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η^1-Silane Complex

Structural and Spectroscopic Characterization of an Unprecedented Cationic Transition-Metal η^1-Silane Complex**

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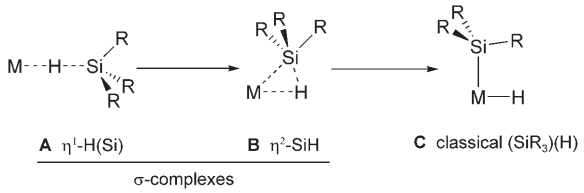
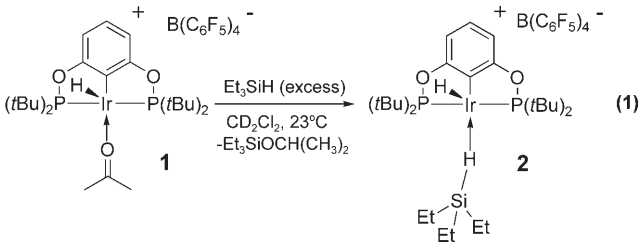
Understanding the coordination of σ bonds to metal centers is of fundamental importance and provides insights useful for developing metal-catalyzed transformations.[1] σ-Complexes between silanes and cationic transition-metal compounds possess highly electrophilic silicon centers and are invoked as key intermediates in catalytic Si–H activation reactions.[2,3] There are examples of isolated neutral silane σ-complexes, but cationic complexes of this type are rarely isolable presumably due to the extreme sensitivity of the electrophilic Si center to nucleophiles.[4,5] Moreover, all of the structurally characterized σ-complexes are η^2-SiH complexes, in which the silane is bound side-on with significant metal–silicon interaction (Scheme 1, **B**).[6,7] We report here the first example of a fully characterized cationic transition-metal η^1-silane complex (Scheme 1, **A**) in which the silane is bound to a metal center in an end-on fashion with no appreciable metal–silicon interaction.



Scheme 1. Interactions of R_3SiH with transition-metal complexes.

During our studies of Ir-catalyzed reduction of alkyl halides by triethylsilane, a cationic iridium(III)–Et_3SiH σ-complex, originally formulated as an η^2-SiH complex, was proposed as a key intermediate.[2a] This intermediate can be generated in situ by treatment of [(POCOP)Ir(H)-(acetone)]$^+$[$B(C_6F_5)_4$]$^-$ (**1**; POCOP = 2,6-[$OP(tBu)_2$]$_2C_6H_3$) with Et_3SiH in CD_2Cl_2 at 23 °C [Eq. (1)].[8]

At 23 °C, the ^{1}H NMR resonances for the terminal (Ir-H) and bridging (Ir-H-Si) hydrides are too broad to be observed due to exchange. At −70 °C, the static spectrum is obtained which shows two hydride resonances in a 1:1 ratio. The singlet at $\delta = -4.9$ ppm with ^{29}Si satellites ($^1J_{Si\text{-}H} = 79$ Hz) is assigned



to a bridging (Ir-H-Si) hydride while the triplet at $\delta = -44.2$ ppm ($^2J_{P\text{-}H} = 11.6$ Hz) is assigned to a terminal (Ir-H) hydride. The upfield shift of $\delta = -44.2$ ppm is indicative of a hydride *trans* to a vacant coordination site.[9] These NMR data, especially the $J_{Si\text{-}H}$ value,[10] suggest that **2** is a square-pyramidal Et_3SiH σ-complex with an apical hydride and silane bound in the square plane.

