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Ruthenacyclic carbamoyl complexes: Highly efficient catalysts for organosilane hydrolysis

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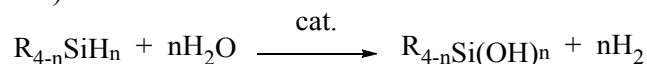
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ABSTRACT: The ruthenacyclic carbamoyl complexes [RuX(2-NHC(O)C₅H₃NR)(CO)₂(NCMe)] (R = H and Me; X = Br and SC₆H₃-o,o-Me₂) are excellent catalysts for the hydrolysis of organosilanes, particularly towards primary silanes, generating hydrogen under ambient conditions within seconds. These complexes are structural mimics of the [Fe]-hydrogenase active site and like the natural enzyme, a labile ligand at the sixth coordination site is essential to the catalytic activity.

INTRODUCTION

Realization of the “hydrogen economy” as an alternative energy source to fossil fuels is contingent upon the solution of a number of challenges.¹⁻⁴ One of these is a cheap and efficient means of production,⁵ for which the hydrogenases, which are capable of generating hydrogen from water, are of interest.⁶⁻⁹ Of the three classes of hydrogenase known, *viz.*, the [NiFe] (Type I), [FeFe] (Type II) and [Fe] (Type III) hydrogenases,¹⁰ more attention has been paid to the [FeFe]-hydrogenase which is more efficient in the production of molecular hydrogen.^{11,12} The [Fe]-hydrogenase is the most recently discovered class of hydrogenase, and much of the research so far has revolved around structural mimics to aid in the elucidation of the nature of its active site,¹³ and there has been much less work on functional mimics.¹⁴⁻¹⁷

A second challenge for the “hydrogen economy” is that of storage.¹⁸ One potential solution is to store the hydrogen in the form of hydrides such as organosilanes, which are able to release hydrogen through catalytic hydrolysis (Scheme 1).¹⁹



Scheme 1. Silane hydrolysis.

The only by-products are organosilanols, which are themselves valuable building blocks for the polymer and materials industry, and in various organic transformations.^{20,21} The use of primary silanes is desirable as it can give up to three equivalents of hydrogen. Although a large number of catalysts for the hydrolysis of organosilanes, based on iron,²² ruthenium,^{20,23,24} rhodium,^{25,26} iridium,^{27,28} rhenium,^{29,30} palladium,³¹ silver,^{32,33} gold³⁴ and zinc,³⁵ have been investigated, these have mainly been with secondary and tertiary silanes. The hydrolysis of primary silanes have only been reported for heterogeneous catalysts based on cobalt,³⁶ copper,³⁷ silver,³⁸ gold,^{39,40} and platinum,⁴¹ and one homogeneous catalyst based on rhenium.⁴²

We have recently embarked on a program to synthesise ruthenium-based structural analogues of the [Fe]-hydrogenase active site, such as the ruthenacyclic carbamoyl complexes **1** (Figure 1b).^{43,44} These complexes share a similarity with the natural [Fe]-hydrogenase in that the ligand at the sixth coordination site (acetonitrile) is labile; in the [Fe]-hydrogenase, this was thought to be responsible for the activation of dihydrogen. We therefore hypothesized that such complexes may be active catalysts. In the process,

we have discovered that they are indeed efficient catalysts for the hydrolysis of organosilanes and, in particular, primary silanes. This study is reported here.

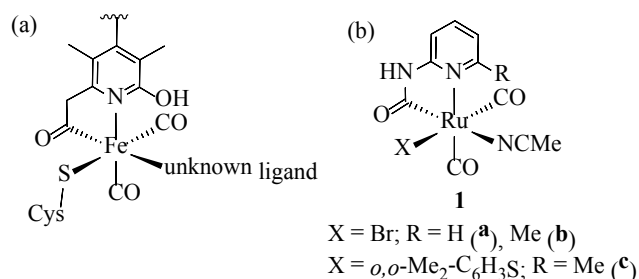
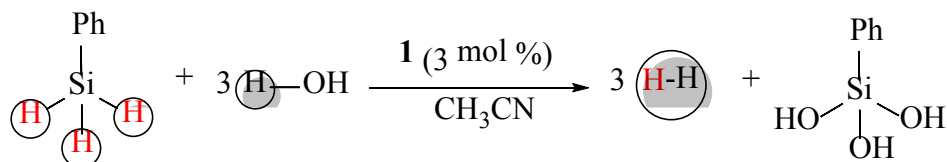


Figure 1. Structure of (a) the active site of [Fe]-hydrogenase, and (b) the ruthenacyclic carbamoyl complexes **1**.

