(1), 1.77(6); Si–H(2), 1.42(6); Si–H(3), 1.41(6); Mo–C(5)–O, 176.9(5); Mo–H(1)–Si, 92(3); Mo–Si–H(1), 42.6(18); Mo–Si–H(2), 118(2); Mo–Si–H(3), 115(2); H(1)–Si–H(2), 111(3); H(1)–Si–H(3), 152(3); H(2)–Si–H(3), 93(4); H(1)–Si–C(50), 85(2); H(2)–Si–C(50), 106(2); H(3)–Si–C(50), 100(2).

comparison to the J_{SiH} values of 20–70 Hz for known η^2-silane complexes,[1,2] the J_{SiH} values of 39–61 Hz for **2–4** clearly indicate that they are better formulated as six-coordinate η^2-silane complexes than as seven-coordinate silyl hydride complexes.

The molecular structure of **2a** in the solid state was determined by a single-crystal X-ray diffraction analysis (Figure 1),[10] and the results confirm the η^2-coordination of the Si–H bond inferred from the solution NMR data. The three hydrogen atoms on the Si were located in the difference Fourier map. The coordination geometry around the molybdenum atom is approximately octahedral, with the midpoint of the Si–H(1) bond occupying a coordination site cis to the CO ligand. The molybdenum-bound Si–H(1) bond is significantly lengthened (1.77(6) Å) relative to the terminal Si–H(2) (1.42(6) Å) and Si–H(3) (1.41(6) Å) bonds, which suggests substantial $Mo(d_\pi)$ to Si–H (σ^*) back-donation leading to appreciable Si–H bond lengthening. The bound Si–H(1) bond distance falls within the range of values (1.61–1.80 Å) found for chromium and manganese complexes $(\eta^5\text{-}C_5R_5)Mn(\eta^2\text{-}H\text{-}SiR_3)L(CO)$ and $(\eta^6\text{-}C_6Me_6)Cr(\eta^2\text{-}H\text{-}SiR_3)(CO)_2$.[2]

It is noteworthy that both the solution NMR data of **2–4** and the X-ray crystal structure of **2a** indicate an octahedral structure in which the η^2-silane ligand and the CO ligand are cis to each other. In contrast, in the corresponding compounds containing an η^2-H_2 ligand or an agostic C–H bond, the CO is trans to the η^2-H_2 ligand or the agostic C–H bond. This structural difference could have both steric and electronic origin. Since an η^2-silane ligand is more bulky than an η^2-H_2 ligand or an agostic C–H bond, it is conceivable that the η^2-silane ligand in **2–4** is placed cis to the small CO ligand in order to minimize the steric repulsion between the silane and the diphosphine substituents. Furthermore, since the Si–H σ^* orbital has lower energy than H–H and C–H σ^* orbitals, a silane is a better π acceptor than H_2 or an agostic C–H bond. Thus, electronic factors may also favor the silane being cis to the strongly π-accepting CO ligand.

In summary, we have found a system in which Si–H, H–H, and agostic C–H bonds can be bound to the same metal fragment in an η^2-fashion. Efforts are underway to explore the chemistry of the η^2-silane complexes **2–4**. We are also looking into the possibility that, by properly adjusting the steric and electronic properties of the metal fragment and of the substituents on silicon, we may be able to observe a hitherto unknown tautomeric equilibrium between an η^2-silane complex and a hydrido silyl complex, which is analogous to the now relatively common equilibrium between an η^2-H_2 complex and a dihydride species.[3,11] Thus, the intriguing question regarding single minimum versus double minima for the reaction trajectory of oxidative addition/reductive elimination of Si–H bonds at transition-metal centers arises and remains to be answered.

Acknowledgment. This work is supported by Los Alamos National Laboratory's LDRD funding. X.L.L. is grateful to the Director of the Laboratory for postdoctoral funding. We thank Professor Ray J. Butcher for assistance with the crystal structure of **2a**.

Supplementary Material Available: Spectroscopic and microanalytical data for complexes **2** and **3** and a summary of X-ray diffraction data, tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters, and a completely labeled diagram for **2a** (11 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.

---

(10) Crystal data for **2a**: light yellow prism, 0.15 × 0.22 × 0.30 mm; $M_r = 644.6$; monoclinic, space group $P2_1/c$; $a = 11.044(3)$ Å, $b = 16.707(4)$ Å, $c = 18.015(5)$ Å, $\beta = 98.59(2)°$, $V = 3287$ Å^3, $Z = 4$; $D_{calcd} = 1.303$ g/cm^3; Enraf-Nonius CAD4 diffractometer; 188 K; Mo Kα radiation ($\lambda = 0.710\,73$ Å); scan method ω; data collection range 4.0–48.0°; total number of reflections measured 9089; number of independent reflections 5152 ($R_{int} = 2.8\%$); number of observed reflections 3421 ($F > 4.0\sigma(F)$). The structure was solved by Patterson methods and refined by a full-matrix least-squares procedure to give final residuals of $R = 0.0430$ and $R_w = 0.0542$; GOF = 1.08. The six carbon atoms of the phenyl group exhibit simple (roughly 50%) positional disorder. The hydrogen atoms bound to Si were located in difference Fourier maps and refined isotropically, except for the thermal parameter for H(1), which consistently refined to values low relative to its estimated standard deviation and thus was fixed at a value roughly averaging those obtained for H(2) and H(3). This was probably caused by the close proximity of the molybdenum atom.

(11) (a) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. F. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (b) Kubas, G. J.; Ryan, R. R.; Unkefer, C. J. *J. Am. Chem. Soc.* **1987**, *109*, 8113. (c) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675. (d) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (e) Luo, X.-L.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990**, 189. (f) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912. (g) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (h) Luo, X.-L.; Michos, D.; Crabtree, R. H. *Organometallics* **1992**, *11*, 237.