X-Ray structure and theoretical studies of $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}H\text{-}SiPh_3)(PCy_3)_2$, a complex with two different η^2-coordinated σ bonds

Khansaa Hussein,[a]† **Colin J. Marsden,**[a] **Jean-Claude Barthelat,**[a] **Venancio Rodriguez,**[b] **Salvador Conejero,**[b]
Sylviane Sabo-Etienne,*[b] **Bruno Donnadieu**[b] **and Bruno Chaudret**[b]

[a] *Laboratoire de Physique Quantique, IRSAMC (UMR 5626), Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 4, France*
[b] *Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 04, France. E-mail: sabo@lcc-toulouse.fr*

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Weak interactions between the silicon and the hydrides are responsible for the stabilization of the title complex bearing two different coordinated σ-bonds, (η^2-H_2) and (η^2-H–$SiPh_3$).

Nowadays the existence of η^2-dihydrogen or η^2-silane coordination to a metal centre is well established.[1–3] These η^2-H–X species (X = H, Si) are often considered as a representation of the arrested oxidative addition of dihydrogen or silanes to a metal center. They are thus often invoked in many catalytic reactions such as hydrogenation or hydrosilylation.[1–4] When considering the small number of complexes accommodating two σ-HX bonds, one important question is to determine the factors that promote the formation of such species. Indeed, there are only two thermally stable bis(dihydrogen) complexes[3] $[RuH_2(H_2)_2(PCy_3)_2]$ **1** and $[Tp^*RuH(H_2)_2]$, and we have recently described a new family of bis(silane) complexes $[RuH_2\{(\eta^2\text{-}H\text{–}SiR_2)_2X\}(PR'_3)_2]$ in which the disilane ligand acts as a chelate and is coordinated to the ruthenium *via* two σ-H–Si bonds.[5]

Here, we present the first structural characterization of a mixed σ-(H–H) and σ-(H–Si) complex $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}H\text{–}SiPh_3)(PCy_3)_2$ **2** as well as theoretical studies highlighting the importance of weak formally non-bonding interactions between the silicon and the classical hydrides.

In 1994, we reported our first results concerning the reactivity of **1** toward weakly coordinating ligands such as N_2 and $HEPh_3$ (E = Si, Ge).[6] Substitution of two or one dihydrogen ligands was observed leading to $RuH_2(N_2)_2(PCy_3)_2$ and $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}H\text{–}EPh_3)(PCy_3)_2$ respectively. The silane complex **2** was obtained by addition of 1 equiv. of $HSiPh_3$ to a pentane suspension of **1**. On the basis of NMR data and T_1 measurements, we proposed a formulation for **2** in which the two phosphine ligands were in a *trans* position, in agreement with the presence of such bulky phosphines. However, we have now succeeded in growing crystals and have obtained new information from the X-ray diffraction study. The molecular structure is shown in Fig. 1 and the principal distances and angles are listed in Table 1.‡ Two molecules are found in the asymmetric unit; however, as no significant differences are observed, we present here only the data concerning one molecule. Surprisingly, the phosphines are in a *cis* configuration with a P1–Ru–P2 angle of 109.71(5)°. The classical hydride H4 is *trans* to one phosphine with a P1–Ru–H4 angle of 166.5(14)° whereas the hydrogen H5 involved in the σ-H–Si bond is *trans* to the other phosphine with a P2–Ru–H5 angle of 170.7(11)°. The second classical hydride H3 is *trans* to the dihydrogen ligand H1–H2 with H3–Ru–H1 and H3–Ru–H2 angles of 163(2) and 168(2)°, respectively.

