2030 *Organometallics* **2002,** *21,* 2030−2032

$[Cp(PMe_3)_2Ru(\eta^2\text{-}HSiCl_3)]^+$: Structure and Bonding of a Rare Cationic η^2-Silane Complex

Samuel T. N. Freeman and Frederick R. Lemke*

Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701-2979

Lee Brammer†

Department of Chemistry and Biochemistry, University of Missouri−St. Louis, 8001 Natural Bridge Road, St. Louis, Missouri 63121-4499

Received January 29, 2002

*Summary: Protonation of $Cp(PMe_3)_2RuSiCl_3$ (**1**) leads to the formation of $[Cp(PMe_3)_2Ru(\eta^2\text{-}HSiCl_3)]^+$ (**2**$^+$), a rare example of a cationic η^2-silane complex. The η^2-silane coordination in **2**$^+$ is confirmed by an X-ray crystallographic study. The short Ru−H and long Si−H interactions in **2**$^+$ model the latter stages of hydrosilane oxidative addition to a metal center.*

The coordination of a Si−H bond to a transition metal center to form η^2-silane metal complexes has been extensively studied and reviewed.[1−6] η^2-Silane complexes represent the incomplete oxidative addition of a Si−H bond to a metal center. The steric and electronic nature of the silane plays an important role in the extent of Si−H bond breaking. These complexes have generally been prepared from the reaction of a hydrosilane with a coordinatively unsaturated metal center. Thus, the majority of η^2-silane metal complexes are neutral; cationic complexes of this type are quite rare. This rarity stems from the tendency of the Si−H bond to undergo heterolytic cleavage in cationic η^2-silane complexes.[7]

The protonation of metal silyl complexes to form cationic η^2-silane metal complexes has been used to a very limited extent. The protonation of $Cp(PMe_3)_2RuSiCl_3$ (**1**) to prepare $[Cp(PMe_3)_2Ru(\eta^2\text{-}HSiCl_3)][BAr^f{}_4]$ (**2**, $Ar^f = 3,5\text{-}C_6H_3(CF_3)_2$) was reported by one of us.[8] Similarly, Brookhart and co-workers reported the observation of $[Cp(CO)(PEt_3)Fe(\eta^2\text{-}HSiEt_3)]^+$ from the protonation of $Cp(CO)(PEt_3)FeSiEt_3$.[9] Structural characterization of such cationic η^2-silane complexes is also rare. Herein we describe the crystal structure of **2** and the nature of the η^2-$HSiCl_3$ bonding in this cationic ruthenium complex. Importantly, we are also able to discuss the structure and bonding of η^2-silane complex **2** relative to the deprotonated silyl complex **1**,[10] just as we have previously been able to make such comparisons between the related hydride, dihydride, and dihydrogen complexes of the "$CpRuP_2$" moiety.[11]

Complex **2** was isolated as a white air- and water-sensitive solid by protonation of **1**[8,10,12] with $[H(OEt_2)_2]BAr^f{}_4$[13] (eq 1).[14] A triplet at δ −9.87 ($^2J_{PH} = 11$ Hz) with ^{29}Si satellites ($^2J_{SiH} = 48$ Hz) was assigned to the hydride ligand on ruthenium in the room-temperature ^1H NMR spectrum of **2**. At lower temperatures, this triplet moves upfield, collapsing to a broad singlet from −40 to −55 °C, and reappears as a triplet (δ −10.13, $^2J_{PH} = 9$ Hz) at −65 °C. In the room-temperature ^{29}Si DEPT NMR spectrum, the silyl group was observed as a doublet at δ 30.61 with $^2J_{SiH} = 49$ Hz and no observable $^2J_{SiP}$. No ^{29}Si signal was observed from −40 to −55 °C but reappeared as a doublet at δ 31.07 ($^2J_{SiH} = 51$ Hz) at −65 °C. The phosphines in **2** were observed as a singlet in the $^{31}P\{^1H\}$ NMR spectrum down to −40 °C. These NMR data for **2**, particularly the small $^2J_{PH}$[15] and apparently large $^2J_{SiH}$[17] values, support the presence of an η^2-$HSiCl_3$ moiety, which is fluxional on the

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* To whom correspondence should be addressed. E-mail: flemke1@ohiou.edu.

† Current address: Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K.

