Inorg. Chem. **2008**, *47*, 8601−8603

Inorganic Chemistry
Communication

Bonding Mode of a Bifunctional P∼Si−H Ligand in the Ruthenium Complex “Ru($PPh_2CH_2OSiMe_2H$)$_3$”

Virginia Montiel-Palma,[†] Olivier Piechaczyk,[‡] Alexandre Picot,[§] Audrey Auffrant,[‡] Laure Vendier,[§] Pascal Le Floch,[*,‡] and Sylviane Sabo-Etienne[*,§]

Centro de Investigaciones Quimicas, Universidad Autónoma del Estado de Morelos, Cuernavaca, Morelos 62210, Mexico, Laboratoire “Hétéroéléments et Coordination”, UMR CNRS 7653 (DCPH), Département de Chimie, Ecole Polytechnique, 91128 Palaiseau Cedex, France, and Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 04, France

Received July 16, 2008

The phosphinosilane compound $PPh_2CH_2OSiMe_2H$ is potentially a bifunctional P∼Si−H ligand. By treatment with the Ru^{II} precursor $RuH_2(H_2)_2(PCy_3)_2$, the complex $Ru(PPh_2CH_2OSiMe_2H)_3$ (**2**), resulting from the coordination of three ligands and the displacement of two PCy_3 and two dihydrogen ligands, was formed. The different bonding modes for each of the three bifunctional P∼Si−H ligands are discussed on the basis of multinuclear NMR, X-ray diffraction, and density functional theory studies. One ligand acts as a monodentate phosphine ligand with a pendant Si−H group, whereas the two others act as bidentate ligands with different Si−H bond activations. Indeed, an intermediate structure between two arrested forms **2a** and **2b** can be proposed: a dihydrido(disilyl)ruthenium(IV) species (form **2a**) resulting from two Si−H oxidative additions or a hydrido(silyl)ruthenium(II) species (form **2b**) presenting an agostic Si−H bond and only one oxidative addition.

Bond activation of a substrate incorporating an H−E bond (E = H, Si, B, C) often results in the oxidative addition of H−E. Formation of a σ-H−E complex is often invoked as an intermediate in the formation of the corresponding hydrido(E) complex and its microscopic reverse, reductive elimination.[1,2] Some of us have been working for several years in determining the boundaries between the two extreme situations, which resulted in the establishment of the σ-CAM mechanism (σ-complexes assisted metathesis mechanism).[3] This mechanism, based on the ability of σ-complexes to undergo dynamic rearrangements, operates at a constant oxidation state and involves at least two discrete σ-complexes as intermediates. We have now launched a new project aimed at designing polyfunctional phosphorus ligands with H−E ancillary functionalities.[4] Besides their potential hemilabile properties,[5] these new ligands are expected to be involved in secondary interactions between the pendant functionality and the metal or any H present in the coordination sphere.[6] More generally, any interaction that could play a role during a catalytic reaction will be examined (hydrogen bonding with the solvent, secondary interactions as in the Noyori system, etc.).[7−9] Recently, we published our first results on the coordination of the phosphinobenzylsilane ligand $Ph_2P(o\text{-}C_6H_4)CH_2SiMe_2H$ to ruthenium complexes.[4] We showed that the bis(agostic) ruthenium complex $RuH_2[\eta^2\text{-(H-SiMe}_2)\text{-}o\text{-CH}_2(C_6H_4)PPh_2]_2$ displaying two rare high-order ϵ-agostic Si−H bonds led finally to the formation of a new complex $Ru[\eta^2\text{-H-SiMe}_2CH(o\text{-}C_6H_4)PPh_2]_2$ featuring two β-agostic interactions and two carbon−metalated bonds. The stepwise H_2 loss process resulted in the formation of this stable bis(carbometalated) complex as a result of C−H activation. Herein we present the coordination of the bifunctional P∼Si−H ligand $PPh_2CH_2OSiMe_2H$ to a ruthenium center studied by multinuclear NMR, X-ray diffraction, and density functional theory (DFT) analysis.

The addition of 3 equiv of $PPh_2CH_2OSiMe_2H$ to the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**) suspended in pentane led to rapid dissolution and precipitation of a gray solid, isolated and characterized as $Ru(PPh_2CH_2OSiMe_2H)_3$ (**2**; Scheme 1).

---

* To whom correspondence should be addressed. E-mail: lefloch@poly.polytechnique.fr (P.L.), sabo@lcc-toulouse.fr (S.S.-E.).

[†] Universidad Autónoma del Estado de Morelos.

[‡] Ecole Polytechnique.

[§] Laboratoire de Chimie de Coordination du CNRS.

(1) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes*; Kluwer Academic/Plenum Publishers: New York, 2001.

(2) Kubas, G. J. *Chem. Rev.* **2007**, *107*, 4152–4205.