RESULT AND DISCUSSION

The complexes **1** catalyse the hydrolysis of a wide range of organosilanes (Table 1).

Table 1. Hydrolysis of various organosilanes catalyzed by 1.



Silane	1a			1b		
	Time (min)	H ₂ yield (%)	Silanol yield (%) ^a	Time (min)	H ₂ yield (%)	Silanol yield (%) ^a
PhSiH ₃	20 sec	93	97	20 sec	92	97
CH ₃ (CH ₂) ₅ SiH ₃	5	96	95	5	97	94
Ph ₂ SiH ₂	20	97	94	20	96	93
Ph(CH ₂ CH ₂ CH ₂) ₂ SiH ₂	25	95	92	25	94	90
(<i>o</i> -ClC ₆ H ₄ CH ₂) ₂ SiH ₂	25	94	92	25	92	88
PhMe ₂ SiH	30	97	90	30	94	90
Et ₃ SiH	40	96	92	40	95	90
Ph ₃ SiH	120	<1	<1	120	<1	<1
(^{<i>i</i>} Pr) ₃ SiH	120	<1	<1	120	<1	<1
PMHS ^b	120	64	54	120	60	50

All reactions were carried out with silane (0.4 mmol), H₂O (4 mmol) and catalyst (3 mol%) in acetonitrile at 25 °C. Complex **1c** showed similar catalytic activity to **1a** and **1b** for the hydrolysis of PhSiH₃, and was not studied further. ^aYields are with respect to amount of organosilane used, with anisole as internal standard. ^bPMHS = Poly(methylhydrosiloxane).

The reaction of phenylsilane with water in the presence of **1a**, for example, gives an immediate and profuse effervescence of hydrogen gas even at room temperature. The reaction proceeds significantly faster in the presence of excess water, but no gas evolution is observed in the absence of **1a** or under anhydrous conditions. A number of different solvents may be used, including acetonitrile, acetone and tetrahydrofuran. The efficiency of **1a** is similar in these solvents, with organosilanol as the only by-product. The secondary and tertiary organosilanols are stable at room temperature,^{22,40} but the primary organosilanols convert slowly to siloxane in these solvents.^{36,42} This is consistent with the earlier report that

tertiary organosilanes are stable in tetrahydrofuran but slowly converted to siloxane in a low dielectric constant solvent such as chloroform.²² An optimization study with phenylsilane shows that the optimal catalyst loading of **1a** is 3 mol% (Table S1). That **1a** shows significant selectivity for primary silanes (R_3SiH_3) is particularly interesting; the rates are much faster than for the secondary (R_2SiH_2) and tertiary silanes (R_3SiH), and is probably related to the steric bulk of the organosilane molecule.²² As mentioned above, although several metal-based catalysts have been reported for organosilane hydrolysis,²²⁻⁴² none of them displayed such fast rates; this is the first example in which hydrolysis is completed within a few seconds, with a TOF estimated at $\sim 6000 \text{ h}^{-1}$ (Table S2).³⁸⁻⁴⁰ Recyclability of the catalyst has been tested for up to five cycles; the yields show an initially slow but steady decline and falls to 68% by the fifth cycle (Figure S1). This is a higher catalyst stability than the iron analogue $[\text{Fe}(2\text{-NHC}(\text{O})\text{C}_5\text{H}_4\text{N})(\text{CO})(\text{MeCN})_3][\text{PF}_6]$.²²

Substitution of the MeCN ligand in **1** with a phosphine (PMe_3) gives the phosphine-substituted derivatives **2**, which have been characterized spectroscopically and their structures have been confirmed by x-ray crystallography (see ESI). These are, however, catalytically inactive and suggest that lability of the MeCN ligand is important for catalytic activity. The ^1H NMR spectrum of a 1:1 mixture of phenylsilane and **1b** in CD_3CN (with adventitious water) shows that while the resonance due to PhSiH_3 (δ 4.16) decreases slowly over time, two new resonances, a singlet at δ 4.57 and a broad singlet at δ 4.32 ppm in a 2:1 integration ratio, begin to appear (Figure 2).⁴⁵ The chemical shift for the latter resonance is temperature-dependent (Figure S2), and hence may be tentatively assigned to a labile hydroxyl group. It is therefore proposed that these two resonances are assignable to $\text{PhSiH}_2(\text{OH})$, a probable intermediate in the reaction. Consistent with this is the observation that the intensities of these resonances increase initially but then decrease and disappear completely later in the course of the reaction.