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(14) In a typical reaction, a 25 mL O-ring Kjeldahl flask was charged with $Cp(PMe_3)_2RuSiCl_3$ (100 mg, 0.313 mmol) and $[H(Et_2O)_2][BAr^f{}_4]$ (285 mg, 0.282 mmol). The flask was cooled with liquid nitrogen, and CH_2Cl_2 (~15 mL) was added via vacuum transfer. The reaction mixture was allowed to warm to room temperature and stir for 1 h. The volume was reduced by ca. two-thirds, then doubled with hexanes. The white precipitate was filtered through a glass frit, washed with hexanes, and vacuum-dried. Typical yields range from 80 to 85%. ^1H NMR (CD_2Cl_2): δ 7.73, 7.57 (m, 12H, $BAr^f{}_4$), 5.43 (s, Cp, 5H), 1.77 (vt, $N = 10.13$ Hz, 18H, PMe_3), −9.87 (t, Ru−H···Si, 1H, $^2J_{PH} = 11.23$ Hz with ^{29}Si satellites $^1J_{SiH} = 48$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 0.421 (s, PMe_3). ^{29}Si DEPT NMR (CD_2Cl_2): δ 30.60 (d, $^1J_{SiH} = 48.2$ Hz). Anal. Calcd for $C_{43}H_{36}BCl_3F_{24}P_2RuSi$: C, 39.22; H, 2.76. Found: C, 39.64; H, 2.55.

(15) The $^2J_{PH}$ value for **2** is small compared to the related ruthenium(IV) dihydrides $[Cp(PMe_3)_2RuH_2]X$ (X = Cl, BF_4, $BAr^f{}_4$), which have $^2J_{PH} = 29$ Hz.[16]

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(17) $^2J_{SiH}$ values are generally <20 Hz for classical H−M−Si interactions. The $^2J_{SiH}$ value for **2** is therefore consistent with a nonclassical interaction between the RuH and Si center and is within the $^2J_{SiH}$ range (38−69 Hz) observed for neutral manganese η^2-hydrosilane complexes.[1,18,19]

10.1021/om020063l CCC: $22.00 © 2002 American Chemical Society
Publication on Web 04/12/2002

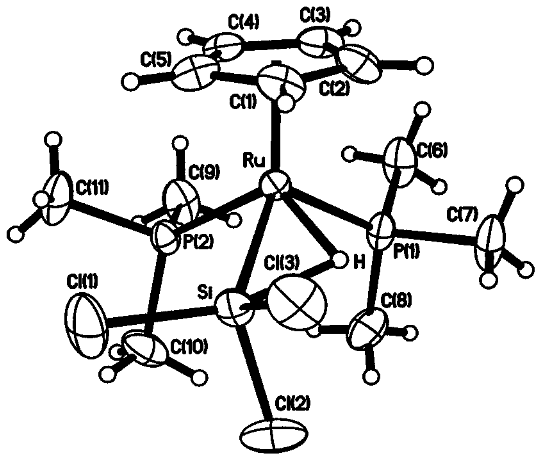
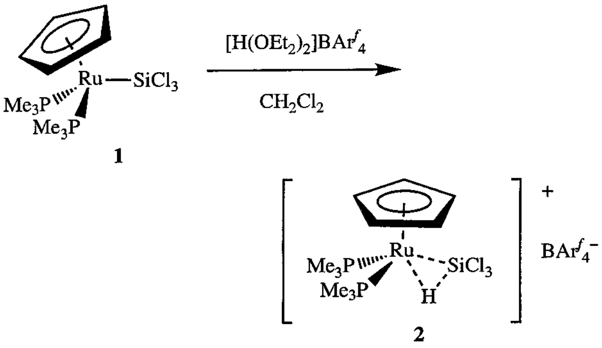


Figure 1. Perspective view of the cation in **2**, $[Cp(PMe_3)_2Ru(\eta^2\text{-}HSiCl_3)]^+$ (30% ellipsoids). Minor orientation of Cp ring not shown. Important bond distances (Å) and angles (deg): Ru−H 1.60(5), Si−H 1.77(5); H−Ru−Si 49.5(16), Ru−Si−H 43.2(16), Si−H−Ru 87.3(16), H−Si−Cl(1) 159.9(16), H−Si−Cl(2) 89.8(14), H−Si−Cl(3) 90.6(16), H−Ru−P(1) 69.7(17), H−Ru−P(2) 116.3(16), Cp(centroid)−Ru−H 122.3.