(3) Perutz, R. N.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 2578–2592.

(4) Montiel-Palma, V.; Munoz-Hernandez, M. A.; Ayed, T.; Barthelat, J.-C.; Grellier, M.; Vendier, L.; Sabo-Etienne, S. *Chem. Commun.* **2007**, 3963–3965.

(5) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, 233–350.

(6) Lachaize, S.; Sabo-Etienne, S. *Eur. J. Inorg. Chem.* **2006**, 4697–4699.

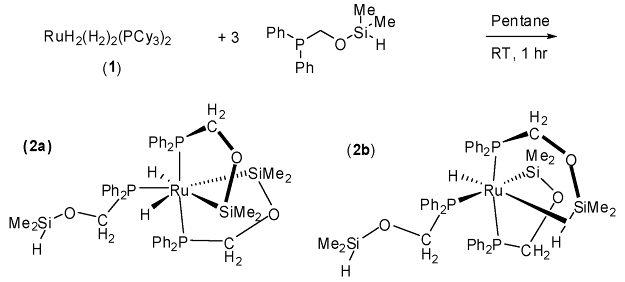
(7) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008–2022.

(8) Abbel, R.; Abdur-Rashid, K.; Faatz, M.; Hadzovic, A.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 1870–1882.

(9) Custelcean, R.; Jackson, J. E. *Chem. Rev.* **2001**, *101*, 1963–1980.

10.1021/ic801327a CCC: $40.75

Scheme 1. Synthesis of **2** Represented by Two Arrested Structures (**2a** and **2b**)



When the reaction was performed in an NMR tube in C_7D_8, $^{31}P\{^1H\}$ NMR spectroscopy attested to the quantitative formation of compound **2** and free PCy_3 (δ 9.3), during the ligand-exchange process. Elucidation of the bonding mode of the three starting phosphinosilane ligands was aided by a combination of different NMR techniques. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet at δ 68.0 and a triplet at δ 42.0 with a J_{PP} of 25 Hz, clearly indicating the coupling of one phosphine cis to two others. On the other hand, the ^1H NMR spectrum exhibits a doublet of triplet at δ −6.28 at room temperature in the hydride region that broadens significantly at 193 K. Furthermore, two different CH_2 resonances are observed as two AB spin system patterns between δ 4.58 and 3.46 in a 2:1 ratio. The latter one assigned to the dangling ligand displays an additional coupling with the phosphorus at δ 42, as shown by selective decoupling experiments. Finally, the dangling Si−H group resonates as a broad septet at δ 4.07. Three heteronuclear multiple-bond correlation $^{29}Si-^{1}H$ experiments were performed with $J = 6$, 30, and 200 Hz, respectively, for a better assignment and determination of the different Si−H coupling constants in **2**. Two Si resonances can be observed at δ 8.2 and 66.8. The resonance at higher field was assigned to the dangling Si−H ligand with a J_{Si-H} value of 200 Hz, whereas the latter correlates with the hydride resonance with a $J_{Si-Happ}$ value of 26 Hz. Finally, HSQC $[^{13}C,^{1}H]\{^{31}P\}$ data confirmed the coordination of two different types of phosphinosilane ligands. The lower field resonances of the methyl substituents at δ 16.8 and 13.8 are indicative of $SiMe_2$ groups in interaction with a metal center as opposed to the resonances near δ −2 for the dangling ligand. All of these data were found in good agreement with the coordination of one phosphinosilane ligand with a dangling Si−H, whereas an advanced oxidative addition process of the other two phosphinosilanes can be assumed because a reduced apparent $J_{Si-Happ}$ coupling value of 26 Hz is observed.[10] Note that such a value is in the lower limit of what is generally observed for σ-silane complexes but high for an oxidative addition product.[11,12]

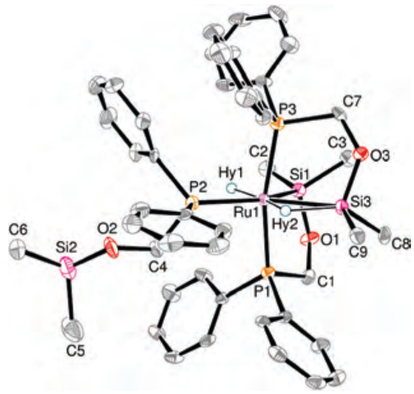


Figure 1. Molecular structure of **2**. Thermal ellipsoid plot (50% probability surface). Hydrogen atoms except hydrides have been omitted for clarity.