An X-ray quality crystal of **2** was obtained by slow diffusion of pentane into a C_6H_5F solution of **1** and excess Et_3SiH at 25 °C under Ar. The ORTEP diagram of **2** is shown in Figure 1.[11] Et_3SiH is coordinated *trans* to the *ipso* carbon

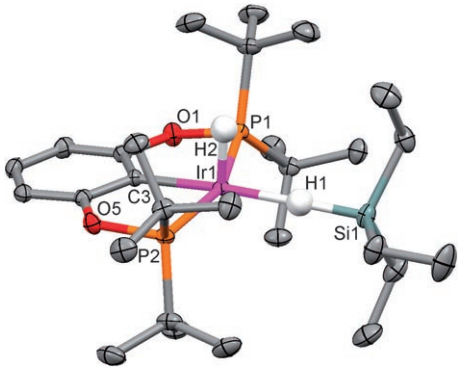


Figure 1. An ORTEP diagram of the cation in **2** (hydrogen atoms omitted). Key interatomic distances [Å] and bond angles [°]: Ir1–C3 2.015(2), Ir1–P2 2.3091(6), Ir1–P1 2.3470(6), Ir1–H1 1.94(3), Ir1–H2 1.425(18), Si1–H1 1.48(3); Ir1···Si1 3.346(1), Ir1-H1-Si1 157(1), P2-Ir1-P1 158.06(2).

of the tridentate POCOP backbone. The hydrogens bound to Ir were located in the final difference map, and their refined positions are consistent with a square-pyramidal geometry at Ir assigned using ^{1}H NMR data. The most striking structural feature of **2** is the orientation of the coordinated silane ligand, characterized by a long Ir···Si distance of 3.346(1) Å (0.97 Å greater than the sum of the covalent radii of Ir and Si)[12] and an Ir-H-Si angle of 157°, both indicative of an end-on η^1-H(Si)

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coordination mode of the silane. In η^2-SiH complexes, the M–Si distances remain relatively short.[4c,b,5a]

To provide insight into the structural and bonding features of the η^1-H(Si) binding mode, DFT studies[13] were performed on the $HSiMe_3$ analogue of **2** (**3**), as well as the $HSiMe_3$ complex of model systems in which Me replaces all four *t*Bu groups (**4**), and Me replaces two *cis* *t*Bu groups distal to the hydride ligand (**5**). Selected metric parameters for the calculated minima are listed in Table 1 and selected minima for **3** and **4** are shown in Figure 2. The potential energy surfaces for the silane complexes show multiple minima corresponding to different rotamers about the Ir–H and Si–H bonds. For each complex, structural data are presented for two distinct minima in which the $SiMe_3$ group is oriented proximal and distal to the hydride ligand (e.g., Figure 2, **4p** and **4d**, respectively). The calculated structure for **3d** agrees well with expectations based on X-ray data. The hydride ligand occupies the apical site in the square pyramid (Ir–H 1.54 Å). The hydrogen of the silane is positioned approximately *trans* to C(aryl) (Ir–H(Si) 1.87 Å). The Si–H distance of 1.57 Å is ca. 0.08 Å longer than the calculated Si–H distance in the parent silane, reflecting activation of the Si–H bond. The calculated Ir···Si non-bonding distance of 3.38 Å for **3d** is similar to the X-ray distance of 3.35 Å. The corresponding Ir-H1-Si angle is 161°. An Ir-H1-Si angle of 180° might be expected for an η^1-H(Si) interaction. The space-filling diagram for **3d** (Figure 2) shows close contact between the SiMe groups and the Me groups on the *t*Bu substituents, and these interactions, together with similar close interactions on the opposite face apparently dictate the Ir-H1-Si angle adopted in **2**.

Table 1: Selected bond lengths [Å] and angles [°] and energies from DFT studies.

Cmpd	Ir-H1	Si-H1[a]	Ir···Si	Ir-H1-Si	E_{rel} [kcal mol^{-1}][b]
3p	1.865	1.572	3.379	158.7	0.0
3d	1.870	1.572	3.395	161.0	−0.1
4p	1.785	1.576	3.169	141.1	0.0
4d	1.753	1.605	2.887	118.5	−0.9
4d′	1.751	1.653	2.619	100.5	−1.9
5d	1.757	1.609	2.871	117.0	0.0
5d′	1.752	1.646	2.626	101.2	−0.9

[a] The calculated Si–H distance in $HSiMe_3$ is 1.493 Å. [b] Difference in electronic energies.

