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Structure and Bonding in a Disilazane Ruthenium Complex. Catalytic Selective Deuteration of Disilazane

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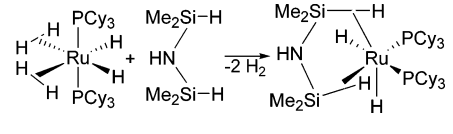
*Summary: The disilazane complex [$RuH_2\{(\eta^2\text{-}HSiMe_2)_2NH\}(PCy_3)_2$] (**2**) was formed by the reaction of the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**) with 1,1,3,3-tetramethyldisilazane. The coordination of the disilazane ligand is discussed on the basis of NMR, X-ray, and DFT studies. The choice of the functional (B3PW91 versus B3LYP) is crucial in this system. **1** is an active catalyst for the selective deuteration of the starting disilazane $(HSiMe_2)_2NH$ into $(DSiMe_2)_2NH$.*

Silanes are used in a wide variety of important chemical processes such as hydrosilylation, dehydrosilylative coupling of alkenes, or silane redistribution to produce useful starting materials for silicon industry and microelectronics.[1,2] Most of these reactions are catalyzed by transition metal complexes, and a good understanding of the nature of the Si−H coordination to the metal center is crucial to achieve better activities and selectivities.[3−6] We have demonstrated that, in ruthenium polyhydride chemistry, silane activation is dominated by the formation of σ-silane complexes.[7] Comparable behavior and structures have been observed for several disilane and disiloxane compounds of general formula [$RuH_2\{(\eta^2\text{-}HSiMe_2)_2Z\}(PCy_3)_2$] (the spacer Z between the two silicons contains two or three atoms, $Z = C_6H_4$, $(CH_2)_n$, $OSiMe_2O$). These compounds have been characterized by NMR, IR, and X-ray diffraction, and the energetics of the reactions have also been computed through a theoretical DFT study. All these complexes adopt the same overall structure, with a characteristic symmetrical coordination of the disilane ligand through two σ-Si−H bonds bonded to the ruthenium in a trans manner and a cis arrangement of the bulky tricyclohexylphosphines.[7] Such a geometry results from stabilizing secondary interactions between the "classical" hydrides and the silicon atoms (SISHA interactions).[8] With smaller spacers such as CH_2 or O, the corresponding complexes have eluded structural characterization so far. However, spectroscopic data were found to be in good agreement with those obtained for larger spacers, whereas DFT analysis showed a dissymmetrical arrangement of the disilane or disiloxane ligand.

Scheme 1



As part of our ongoing interest in silane activation, we were interested in exploring the reactivity of our ruthenium precursor with disilazanes. It is noteworthy that disilazanes find interesting applications as starting materials for ceramics and in organic synthesis.[9−11] Furthermore, we reasoned that the disilazane derivatives (with thus a short spacer between the two silicon atoms) could lead to the isolation of a new family of compounds, benefiting from the possibility of further functionalization of the nitrogen atom. We describe in this communication the synthesis and properties of a disilazane ruthenium complex, as well as preliminary catalytic results that concern the selective deuteration of a disilazane.

A pentane suspension of the bis(dihydrogen) complex[12] $RuH_2(H_2)_2(PCy_3)_2$ (**1**) reacts rapidly with 1,1,3,3-tetramethyldisilazane to produce a homogeneous solution, followed by the formation of a solid within 5 min. After workup, the white powder was isolated and analyzed as [$RuH_2\{(\eta^2\text{-}HSiMe_2)_2NH\}(PCy_3)_2$] (**2**) (see Scheme 1).

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(1) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; p 1479.

(2) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Vol. 3, p 1415.

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

(4) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151.

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

(6) Lachaize, S.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B. *Chem. Commun.* **2003**, 214.

(7) Delpech, F.; Sabo-Etienne, S.; Daran, J.-C.; Chaudret, B.; Hussein, K.; Marsden, C. J.; Barthelat, J.-C. *J. Am. Chem. Soc.* **1999**, *121*, 6668.

(8) Atheaux, I.; Delpech, F.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B.; Hussein, K.; Barthelat, J.-C.; Braun, T.; Duckett, S. B.; Perutz, R. N. *Organometallics* **2002**, *21*, 5347.

(9) Wrobel, A. M.; Blaszczyk, I.; Walkiewicz-Pietrzykowska, A.; Tracz, A.; Klemberg-Sapieha, J. E.; Aoki, T.; Hatanaka, Y. *J. Mater. Chem.* **2003**, *13*, 731.

(10) Rasul, T.; Son, D. Y. *J. Organomet. Chem.* **2002**, *655*, 115.

(11) Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712.