The (η^2-Si–H) coordination is confirmed by a significant lengthening of the Si–H5 bond: 1.72(3) Å (*ca.* 1.49 Å in free silanes). The Ru–H bond lengths vary from 1.47(4) to 1.66(2) Å with the two Ru–H distances involving the dihydrogen ligand markedly higher. The dihydrogen ligand is characterized by a H1–H2 distance of 0.82(2) Å, a value in agreement with an unstretched dihydrogen complex as highlighted by its high reactivity [addition of H_2 or N_2 results in immediate elimination of the silane and formation of the corresponding bis(dihydrogen) or bis(dinitrogen) complex]. The Si···H4 distance of 1.83(3) Å is below the limit of 2 Å normally admitted for σ-Si–H bonds. Thus the silicon is almost symmetrically bonded to H5 and H4, as can be seen from the H–Ru–Si angles of 45.9(11) and 50.2(10)°. In addition the Si···H3

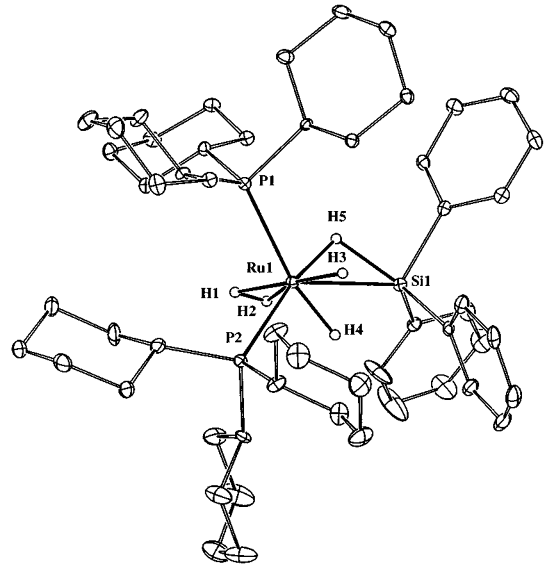

Fig. 1 ORTEP[12] drawing of compound **2**.

Table 1 Calculated geometrical parameters for the $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}H\text{–}SiH_3)(PH_3)_2$ ground-state isomer and X-ray data for **2**[a]

	B3LYP	X-ray		B3LYP	X-ray
Ru–H1	1.807	1.66(2)	Ru–H2	1.785	1.64(2)
Ru–H3	1.626	1.49(4)	Ru–H4	1.641	1.47(4)
Ru–H5	1.643	1.54(4)	Si–H5	1.946	1.72(3)
Si···H3	2.116	2.40(4)	Si···H4	2.071	1.83(3)
H1–H2	0.849	0.82(2)	Ru–Si	2.394	2.3846(18)
Ru–P1	2.370	2.4058(17)	Ru–P2	2.367	2.3921(16)
H3···H4	2.301	2.22(2)			
P1–Ru–P2	98.9	109.71(5)	P1–Ru–H4	171.8	166.5(14)
P2–Ru–H5	177.6	170.7(11)	Si–Ru–H5	53.8	45.9(11)
Si–Ru–H3	60.0	72.6(14)	Si–Ru–H4	58.3	50.2(10)
H1–Ru–H2	27.4	28.9(8)	H2–Ru–H3	162.9	168(2)
P1–Ru–Si	114.4	118.49(6)	P2–Ru–Si	124.9	124.85(6)

[a] See Fig. 1 for labelling of the atoms. Distances are in Å and angles in °.

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† Permanent address: Department of Chemistry, Faculty of Sciences, University Al Baath, Homs, Syria.

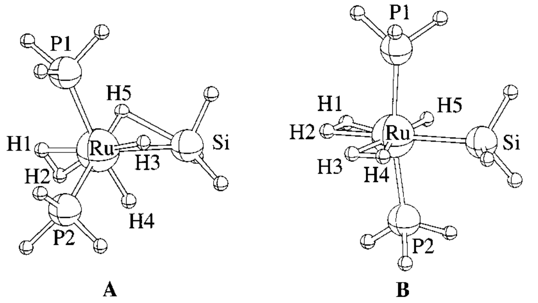

Fig. 2 The B3LYP-optimized structures of isomers **A** and **B**.

distance is 2.40(3) Å, allowing further Si···H interactions as also found by theoretical calculations. Similar interactions are also responsible for the *cis* geometry for the two PCy_3 ligands in the ruthenium complexes $RuH_2\{(\eta^2\text{-H–SiR}_2)_2X\}(PR'_3)_2$ accommodating two σ-Si–H bonds.[5b]