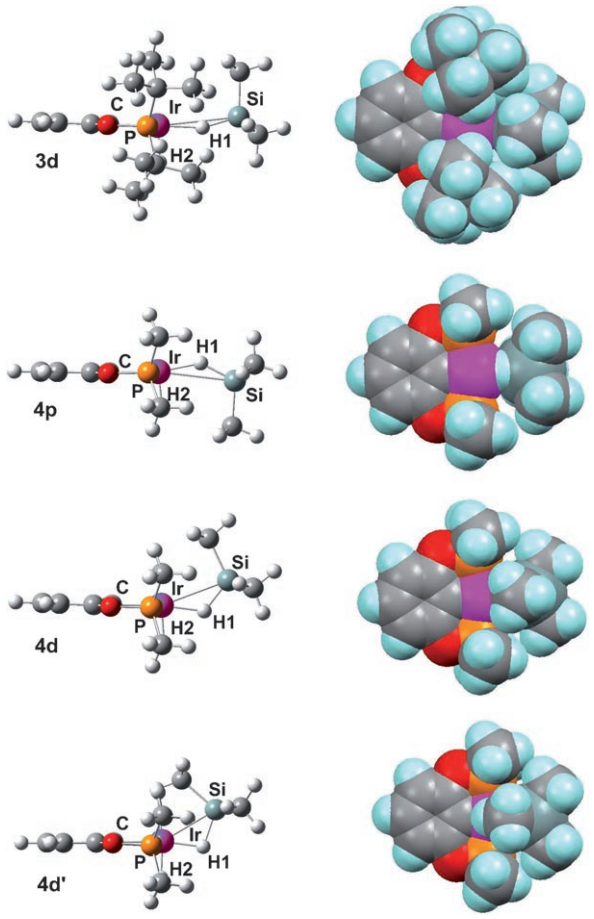

Figure 2. Selected minima for **3** and **4**, and corresponding space-filling diagrams (top view).

The reduced ligand steric bulk in trimmed **4** allows the silicon in **4d** to more closely approach Ir (Ir···Si 2.89 Å). Moreover, **4** shows a distinct minimum (**4d′**) with an even shorter Ir–Si distance (Ir···Si 2.62 Å), in which the silane coordination is assisted by the formation of an axial agostic interaction with a SiMe group (Figure 2) (H···Ir 2.25 Å). The development of the η^2-SiH interaction is demonstrated by the structural parameters of the series of complexes, **4p**, **4d**, and **4d′**, with progressively longer H1–Si distances, shorter Ir–H1 and Ir–Si distances, and smaller Ir-H1-Si angles along the series (see Table 1). The relative energies of **4p**, **4d**, and **4d′** are 0, −0.9, and −1.9 kcal mol^{-1}, respectively, indicating that the stabilization afforded by the η^2-SiH interaction is small. Trimmed **5** is electronically intermediate between **3** and **4**. The similar structural parameters and energetics of the **d** and **d′** minima for **4** and **5** are consistent with the assertion that the steric properties of the ligand are driving the structural changes in the trimmed complexes.

An NBO analysis[14] was conducted on the silane complexes, and the natural charges are shown in Table 2. Formation of the η^1-H(Si) silane complex increases the polarization of the Si–H bond, with an accompanying increase in charge on silicon by ca. 0.2 in comparison to the free silane, and a decrease in the charge on hydrogen.

Table 2: Natural charges and NBO populations in the silane complexes.[a]

	Natural Charges			NBO Populations			
	Ir	Si	H(Si)	σ Si-H	σ* Ir-C	Ir(dπ*)	σ* Si-H
3p	0.021	1.563	−0.281	1.796	0.313	1.952	0.063
3d	0.011	1.554	−0.275	1.796	0.313	1.954	0.063
4p	−0.011	1.540	−0.255	1.763	0.336	1.947	0.071
4d	−0.051	1.476	−0.175	1.712	0.380	1.931	0.084
4d′	−0.116	1.441	−0.115	1.673	0.426	1.916	0.093
5d	−0.038	1.490	−0.180	1.720	0.376	1.933	0.079
5d′	−0.123	1.449	−0.115	1.674	0.429	1.916	0.092

[a] In $HSiMe_3$, the natural charges on Si and H are 1.345 and −0.196, respectively.

