A Unique Coordination of SiH_4: Isolation, Characterization, and Theoretical Study of $(PR_3)_2H_2Ru(SiH_4)RuH_2(PR_3)_2$

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Received January 21, 2000

Since the report of the first silane σ-complex in 1969,[1] the activation of Si−H bonds has been the focus of intense research effort.[2,3] Hydrosilylation, dehydrogenative silylation, and dehydrogenative polymerization of silanes represent the most important applications and involve a wide variety of silanes.[4] However, the scarcity of publications on reactions using SiH_4, the simplest silane, and transition metals is probably the result of safety concerns. The only transition metal η^2-SiH_4 complex $Mo(\eta^2\text{-}SiH_4)(CO)(R_2PC_2H_4PR_2)_2$ was reported in 1995 by Luo, Kubas et al.[5] This compound was obtained by direct reaction of SiH_4 on the molybdenum complex $Mo(CO)(R_2PC_2H_4PR_2)_2$. To circumvent any hazard associated with the use of SiH_4, its in situ generation by catalytic redistribution of $HSi(OEt)_3$ by Cp_2TiMe_2 was exploited by Harrod et al.[6] Such alkoxyhydrosilane redistributions were also catalyzed by zirconium and hafnium complexes as shown by Tilley et al.[7]

Within the last three years, we have made a lot of progress on the isolation of unusual complexes involving in particular more than one σ-bond. We have described a series of bis(silane) mononuclear complexes $[RuH_2\{(\eta^2\text{-}H{-}SiR_2)_2X\}(PR'_3)_2]$ with two σ-Si−H bonds and demonstrated that these compounds are stabilized by secondary H···Si interactions.[8] These additional interactions are also responsible for the stability of another complex incorporating two different σ-bonds $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}H{-}SiPh_3)(PCy_3)_2$ (**1**).[9] We present in this contribution our first studies on the reactivity of dihydrogenosilanes with ruthenium complexes, and the isolation of the two complexes $(PR_3)_2H_2Ru(SiH_4)RuH_2(PR_3)_2$ (R= Cy, **2a**; R = ^{i}Pr, **2b**) with a SiH_4 ligand trapped by two dihydridobis(phosphine)ruthenium units.

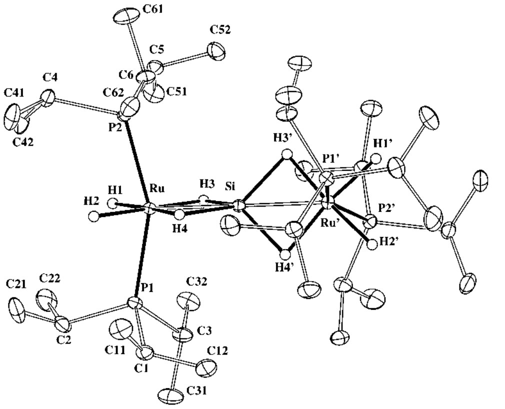

Figure 1. ORTEP drawing of compound **2b**.