Table 1. Comparison between Selected Geometrical Parameters (Distances in Å and Angles in deg) for the Experimental and Calculated Structures of **2**[a]

	exptl	calcd	TS
Ru−P1	2.3137(11)	2.29	2.29
Ru−P2	2.3753(11)	2.33	2.33
Ru−P3	2.3257(10)	2.29	2.29
Ru−Hy1	1.60(3)	1.64	1.64
Ru−Hy2	1.61(3)	1.65	1.64
Ru−Si1	2.4240(11)	2.45	2.47
Ru−Si3	2.4647(11)	2.50	2.46
Si1−Hy1	2.28(3)	2.27	2.06
Si3−Hy2	1.75(3)	1.85	2.04
P1−Ru−P2	98.03(4)	96.6	97.0
P1−Ru−P3	166.04(4)	166.1	166.6
P2−Ru−P3	95.91(4)	97.0	96.4
P3−Ru−Hy2	87.7(10)	91.3	96.4
P3−Ru−Hy1	91.9(10)	91.7	93.1
P2−Ru−Hy2	85.2(10)	80.8	77.6
P2−Ru−Hy1	78.5(10)	77.7	80.9
P2−Ru−Si1	143.89(4)	141.4	136.9
P2−Ru−Si3	130.23(4)	128.4	132.7
P3−Ru−Si1	88.42(4)	86.4	88.4
P3−Ru−Si3	81.90(4)	82.4	82.1
P2−Ru−Hy1−Si1	−177.0	−178.1	−178.1
P2−Ru−Hy2−Si3	−177.0	−175.4	−177.9

[a] Calculated geometrical parameters for the transition state TS are also given.

The molecular structure of **2** is shown in Figure 1 and confirms that the two PCy_3 ligands have been displaced. Selected geometrical parameters are listed in Table 1. Whereas one phosphinosilane is η^1-coordinated to the ruthenium center through the phosphorus atom, leaving one pendant Si−H group, the coordination modes of the two other ligands are not clear-cut. Two formulations can be proposed (Scheme 1). First, we can consider that the two Si−H bonds have been broken, leading formally to a dihydrido(disilyl)ruthenium(IV) species (**2a**). A second possibility is to assume that one Si−H bond has been oxidatively added, leading to a hydrido(silyl)ruthenium (II) complex with one agostic Si−H bond (**2b**). In the first case, the geometry can be considered as a pentagonal bipyramid, whereas in the second hypothesis, a highly distorted octahedral complex would have been formed, with the agostic Si−H bond occupying one coordination site in the equatorial plane. The two Ru−Si bonds [2.4240(11) and 2.4647(11) Å] and the two P−Ru−Si angles [143.89(4°) and 130.23(4)°] are notably different. The two hydrogen atoms were located and the Si−H bond distances are in favor of a different degree of activation. The Si3−Hy2 bond length of 1.75(3) Å is in agreement with an agostic interaction and in the range found for other σ-silane ruthenium complexes, whereas the Si1−Hy1 bond length of 2.28(3) Å is characteristic of an advanced activation process, leading to a hydrido(silyl) formulation

---

(10) Schubert, U.; Gilges, H. *Organometallics* **1996**, *15*, 2373–2375.
(11) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175–292.
(12) Alcaraz, G.; Sabo-Etienne, S. *Coord. Chem. Rev.* 2008, in press., doi: 10.1016/j.ccr.2008.1002.1006.

with one SISHA (secondary interaction between a silicon and a hydrogen atom) interaction.[6,13]

The location of hydrogen atoms by X-ray diffraction is always subject to debate, and DFT studies proved to be very useful to discuss the bonding modes of hydrogen involved in σ bonds. DFT calculations were carried out on the model complex $Ru(PH_2CH_2OSiMe_2H)_2(PH_3)$ using the *Gaussian 03W* set of programs[14] with the B3PW91 functional[15,16] and the 6-31G(d,p) basis set for all nonmetallic atoms. For ruthenium, the core electrons were represented by a relativistic small-core pseudopotential using the Durand−Barthelat method.[17] The PH_3 ligand was used to model the η^1-coordinated phosphinosilane, assuming that the dangling silane has no effect on the coordination around the ruthenium. Hydrogen atoms were used in place of the phenyl groups for the two other phosphine ligands. As shown in Table 1, a good agreement was found between experimental and theoretical data. The dissymmetry concerning the activation of the Si1−Hy1 and Si3−Hy2 bonds is particularly well reproduced, with the Si3−Hy2 distance being found significantly shorter (1.85 Å) than the Si1−Hy1 (2.27 Å). The nature of the ruthenium−silane interaction was studied by a NBO analysis (using the NBO 3.1 program as implemented in *Gaussian 03W*).[18] Importantly, the reduction of the Wiberg bond index for Si1−Hy1 ($WBI_{Si1-Hy1} = 0.15$) by comparison to the value calculated for Si3−Hy2 ($WBI_{Si3-Hy2} = 0.33$) suggests a stronger bonding of Hy2 to Si3, in agreement with the bond distances recorded. Conversely, stronger $WBI_{Ru-Si1} = 0.42$ (vs $WBI_{Ru-Si3} = 0.34$) and $WBI_{Ru-Hy1} = 0.44$ (vs $WBI_{Ru-Hy2} = 0.35$) were found. These data show that complex **2** cannot be simply viewed as a ruthenium(IV) dihydride species because a Si3−Hy2 bonding is still clearly present. On the other hand, the observed structure is also far from that expected for a d^6 complex adopting an ideal octahedral geometry (structure **2b**; Scheme 1). Indeed, as shown by the analysis of its molecular orbital scheme, the d_{xy} orbital is not purely nonbonding and involved in both the σ-Ru−Si (HOMO-5) and Ru−H (HOMO-6) bonds (Figure 2). Thus, this complex might be better described as an intermediate between the two arrested structures presented in Scheme 1.