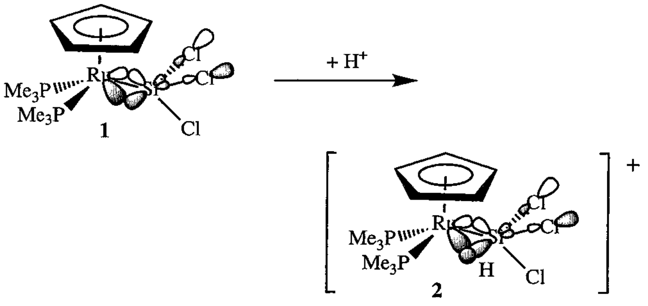
NMR time scale. However, the NMR data does not indicate the orientation of the η^2-$HSiCl_3$ group on the $Cp(PMe_3)_2Ru^+$ fragment.



(1)

The orientation of the η^2-$HSiCl_3$ group was determined by X-ray crystallography.[20] Crystals of **2** suitable for X-ray diffraction were grown via diffusion of hexanes into a concentrated CH_2Cl_2 solution of **2** at −30 °C. The molecular structure of the cation in **2** is shown in Figure 1. The hydrogen atom attached to ruthenium was located in the difference Fourier map and its position freely refined; it lies *cis* to the silicon atom. The geometry of **2** can be described as a "four-legged piano stool" with the "legs" comprising the hydride, silyl, and two phosphine ligands; alternatively, **2** could be considered a "three-legged piano stool" with the η^2-$HSiCl_3$ and phosphine ligands comprising the "legs". The three chlorides and the Ru−H bond form a distorted tetrahedral geometry around the Si. While the Ru−H distance (1.60(5) Å) is consistent with that of a terminal ruthenium hydride,[11,16,21] the hydride is only 1.77(5) Å from the silicon atom, indicating a significant Si⋯H interaction. This Ru⋯H⋯Si interaction shows dimensions similar to those observed in $RuH_2\{(\eta^2\text{-}HSiMe_2)_2O\}(PCy_3)_2$ (Si⋯H 1.83(3) and 1.88(3) Å)[22] and the cation $\{Cp^*Ru(H)[\eta^5\text{-}Me_4C_4SiSi(SiMe_3)_3]\}^+$ (Si⋯H 1.70(7) Å).[23]

Scheme 1



The structure of **2** exhibits some interesting differences from that of the previously characterized deprotonated form **1**.[10] A comparison of selected bond distances and angles between **1** and **2** is given in Table 1. The Ru−Si distance is markedly longer in **2** than in **1**, while the average Si−Cl distances are shorter in **2** (2.043 Å) than in **1** (2.119 Å). In a similar manner, Ru−P distances in **2** increase and P−C distances decrease in length relative to those in **1**. Also, as one might anticipate, the longer Ru−Si distance and shorter Si−Cl distances are accompanied by an increase in the average Cl−Si−Cl angle in **2** (from 98.2° in **1** to 102.4°) with a concomitant decrease in the average Ru−Si−Cl angle (from 119.1° in **1** to 115.9°).

The η^2-silane bonding in **2** can be described as a $Cp(PMe_3)_2Ru^+$ fragment interacting with $HSiCl_3$.[1] The LUMO of $Cp(PMe_3)_2Ru^+$ is composed primarily of the ruthenium d_{z^2} orbital[24,25] and undergoes a σ-type interaction with the σ(Si−H) orbital of $HSiCl_3$. A π-type interaction (back-bonding) occurs from the interaction of the HOMO (primarily ruthenium d_{yz} in character)[24,25] of $Cp(PMe_3)_2Ru^+$ with the σ^*(Si−H) orbital of $HSiCl_3$. Both interactions result in the weakening (lengthening) of the Si−H bond. As a consequence, the Si−H distance in **2** (1.77 Å) is considerably longer than the Si−H distance (1.48 Å)[26] in free hydrosilanes. The longer Si−Cl distances in **2** (2.04 Å) compared to free polychlorosilanes (2.02 Å)[27] is consistent with a change in

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(20) Crystal data for **2**: colorless blocks; $M = 1316.98$, monoclinic, $P2_1/n$, $a = 12.668(5)$ Å, $b = 26.906(10)$ Å, $c = 14.881(6)$ Å, $\beta = 98.65(2)°$, $U = 5014(3)$ Å^3, $Z = 4$, $D_c = 1.744$ Mg m^{-3}, $T = 203(5)$ K; $R_1(F) = 0.053$ for 6487 $F^2 > 2\sigma(F^2)$, $wR_2(F^2) = 0.138$, $S(F^2) = 1.25$ for all 8564 data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Orientational disorder in the cyclopentadienyl ring was modeled using two orientations (60:40) in which the rings were constrained to be idealized pentagons. Rotational disorder in one of the CF_3 groups of the anion was modeled using two orientations (57:43). The hydride hydrogen was located from the difference density map and refined using unconstrained positional parameters and a fixed isotropic displacement parameter. C−H hydrogen atoms were placed in idealized positions and refined using a riding model. Further details concerning the crystallographic analysis of **2** are given in the Supporting Information.