Addition at room temperature of 2 equiv of $H_2SiPhMe$ to a suspension of the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ (**3**)[10] in pentane results in immediate gas evolution, and $(PCy_3)_2H_2Ru(SiH_4)RuH_2(PCy_3)_2$ (**2a**) is isolated as a white powder in 32% yield.[11] The ^1H NMR spectrum of **2a** in C_6D_6 solution at room temperature exhibits a pseudotriplet at δ −7.89 that transforms into a singlet upon phosphorus decoupling with satellites due to coupling to a single silicon (J_{Si-H} = 36 Hz). Upon cooling, two separate broad signals of equal intensities are observed at δ −6.0 and δ −8.6. The $^{29}Si\{^1H\}$ NMR shows a singlet at δ 290.2, and the ^{29}Si INEPT spectrum shows a nonet (J_{Si-H} = 36 Hz) in agreement with eight hydrogen atoms (in fast exchange) coupled to the silicon. We were able to obtain an X-ray structure of the analogous complex **2b** with the triisopropylphosphine in place of PCy_3.[11,12] **2b** and **2a** display the same basic NMR features. An ORTEP plot is shown in Figure 1. **2b** is a dinuclear ruthenium complex with each ruthenium in a roughly octahedral geometry. The figure clearly depicts the unique geometry of the SiH_4 ligand. The two ruthenium and the silicon atoms are linear (*z* axis) with one of the shortest Ru−Si distances ever reported (2.1875(4) Å),[2] even slightly shorter than in $[Cp^*(PMe_3)_2Ru{=}SiMe_2]^+$ (2.238(2) Å).[13] Moreover, highly downfield ^{29}Si NMR resonances have been associated with the presence of a silylene ligand.[13b] The four hydrogen atoms H1, H2, H3, and H4 are in a plane (*xz*) perpendicular to the plane (*yz*) containing the four other ones (H1′−H4′). The Si−H3 and Si−H4 distances, 1.69(3) and 1.73(3) Å respectively, indicate significant Si−H bond lengthening (1.48 Å for organosilicon compounds).[2,3] If we consider a complex incorporating four σ-Si−H bonds (4 $^1J_{Si-H}$) and four classical hydrides (4 $^2J_{Si-H}$), one can estimate a $J_{\sigma-Si-H}$ value in the range 50−70 Hz.[14] This is in perfect agreement with the Si−H distances found by X-ray and can be compared to previous data.[2,3,5,8]

To better understand the nature of the bonding between SiH_4 and the two metal-containing units, we have performed DFT/

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(1) Hoyano, J. K.; Elder, M.; Graham, W. A. G. *J. Am. Chem. Soc.* **1969**, *91*, 4569.

(2) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

(3) (a) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (b) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151.

(4) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Brown, S. S.; Kendrick, T. C.; McVie, J.; Thomas, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon press: New York, 1994; Vol. 2, Chapter 4. (c) West, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Chapter 19. (d) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Chapter 25. (e) Lapointe, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906. (f) Woo, H. G.; Waltzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (g) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 177.

(5) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 1159.

(6) (a) Xin, S.; Aitken, C.; Harrod, J. F.; Mu, Y.; Samuel, E. *Can. J. Chem.* **1990**, *68*, 471. (b) Hao, L.; Lebuis, A.-M.; Harrod, J. F.; Samuel, E. *Chem. Commun.* **1997**, 2193. (c) Hao, L.; Lebuis, A.-M.; Harrod, J. F. *Chem. Commun.* **1998**, 1089.

(7) Woo, H. G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698.

(8) (a) Delpech, F.; Sabo-Etienne, S.; Chaudret, B.; Daran, J. C *J. Am. Chem. Soc.* **1997**, *119*, 3167. (b) Delpech, F.; Sabo-Etienne, S.; Chaudret, B.; Daran, J. C.; Hussein, K.; Marsden, C. J.; Barthelat, J.-C. *J. Am. Chem. Soc.* **1999**, *121*, 6668.

(9) Hussein, K.; Marsden, C. J.; Barthelat, J.-C.; Rodriguez, V.; Conejero, S.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B. *Chem. Commun.* **1999**, 1315.

(10) Sabo-Etienne, S.; Chaudret, B. *Coord. Chem. Rev.* **1998**, *178−180*, 381.

(11) See Supporting Information for details on the synthesis and characterization of **2a** and **2b**.

(12) Crystal data for **2b**: pale yellow crystal, *T* = 160 K, monoclinic, *C*2/*c*, *a* = 19.588(2) Å, *b* = 12.1805(15) Å, *c* = 19.823(3) Å, β = 98.066 (15) °, *Z* = 8, R1 = 0.0281, GOF = 1.034.

(13) (a) Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 5495. (b) Grumbine, S. K.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **1998**, *17*, 5607.