Interestingly, a low-energy-lying transition state ($\Delta G^{\ddagger} = 3.8$ kJ.mol^{-1}) corresponding to the exchange of coordination modes between the two Si−H bonds was located, with its structure being close to a C_2 geometry (Figure 3). This very low activation barrier is in very good agreement with the recorded ^{1}H NMR data because the two ligands involved in the Si−H bonding to ruthenium were found to be equivalent on the NMR time scale.

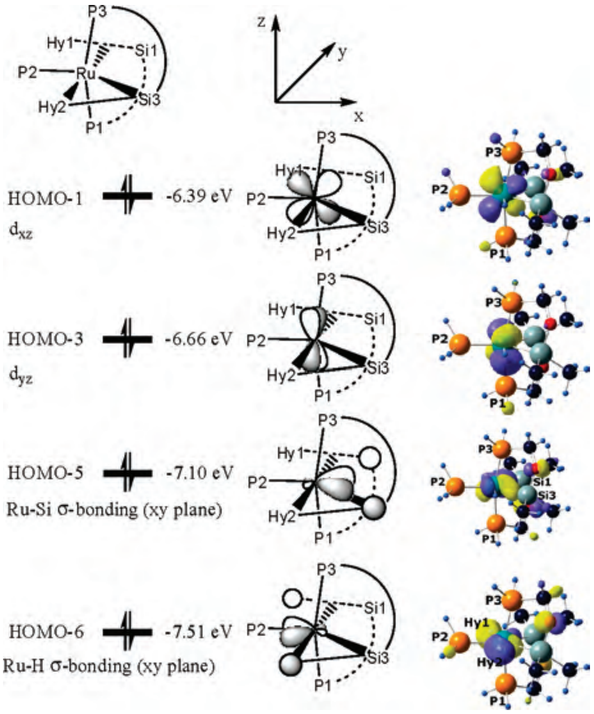


Figure 2. Selected occupied orbitals of the model complex.

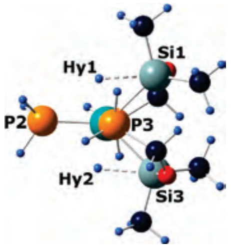


Figure 3. View of the transition state corresponding to the inversion of the Si−H bonding modes.

In summary, we show here that the phosphinosilane can coordinate to a ruthenium center via different modes. The dangling Si−H ligand should allow further reactivity, whereas the coordination of the two other ligands results in an advanced Si−H bond activation step. The two bonding modes observed here illustrate the difficulty in assigning an arrested structure. From NMR data, one might conclude that a dihydrido(disilyl)complex (Ru^{IV} species) with SISHA interactions was formed, whereas X-ray diffraction and DFT calculations indicate a different Si−H bond activation, in agreement with a structure representing a continuum between a $Ru^{II}H(SiMe_2OCH_2PPh_2)(\eta^2\text{-}HSiMe_2OCH_2PPh_2)(PPh_2CH_2OSiMe_2H)$ (**2b**) and a $Ru^{IV}H_2(SiMe_2OCH_2PPh_2)_2(PPh_2CH_2OSiMe_2H)$ (**2a**) species. Studies dealing with the reactivity of complex **2** are currently ongoing in our laboratories and will be reported in due course.

Acknowledgment. We thank the ANR (Programme blanc “In−Out Tuning” ANR-06-BLAN-0060) and CNRS/CONACYT (Grant 16873) for support.

Supporting Information Available: X-ray crystallographic data in CIF format for **2**, free energies and three lower frequencies of DFT-calculated extrema, and a complete Gaussian reference, as well as experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC801327A

---

(13) Lin, Z. *Chem. Soc. Rev.* **2002**, *31*, 239–245.

(14) Frisch, M. J.; et al. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2004.

(15) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(16) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244–13249.

(17) Durand, P.; Barthelat, J. C. *Theor. Chim. Acta* **1975**, *38*, 283–302.

(18) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.