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Table 1. Selected Bond Distances (Å) and Angles (deg) for $Cp(PMe_3)_2RuSiCl_3$ (1) and $[Cp(PMe_3)_2Ru(\eta^2\text{-}HSiCl_3)][BAr^f_4]$ (2)

	1[a]	**2**
	Interatomic Distances[b]	
Ru−Si	2.265(2)	2.329(1)
Ru−P(1)	2.273(2)	2.335(1)
Ru−P(2)	2.280(2)	2.322(1)
Ru−Cp(c)	1.887	1.879
Si−Cl(1)	2.122(3)	2.052(2)
Si−Cl(2)	2.114(3)	2.046(2)
Si−Cl(3)	2.121(3)	2.030(2)
P−C (av)	1.823	1.798
P−C (range)	1.808(8) − 1.84(1)	1.786(5) − 1.809(5)
	Bond Angles[b]	
P(1)−Ru−P(2)	95.80(7)	91.11(5)
P(1)−Ru−Si	92.60(7)	109.08(5)
P(2)−Ru−Si	93.00(7)	86.83(6)
Cp(c)−Ru−Si	121.2	119.6
Cp(c)−Ru−P (av)	123.2	120.8
Ru−Si−Cl(1)	116.8(1)	116.76(8)
Ru−Si−Cl(2)	115.0(1)	117.19(8)
Ru−Si−Cl(3)	125.6(1)	113.62(8)
Cl(1)−Si−Cl(2)	99.0(1)	103.4(1)
Cl(2)−Si−Cl(3)	98.8(1)	100.9(1)
Cl(1)−Si−Cl(3)	96.9(1)	102.9(1)

[a] Interatomic distances and angles from ref 10. [b] Cp(c) represents the centroid of the cyclopentadienyl group.

hybridization at silicon due to an increase in coordination number.[28] On the basis of these structural characteristics, **2** represents a model for the latter stage of oxidative addition of a hydrosilane to a transition metal center.

An alternative but similar view of the bonding interaction in **2** arises by considering the changes induced upon protonation of **1**. Silyl **1** contains short Ru−Si and long Si−Cl distances due to π-back-bonding between the d-orbital based HOMO and SHOMO of the $Cp(PMe_3)_2$-Ru fragment and the linear combinations of σ^*(Si−Cl) orbitals on the $SiCl_3$ group.[10] (One of these π-back-bonding interactions in **1** is shown in Scheme 1.) Protonation of **1** forms a relatively normal Ru−H bond and a long Si−H bond and formally oxidizes the ruthenium center to Ru(IV). Consequently, the direct Ru−$SiCl_3$ π-back-bonding interaction is substantially weakened, resulting in a marked lengthening of the Ru−Si bond and shortening of the Si−Cl bonds in **2** relative to **1**. The accompanying but much smaller changes in Ru−P and P−C distances upon protonation can also be accounted for by a decrease in the Ru−PMe_3 π-back-bonding interaction[29] (Table 1).

In summary, the rare cationic η^2-silane complex **2**, prepared by the protonation of the neutral ruthenium silyl complex **1**, has been characterized in detail by X-ray crystallography and compared with the deprotonated species **1**. The structural data for **2** indicate the η^2-silane is arrested in its oxidative addition to the ruthenium center and models the latter stages of such a reaction wherein the M−H is short and the Si−H bond is substantially elongated.

We are continuing efforts to obtain more structural and chemical information on cationic η^2-silane complexes of ruthenium.

Acknowledgment. F.R.L. and S.T.N.F. would like to thank the Research Challenge and Condensed Matter and Surface Science programs at Ohio University, and Dow Corning Corporation for financial support. L.B. is grateful to the National Science Foundation for research support (CHE-9988184) and for support of the SMART CCD diffractometer at UMSL (CHE-9309690).

Supporting Information Available: General experimental procedures, variable-temperature NMR data, and tables of crystal data, data collection and refinement parameters, and interatomic distances and angles for **2**. Full crystallographic data in CIF format for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020063L

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