10.1021/ja000223p CCC: $19.00

Table 1. Selected Optimized Geometrical Parameters for $(PH_3)_2H_2Ru(SiH_4)RuH_2(PH_3)_2$ **2** and X-ray Data for $(P^iPr_3)_2H_2Ru(SiH_4)RuH_2(P^iPr_3)_2$ **2b**[a]

	DFT/B3LYP	X-ray
Ru−H1(H2)	1.626	1.49(2); 1.52(3)
Ru−H3(H4)	1.812	1.62(3); 1.62(3)
Si−H3(H4)	1.685	1.69(3); 1.73(3)
Ru−Si	2.229	2.1875(4)
Ru−P1(P2)	2.308	2.3119(7); 2.3129(7)
H1−Ru−H2	86.0	86.6(15)
H3−Ru−H4	95.9	101.4(14)
H3−Si−H4	105.9	94.2(14)
P1−Ru−P2	155.4	155.18(2)
Ru−Si−Ru′	180.0	179.40(4)

[a] See Figure 1 for labeling of the atoms. Distances are in Å and angles in degrees.

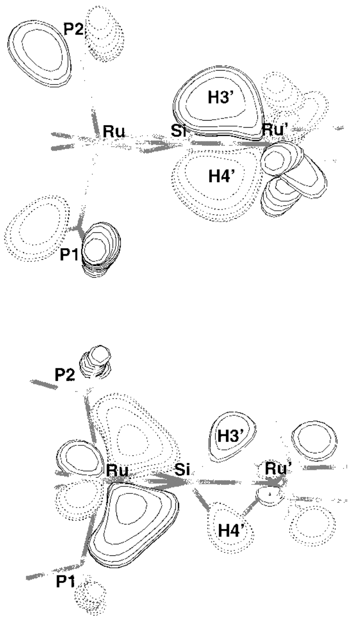

Figure 2. Isovalue representation of the 4e and 7e valence molecular orbitals of **2** involved in the σSi−H → d_{yz} Ru′ (top) and d_{yz} Ru → σ^*Si−H (bottom) interactions. The surfaces correspond to 0.05 $(ea_0^{-3})^{1/2}$.

B3LYP calculations on the model complex $(PH_3)_2H_2Ru(SiH_4)RuH_2(PH_3)_2$ (**2**).[15] A geometry optimization followed by a vibrational frequency analysis results in a D_{2d} geometry with no imaginary frequencies. Optimized geometrical parameters and X-ray data for **2b** are compared in Table 1. Our calculation confirms the overall structure found by X-ray diffraction. As expected, X-ray Ru−H distances are found shorter than the calculated ones. However, the calculated Ru−Si distance (2.229 Å) is in good agreement with the experimental one. The comparison with optimized Ru−Si bond lengths in η^2-silane complexes (2.425 Å in $[RuH_2\{(\eta^2\text{-H}-SiH_2)_2(C_6H_4)\}(PH_3)_2]$ (**A**),[8b] 2.394 Å in $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-H}-SiH_3)(PH_3)_2$ (**B**))[9] reveals an unusual short distance in **2**, suggesting some double bond character. The nature of this Ru−Si interaction was first studied by a natural bond orbital (NBO) analysis:[18] it appears that in **2** as well as in **A** and **B**, the Ru−Si bond would be highly polar with a bond order smaller than 1. Moreover, analysis of the molecular orbitals reveals that the bonding interactions between SiH_4 and the two ruthenium fragments occur through the σ Si−H bonds. In each *xz* and *yz* planes, the two Si−H hybrid orbitals interact with the empty d orbital of one ruthenium center, whereas a back-bonding delocalization occurs from the occupied d orbital of the other Ru center into the σ^* Si−H antibonding orbitals. This double interaction is shown in Figure 2 where the two molecular orbitals involving the metal orbitals of primarily d_{yz} character are depicted. The short Ru−Si distances cannot be considered as classical double bonds but are the result of these multiple σ-interactions. A high binding energy of 255 kJ.mol^{-1} between SiH_4 and the $RuH_2(PH_3)_2$ fragments is calculated.