DFT/B3LYP calculations using a relativistic small-core pseudopotential and a [5s,5p,3d] contracted Gaussian basis for ruthenium[7] were performed on the model complex $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-H–SiH}_3)(PH_3)_2$.§ Geometry optimizations followed by vibrational frequency analyses allow identification of five singlet local minima. The structure of the most stable isomer **A** in Fig. 2 (C_1 symmetry) closely resembles that found by X-ray diffraction for **2**; we note that location of H atoms by X-ray diffraction is subject to considerable uncertainties, and that the computed P1–Ru–P2 bond angle would increase by about 7° if the PH_3 ligands were replaced by a more realistic model, such as PMe_3.[5b] Optimized geometrical parameters are listed in Table 1 for comparison. The origin of the unusual *cis* geometry for the two phosphines can be found in the presence of two attractive non-bonded interactions between the silicon atom and the two classical hydrides H3 and H4;[10] the attractive nature of these interactions is shown by the Mulliken population analysis.¶ Indeed, the calculated Si···H3 and Si···H4 distances, 2.116 and 2.071 Å, respectively, are much shorter than the sum of the van der Waals radii of silicon and hydrogen (3.3 Å). Such interactions are precluded geometrically in the four other isomers (all having *trans* phosphines). The lowest-energy of these is better described as a hydrido(silyl) complex $RuH(SiH_3)(\eta^2\text{-}H_2)_2(PH_3)_2$ (**B** in Fig. 2); it is only 8 kJ mol^{-1} above **A** [17 kJ mol^{-1} by single-point CCSD(T) calculations]. Relative B3LYP energies of the other isomers vary from 16 to 41 kJ mol^{-1}. Binding energies of the SiH_4 and H_2 ligands have been calculated from the $RuH_2(\eta^2\text{-}H_2)(PH_3)_2$ and $RuH_2(\eta^2\text{-H–SiH}_3)(PH_3)_2$ fragments.‖

As pointed out very recently by Corey and Braddock-Wilking in their impressive review on the reactions of hydrosilanes with transition-metal complexes, 'Several variations of interactions seem to occur between silanes and metals, from full oxidative addition to that of arrested addition with an interaction between a metal orbital and a Si–H sigma bond'.[2b] We have shown here how important additional Si···H interactions are; they control the coordination geometry at the metal centre. This type of bonding deserves special attention for future studies, given that it involves energies comparable to those in the 'dihydrogen bonds'** recently described by several groups,[11] and that it might well be of primary importance in catalytic silicon transformations.

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Notes and references

‡ *Crystal data* for **2**: $C_{58}H_{91}OP_2SiRu$, M = 995.59, triclinic, space group $P\bar{1}$, T = 160(2) K, a = 12.7694(16), b = 20.991(3), c = 21.691(2) Å, α = 94.763(14), β = 103.677(14), γ = 98.202(15)°, V = 5550.0(12) Å^3, Z = 4, μ = 0.342 mm^{-1}, reflections collected/unique = 44792/16676, $R1$ = 0.0381, $wR2$ = 0.0626. The H1–H5 atoms were located on difference Fourier syntheses; their coordinates were refined with isotropic thermal parameters. CCDC 182/1287. See http://www.rsc.org/suppdata/cc/1999/1315/ for crystallographic files in .cif format.

§ All calculations were performed with the Gaussian 94 program.[8] The Si and P atoms were described by standard pseudo-potentials developed in Toulouse[9] with a double-zeta plus polarization basis set. A double-zeta plus polarization basis was used for the hydrogen atoms, except for those of the phosphine ligands (DZ only).

¶ We obtain non-negligible positive overlap populations between Si and H3 or H4 of 0.05 and between Si and H5 of 0.09 (0.40 in free SiH_4).

‖ The energy differences between the products and the reactants are −92.7 kJ mol^{-1} for SiH_4 and −73.8 kJ mol^{-1} for H_2. Further details on related complexes will be published elsewhere.

** Intramolecular hydrogen bonding between a hydride and a hydrogen bond donor.

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