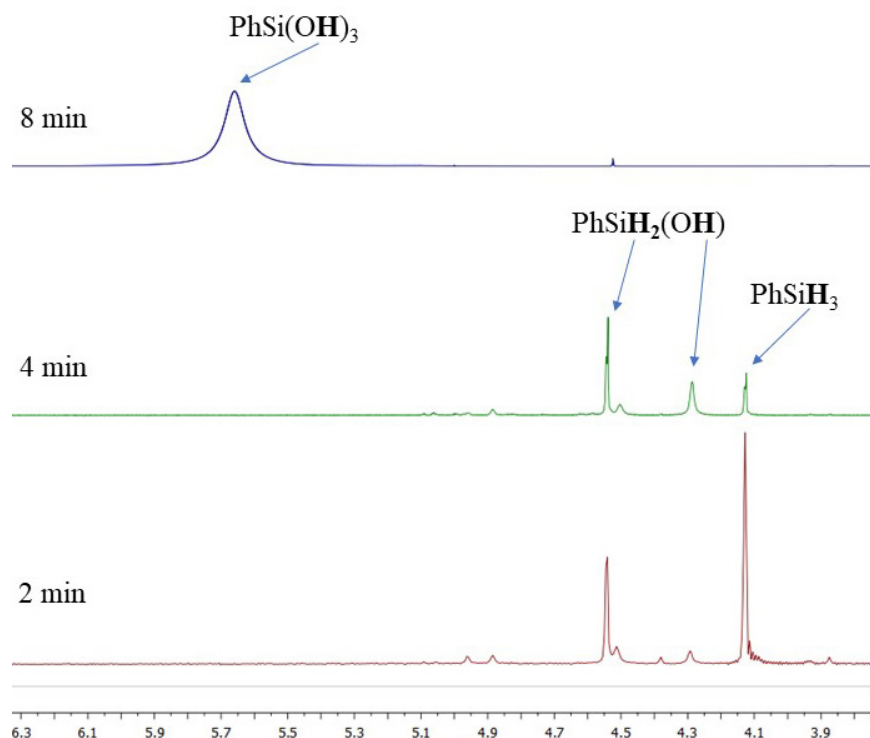
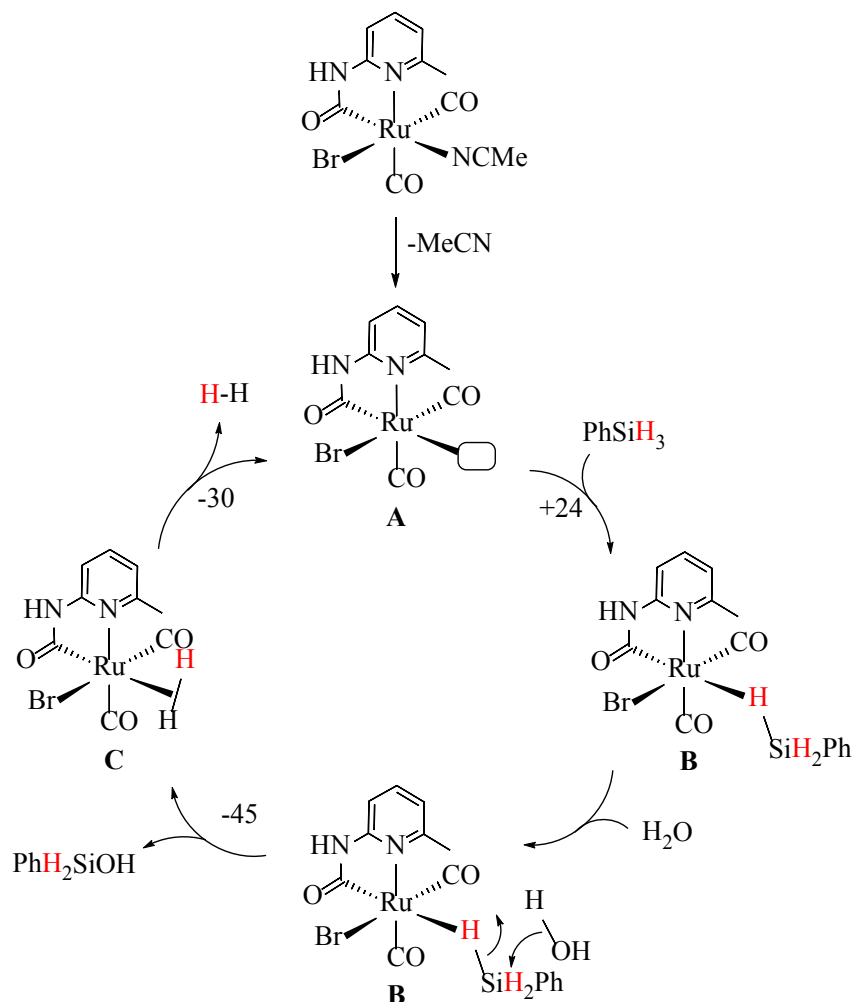