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Adoption of the η^2-SiH coordination mode reduces the positive charge on silicon, and increases the charge on hydrogen. Therefore the η^1-H(Si) coordinated silane, with little Ir to SiH σ* backbonding, is expected be a more potent source of electrophilic silicon than an η^2-SiH complex. The NBO populations of the relevant orbitals for interaction with the silane (see Figure 3) are summarized in Table 2. The NBO

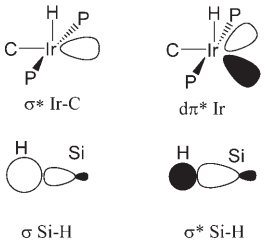

Figure 3. Relevant orbitals for interaction between the silane and iridium.

populations are consistent with greater donation from σ SiH to σ* IrC and greater back-donation from dπ* Ir to σ* SiH as the silane coordination geometry changes from **4p**, **4d**, to **4d′**.

In summary, we report structural, spectroscopic, and computational characterization of a cationic η^1-H(Si) silane complex, **2**. The $\delta(^1H)$ and $J_{Si\text{-}H}$ values for **2** fall into the range observed for η^2-SiH complexes, therefore these data alone do not allow assignment of the η^1-H(Si) coordination mode. Computational studies indicate that the bulky substituents on phosphorus in the POCOP ligand dictate the coordination mode of the silane and in complexes with trimmed ligands η^2-SiH conformers are energy minima. The small energy difference between η^1-H(Si) and η^2-SiH conformers indicates that backbonding from Ir to SiH σ* in these cationic complexes is not a very important stabilizing interaction.

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[1] a) G. J. Kubas, *Metal Dihydrogen and σ-Bond Complexes*, Kluwer/Plenum, New York, **2001**; b) J. E. Bercaw, J. A. Labinger, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 6899 – 6900, and the following articles in this special feature "Coordination Chemistry of Saturated Molecules".

[2] a) J. Yang, M. Brookhart, *J. Am. Chem. Soc.* **2007**, *129*, 12656 – 12657; b) M. D. Doherty, B. Grant, P. S. White, M. Brookhart, *Organometallics* **2007**, *26*, 5950 – 5960.

[3] a) R. N. Perutz, S. Sabo-Etienne, *Angew. Chem.* **2007**, *119*, 2630 – 2645; *Angew. Chem. Int. Ed.* **2007**, *46*, 2578 – 2592; b) S. L. Matthews, V. Pons, D. M. Heinekey, *Inorg. Chem.* **2006**, *45*, 6453 – 6459; c) G. J. Kubas, *Catal. Lett.* **2005**, *104*, 79 – 101; d) G. J. Kubas, *Adv. Inorg. Chem.* **2004**, *56*, 127 – 177; e) M. Buhl, F. T. Mauschick, *Organometallics* **2003**, *22*, 1422 – 1431; f) X. Fang, J. Huhmann-Vincent, B. L. Scott, G. J. Kubas, *J. Organomet. Chem.* **2000**, *609*, 95 – 103; g) S. Chang, E. Scharrer, M. Brookhart, *J. Mol. Catal. A* **1998**, *130*, 107 – 119; h) E. Scharrer, S. Chang, M. Brookhart, *Organometallics* **1995**, *14*, 5686 – 5694; i) M. Brookhart, B. E. Grant, *J. Am. Chem. Soc.* **1993**, *115*, 2151 – 2156; j) X.-L. Luo, R. H. Crabtree, *J. Am. Chem. Soc.* **1989**, *115*, 2527 – 2535.