When the reaction of two equiv of $H_2SiPhMe$ to (**3**) is performed in an NMR tube in C_6D_6 solution, two major ruthenium compounds are identified by ^1H and ^{31}P NMR as **2a** and $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-H}-SiPh_3)(PCy_3)_2$ (**1**), together with the two silicon compounds $HSiPh_2Me$ and $HSiMe_2Ph$ in a 1:1.3:2.2:3.4 ratio, respectively. A small amount of an unidentified hydride complex was also detected as well as traces of $HMe_2SiSiMe_2H$. Clearly this reaction undergoes redistribution at silicon with Si−C bond breaking allowing the generation of SiH_4 immediately trapped by two dihydride ruthenium units. In situ generation of $HSiPh_3$ also results in its coordination to ruthenium producing the known complex **1**. It is remarkable that formation of **2a** is also observed when using a dihydrogenosilane such as H_2SiEt_2.[19]

In summary, we report here a unique mode of coordination of the simplest silane SiH_4 to a transition metal complex. In our system, in situ generation of SiH_4 by redistribution of H_2SiRR' is catalyzed by a ruthenium complex; the redistribution mechanism has still to be elucidated. In view of the structural and theoretical data, $(PR_3)_2H_2Ru(SiH_4)RuH_2(PR_3)_2$ can be formulated as complexes in which SiH_4 is trapped by two $RuH_2(PR_3)_2$ units and acts as a bridging ligand via four σ-Si−H bonds. These novel interactions involve in each case σ-donation to a ruthenium and back-bonding from the other ruthenium, and they are indeed responsible for the very short Ru−Si distances. They represent the first examples of a new mode of bonding of a silane, in addition to full oxidative addition and to usual σ-bond coordination. Reactivity and catalytic activity studies of **2a**,**b** are in progress.

Acknowledgment. This work is supported by the CNRS. We thank the CINES (Montpellier, France) for a generous allocation of computer time.

Supporting Information Available: X-ray structural information on **2b**. A table of natural atomic charges and bond orders for **2**, **A** and **B**. Synthesis and characterization data for **2a** and **2b** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) $J_{H-Si}obs = 1/8(4\ ^1J_{H-Si} + 4\ ^2J_{H-Si}) = 36$ Hz. Assuming a $^2J_{H-Si}$ value in the range 0−20 Hz for the coupling between the silicon and the classical hydrides H1, H2, H1′, and H2′, one can estimate a J_{H-Si} value of 52 to 72 Hz for the coupling between the silicon and the hydrides H3, H4, H3′, and H4′.

(15) Ruthenium centers were described with a relativistic small-core pseudopotential and a [5s,5p,3d] contracted Gaussian basis set.[16] Pseudopotentials developed in Toulouse[17] were used to represent the 10-electron core of the Si and P atoms. For these atoms and for the hydrogen atoms directly attached to Si and Ru, double-ζ plus polarization basis sets were used. All calculations were carried out with the Gaussian 98 program (see Supporting Information).

(16) Rodriguez, V.; Sabo-Etienne, S.; Chaudret, B.; Thoburn, J.; Ulrich, S.; Limbach, H.-H.; Eckert, J.; Barthelat, J.-C.; Hussein, K.; Marsden, C. J. *Inorg. Chem.* **1998**, *37*, 3475.

(17) Bouteiller, Y.; Mijoule, C.; Nizam, M.; Barthelat, J.-C.; Daudey, J.-P.; Pélissier, M.; Silvi, B. *Mol. Phys.* **1988**, *65*, 2664.

(18) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(19) For redistributions at silicon, see refs 6, 7, and 20. Interestingly, Suzuki et al. have described in 1995 the activation of $^tBu_2SiH_2$ by $Cp^*Ru(\mu\text{-H})_4RuCp^*$ in which case, the dinuclear ruthenium complex $[Cp^*Ru(\mu\text{-H})]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2Si^tBu_2)$ is obtained with the dihydrogenosilane bound to each ruthenium via two σ-Si−H bonds.[21]

(20) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

(21) Takao, T.; Yoshida, S.; Suzuki, H.; Tanaka, M. *Organometallics* **1995**, *14*, 3855.