Figure 2. ^1H NMR spectra of a 1:1 mixture of phenylsilane and **1b** in CD_3CN .

Given the variety of metal-catalysed hydrolysis of organosilanes which have been investigated, both homogeneous and heterogeneous, a large variety of mechanisms have been proposed.^{23,29-31,38,41} In this work, the only intermediate identified is $\text{PhSiH}_2(\text{OH})$. We propose a catalytic pathway which is somewhat similar to that previously proposed for a ruthenium-catalysed hydrolysis of secondary and tertiary silanes; the reaction free energies have been calculated using density functional theory (Scheme 2). Initial dissociation of the CH_3CN ligand generates the catalytically-active, 16-electron species **A**. Coordination of the

silane can be via either an end-on η^1 or a side-on η^2 coordination mode. Optimization of an η^2 coordination mode of the silane leads to the σ -complex **B**, suggesting that η^1 coordination is favoured and is consistent with earlier reports.^{23,29} An alternative pathway, involving substitution of the bromide,^{23,24} is ruled out as the thiolate derivative **1c** shows similar catalytic activity to **1a** and **1b**.



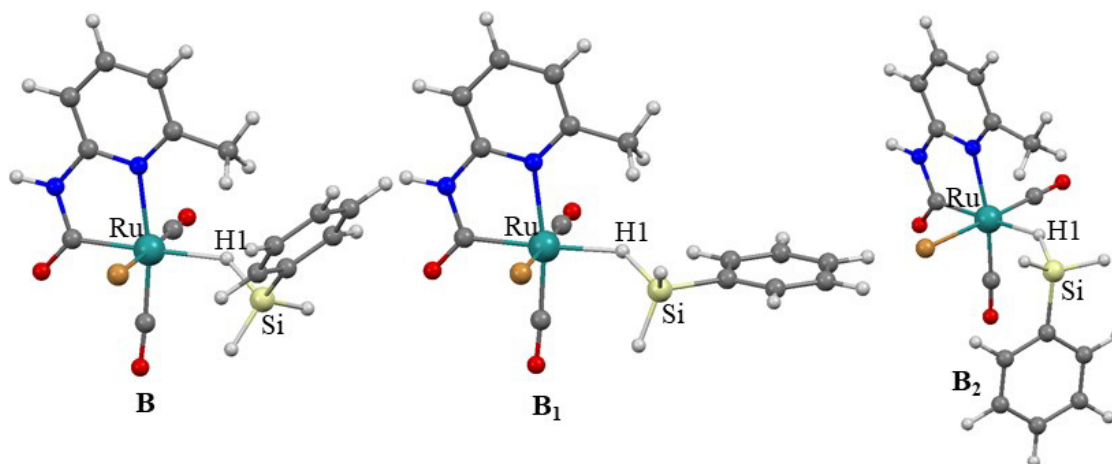
Scheme 2. Proposed mechanism for the catalytic hydrolysis of phenylsilane with **1b**. Reaction free energies given (kJ/mol) are for solvated species in acetonitrile.

Attack of water at the silicon atom in **B** generates the intermediate PhSiH₂(OH), together with a dihydrogen complex **C**.²⁴ The dihydrogen ligand is most likely formed from a (hydridic) hydrogen atom from the silane and a proton from water.²³ An alternative to this step, which is a nucleophilic attack of water at the silicon center to produce an ionic species (Scheme S1),^{23,29} is endergonic ($\Delta G^\circ = +125$ kJ/mol). The final step is the elimination of the H₂ ligand to regenerate **A**. The intermediate PhSiH₂(OH) produced in this cycle should be hydrolysable through the same pathway to produce two more molecules of dihydrogen together with phenylsilanetriol.