(12) Borowski, A. F.; Sabo-Etienne, S.; Christ, M. L.; Donnadieu, B.; Chaudret, B. *Organometallics* **1996**, *15*, 1427.

10.1021/om050361t CCC: $30.25

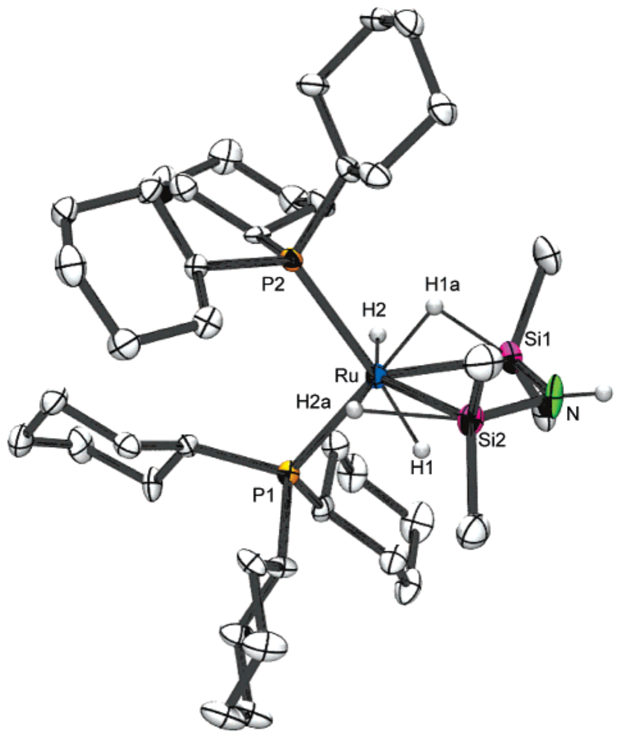


Figure 1. X-ray crystal structure of complex $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2NH\}(PCy_3)_2]$ (**2**).

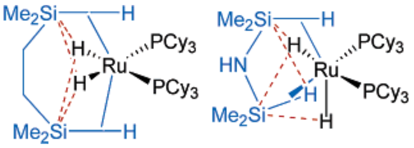
The complex was characterized by NMR and by single-crystal X-ray diffraction. NMR data are very similar to those reported for the analogous disiloxane complex $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2O\}(PCy_3)_2]$ (**3**).[7] The ^1H NMR spectrum displays a singlet at δ 0.86 corresponding to the four methyl groups, and a broad signal at high field at δ −9.80 integrating for four hydrogens and corresponding to the two hydrides and the two hydrogens of the (η^2-H−Si) ligands in fast exchange. A variable-temperature study shows a first decoalescence at 273 K, leading to a broad singlet at δ −8.72 and a broad triplet at δ −10.39 (J_{H-P} = 40 Hz) resolved at 233 K. This process is characterized by a $\Delta G^‡$ of 45 kJ·mol^{-1} (47.5 kJ·mol^{-1} for **3**). A second decoalescence is achieved at 213 K, and the slow exchange limit is obtained at 193 K with four broad signals of equal intensity at δ −8.36, −8.62, −9.93, and −10.76. The decoalescence temperature combined with the $\Delta\nu$ = 331 and 107 Hz, respectively, for the two types of protons gave the same $\Delta G^‡$ value obtained for **3**, ca. 38 kJ·mol^{-1}. One signal is observed at δ 53.5 at room temperature in the $^{31}P\{^1H\}$ spectrum. Decoalescence is achieved at 213 K, leading to a poorly resolved AB system at δ 52.3 and 50.5 (J_{P-P} = 28 Hz) at 193 K, in agreement with a cis disposition of the two phosphines and indicative of an arrested structure. The X-ray structure of **2** is shown in Figure 1 (see Table 1).[13]

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2NH\}(PCy_3)_2]$ (2): Comparison of X-ray Data for 2 versus DFT/B3PW91 Data for the Optimized Disilazane Isomers $[RuH_2\{(\eta^2\text{-}HSiH_2)_2NH\}(PH_3)_2]$ (2′) and $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2NH\}(PCy_3)_2]$ (2″) and the Optimized Disiloxane Isomer $[RuH_2\{(\eta^2\text{-}HSiH_2)_2O\}(PH_3)_2]$ (3′)