[4] For reviews: a) G. Nikonov, *Adv. Organomet. Chem.* **2005**, *53*, 217 – 309; b) J. Y. Corey, J. Braddock-Wilking, *Chem. Rev.* **1999**, *99*, 175 – 292; c) U. Schubert, *Adv. Organomet. Chem.* **1990**, *30*, 151 – 187; d) S. Lachaize, S. Sabo-Etienne, *Eur. J. Inorg. Chem.* **2006**, 2115 – 2127; e) Z. Lin, *Chem. Soc. Rev.* **2002**, *31*, 239 – 245; f) J. J. Schneider, *Angew. Chem.* **1996**, *108*, 1132 – 1139; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1068 – 1075; g) R. H. Crabtree, *Angew. Chem.* **1993**, *105*, 828 – 845; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789 – 805.

[5] Isolated cationic silane σ-complexes with X-ray analysis: a) S. T. N. Freeman, F. R. Lemke, L. Brammer, *Organometallics* **2002**, *21*, 2030 – 2032; isolated cationic silane σ-complexes without X-ray analysis: b) X. Fang, B. L. Scott, K. D. John, G. J. Kubas, *Organometallics* **2000**, *19*, 4141 – 4149.

[6] Calculations have identified complexes with minima showing smaller Si–M interactions: a) C. M. Nagaraja, P. Parameswaran, E. D. Jemmis, B. R. Jagirdar, *J. Am. Chem. Soc.* **2007**, *129*, 5587 – 5596; b) S. F. Vyboishchikov, G. I. Nikonov, *Organometallics* **2007**, *26*, 4160 – 4169; c) S. K. Ignatov, N. H. Rees, B. R. Tyrrell, S. R. Duberley, A. G. Razuvaev, P. Mountford, G. I. Nikonov, *Chem. Eur. J.* **2004**, *10*, 4991 – 4999; d) H. Rabaâ, J.-Y. Saillard, U. Schubert, *J. Organomet. Chem.* **1987**, *330*, 397 – 413.

[7] A neutral Zr dimer with a linear Si-H-Zr interaction has been observed in solid state but does not persist in solution: G. Ciruelo, T. Cuenca, R. Gómez, R. Gomez-Sal, A. Martin, *J. Chem. Soc. Dalton Trans.* **2001**, 1657 – 1663.

[8] See Supporting Information for experimental details including complete ^1H, ^{31}P and ^{29}Si NMR characterization.

[9] a) I. Goettker-Schnetmann, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 9330 – 9338; b) I. Goettker-Schnetmann, P. White, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 1804 – 1811; c) I. Goettker-Schnetmann, P. White, M. Brookhart, *Organometallics* **2004**, *23*, 1766 – 1776.

[10] Usually $J_{Si\text{-}H} < 20$ Hz for classical H-M-Si interactions, see ref. [3]; $J_{Si\text{-}H} = 175$ Hz for free Et_3SiH.

[11] Crystallographic data for **2**: $C_{52}H_{56}BF_{20}IrO_2P_2Si$, $M_r = 1386.01$, collection temperature 100(2) K, triclinic, space group $P\bar{1}$, $a = 12.4133(7)$, $b = 13.9005(8)$, $c = 17.0525(9)$ Å, $\alpha = 70.938(2)$, $\beta = 87.821(2)$, $\gamma = 88.840(2)°$, $V = 2779.0(3)$ Å^3, $Z = 2$, $R1 = 0.0246$ [$I > 2\sigma(I)$]. CCDC 676582 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] For example, Ir–Si 2.390(1) Å in $[Cp'Ir(H)_2(SiEt_3)_2]$: J. S. Ricci, T. F. Koetzle, M. J. Fernandez, P. M. Maitlis, J. C. Green, *J. Organomet. Chem.* **1986**, *299*, 383 – 389.

[13] Gaussian 03, Revision D.02; B3LYP; LANL2DZ on Ir(+f polarization); 6-311G** on other atoms. For details regarding the DFT study, see Supporting Information.

[14] a) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899 – 926; b) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735 – 746.

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