	X-ray	DFT/B3PW91		
	2	**2′**	**2″**	**3′**
Ru−Si1	2.395(2)	2.448	2.416	2.431
Ru−Si2	2.434(2)	2.546	2.490	2.558
Ru−P1	2.442(1)	2.312	2.463	2.321
Ru−P2	2.434(1)	2.347	2.487	2.349
Si1−N (O for **3′**)	1.733(7)	1.747	1.748	1.684
Si2−N (O for **3′**)	1.743(7)	1.740	1.757	1.672
Si1−Ha1	1.93(5)	1.778	1.922	1.818
Si2−Ha2	1.91(5)	1.674	1.775	1.670
Si1−Ha2	3.53(4)	3.181	3.467	3.178
Si2−Ha1	2.35(6)	3.060	2.510	2.985
Si1−H1	2.25(6)	2.122	2.191	2.112
Si2−H2	3.68(5)	4.019	3.900	4.032
Si1−H2	2.39(5)	2.880	2.500	2.874
Si2−H1	2.09(6)	2.511	2.367	2.551
Ha1−Ru−Ha2	96(3)	90.7	89.7	91.3
Si1−Ru−Si2	68.91(4)	68.4	69.3	65.7
P1−Ru−P2	103.00(3)	96	105.9	96.4

All the hydrides in the coordination sphere of the ruthenium could be located. The ruthenium is in a pseudo-octahedral environment with a C_{2v} arrangement for the core P_2RuSi_2. The disilazane coordination to ruthenium is characterized by a similar activation of the two Si−H bonds, as illustrated by the Ru−Si bond distances (2.395(2) and 2.434(2) Å) and the identical σ-Si−H bond lengths of 1.91(5) and 1.93(5) Å. The Ru−Si bond lengths are in the normal range for σ-silane or silyl complexes, whereas the σ-Si−H bond distances are at the higher limit for σ-coordination.[3] The main difference between the coordination of the disilazane ligand and the disilane ligand in all the previous structures obtained for the series of disilane complexes[7] $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2Z\}(PCy_3)_2]$ is the coordination of the disilazane to the ruthenium via two (η^2-H−Si) ligands in a cis disposition (see Scheme 2).

Scheme 2. Comparison of Disilane Coordination (two Si−H bonds in trans position) versus Disilazane Coordination (two Si−H bonds in cis position) in Ruthenium Complexes (the SISHA interactions are represented as red dotted lines)



This is the result of a steric constraint, as illustrated by the smaller value of the Si−Ru−Si angle (69°) by comparison to 88° for Z = C_6H_4 and 97° for Z = $OSiMe_2O$. A Si−Ru−Si angle similar to that in **2** is found in the osmium complex $Os(SiMe_2NMe_2SiMe_2)Cl(CO)(PPh_3)_2$.[14] The disilane complexes $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2Z\}(PCy_3)_2]$, with 2 or 3 atoms between the two silicons, display the same overall structure with the disilane bonded to the ruthenium via two trans (η^2-H−Si) bonds. When comparing these X-ray data with the theoretical study we previously published on the disiloxane compound **3**, using the model $[RuH_2\{(\eta^2\text{-}HSiH_2)_2O\}(PH_3)_2]$ (**3′**) at the DFT /B3LYP level,[7,8] we were surprised to

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(13) Crystal data for **2**: $C_{40}H_{83}NP_2Si_2Ru$, M = 797.26, orthorhombic, space group $C\,2\,2\,2_1$, T = 180(2) K, a = 17.443(3) Å, b = 20.752(4) Å, c = 23.465(5) Å, α = β = γ = 90°, V = 1701.9(6) Å^3, Z = 8, μ = 0.529 mm^{-1}, reflections collected/unique = 27 641/6749, R1 = 0.0387, wR2 = 0.0575, GOF = 0.864.

(14) Choo, T. N.; Kwok, W.-H.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2002**, *645*, 235.

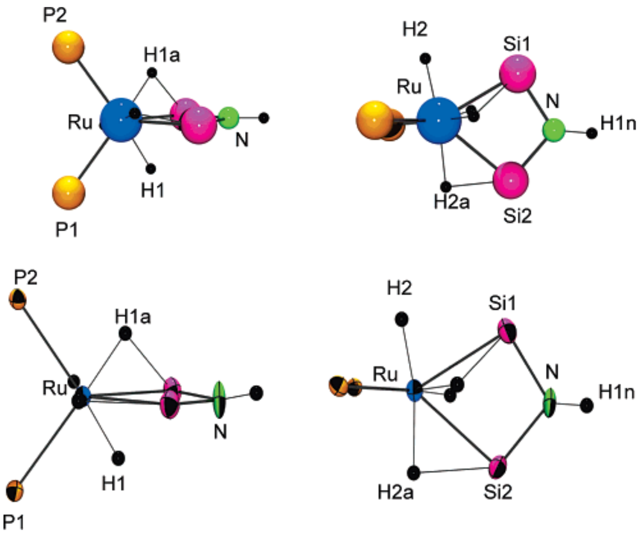
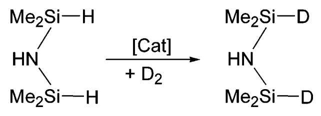


Figure 2. X-ray crystal structure of complex $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2NH\}(PCy_3)_2]$ (**2**) (bottom section) and optimized geometry of $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2NH\}(PCy_3)_2]$ (**2′′**) using DFT/B3PW91 (upper section). All the carbons have been omitted for clarity.

see some important differences. We found that not only the geometrical parameters associated with the hydrides are different, but the positions of the heavy atoms are also different. In particular, the Ru−Si distances in **3′** of 2.442 and 2.700 Å indicate a difference in the activation of the two Si−H bonds. Moreover, the higher value (2.700 Å) is at the very high limit of what is normally found in σ-complexes. To understand these differences, we performed a more detailed theoretical study on the disilazane system (see Supporting Information for computational details). Full details will be reported in due course, but the most significant change was observed by using the B3PW91 functional instead of B3LYP. It is noteworthy that in all the previous cases in silane chemistry we never observed any effect. Indeed, optimization of the disilazane complex $[RuH_2\{(\eta^2\text{-}HSiH_2)_2NH\}(PH_3)_2]$ (**2′**) analogous to **3′** leads to the same result at the DFT/B3LYP level, whereas when using B3PW91, the geometry resembled the one obtained by X-ray diffraction and the geometrical parameters were more in agreement with a similar degree of activation of the two σ-Si−H bonds (see Table 1). In particular, the Ru−Si distances are 2.474 and 2.646 Å with B3LYP and 2.448 and 2.546 Å with B3PW91. The trend was even better when the optimization (DFT/B3PW91) was carried out by using PCy_3 itself. The geometry of $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2NH\}(PCy_3)_2]$ (**2′′**) was optimized and characterized as a minimum on the potential energy surface. The structure is depicted in Figure 2. Theoretical values closely match the experimental parameters obtained from the X-ray data (see Table 1) with in particular the key Ru−Si bond lengths close to those in **2** (2.416 and 2.490 Å by DFT versus 2.395(2) and 2.434(2) Å by X-ray). In view of these differences, we have revisited the case of the disiloxane compound. When performing the DFT calculations at the B3PW91 level, using the disiloxane **3′** as a model, we indeed obtained results comparable to the disilazane isomer **2′**. The change in the Ru−Si distances is again noticeable with values of 2.442 and 2.700 Å with B3LYP and values of 2.431 and 2.558 Å with B3PW91.

Scheme 3



[Cat]: $RuH_2(H_2)_2(PCy_3)_2$ 1% mol

NMR studies show that exchange between the different types of hydrides is rapid at room temperature. This led us to investigate the possibility for a selective deuteration of the starting disilazane. A catalytic experiment was performed by pressurizing **1** (1 mol %) and the disilazane under 3 bar D_2 without any solvent (see Scheme 3).

Deuteration of the Si−H bonds is evidenced by IR and NMR. The Si−D bond is characterized by a strong stretching band at $\nu = 1539$ cm^{-1}, with the NH stretching band at $\nu = 3386$ cm^{-1} remaining unchanged after deuteration. The ^{1}H NMR spectrum shows a singlet at δ 0.42 corresponding to the methyls and a broad triplet at δ 0.12 with $J_{NH} = 42$ Hz. Very small traces of a Si−H resonance have been detected, indicating that Si−H bonds have been converted into Si−D, leading thus to the production of $(DSiMe_2)_2NH$. The ^{29}Si NMR spectrum shows a triplet at δ −11.5 with $J_{SiD} = 30$ Hz. The ^{2}H NMR spectrum shows a pseudooctuplet at δ 4.82 corresponding to the coupling with the methyls and the NH proton ($J_{DH\ app} = 0.5$ Hz). The silicon satellites are also clearly identified ($J_{SiD} = 30$ Hz).

In conclusion, for the first time in silane ruthenium chemistry, the choice of the functional for DFT calculations appears to be crucial. Better results are obtained with the hybrid B3PW91 density functional, whereas the use of B3LYP leads to major differences in the overall geometry and overestimates in particular the Ru−Si distances. This dramatic effect could be important for other systems. Moreover, we have reported the catalytic selective deuteration of $(HSiMe_2)_2NH$, and the use of the deuterated isomer could give key information in mechanistic issues. Our work will be extended to the design of functionalized silazane complexes toward the goal of obtaining polydentate ligands bearing different functionalities and developing new active catalysts.

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Supporting Information Available: Experimental details and characterization data for $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2NH\}(PCy_3)_2]$ (**2**). Computational details. Complete crystallographic details (CIF files) for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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