The proposed mechanism resembles what has been described as an outer sphere mechanism in the context of hydrosilylation reactions, and the η^1 -coordinated silane in **B** has also been suggested in computational studies.^{46,47} Three conformations, differing in the orientation of the phenyl group of the silane, for **B** have been studied computationally. The most stable conformation has the phenyl ring on the same side of the pyridinyl as the Br ligand (Table 2). The Ru...HSi≡ vector is significantly longer than that in the reported ruthenium η^2 -silane complex [[RuH₂{(η^2 -HSiMe₂)₂(C₆H₄)}(PCy₃)₂] (**3**) (2.03 Å vs 1.65 Å, respectively),⁴⁸⁻⁵⁰ whereas the H-Si bond length is significantly shorter (1.51 Å vs 1.88 Å, respectively).

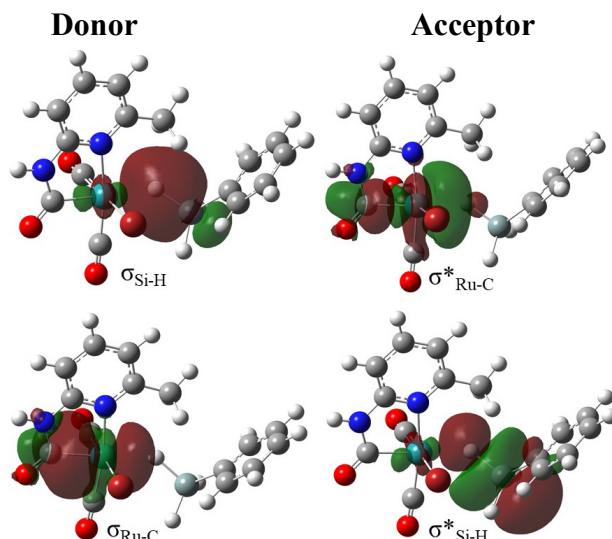
The Ru \cdots Si distance is also significantly longer than that in **3** (3.31 Å vs 2.43 Å), indicating that there is no bonding interaction between the ruthenium and silicon centers.

Table 2. Computed optimized structures and selected bond parameters of the conformers of **B**.



Compound	Ru-H1(Å)	Si-H1(Å)	Ru \cdots Si(Å)	Ru-H1-Si(°)	E (kJ/mol)
B	2.027	1.514	3.311	138.0	0.0
B₁	1.978	1.507	3.241	136.4	4.3
B₂	2.005	1.512	3.315	140.6	5.6

A second order perturbative analysis through a natural bond orbital (NBO) calculation on **B** shows that the bonding interaction in the Ru- η^1 -HSiPhH₂ unit comprises a σ -donation from the H-Si σ bond to an antibonding Ru-C(carbamoyl) orbital, and a weaker back-donation from the Ru-C(carbamoyl) bonding orbital to the H-Si σ^* orbital (Figure 3).⁵¹ The Si-H bond is more polarized in **B** than in the free silane, as reflected in the natural charges on the silicon and hydrogen atoms (Table S3).



NBO	$\sigma_{\text{H-Si}}$	$\sigma^*_{\text{Ru-C}}$	$\sigma_{\text{Ru-C}}$	$\sigma^*_{\text{H-Si}}$
Occupancy	1.8	0.3	1.9	0.0
Energy (kJ/mol)	-1.7	1.0	-1.5	0.9
Interaction (kJ/mol)	104		9	

Figure 3. MOs involved in the Ru- η^1 -HSiPhH₂ bonding interaction.

CONCLUSION

In this study, we have described the catalytic activity of the ruthenacyclic carbamoyl complexes [RuBr(2-NHC(O)C₅H₃NR)(CO)₂(L)] for the hydrolysis of organosilanes. These ruthenium complexes turned out to be very efficient and robust catalysts for the hydrolysis of organosilanes, with very high TOF for primary silanes.

EXPERIMENTAL SECTION

General procedures. All experiments were performed under an argon atmosphere using standard Schlenk techniques. Chemicals were obtained from Sigma Aldrich and were used as received. Compounds **1** were synthesized by following a previous work reported by our group.^{43,44} Solvents that were used for reactions were distilled over the appropriate drying agents under argon before use. HRMS were recorded in ESI mode on a Waters UPLC-Q-ToF MS mass spectrometer. ¹H and ¹³C{¹H} NMR spectra were obtained on a JEOL 400 MHz spectrometer at room temperature unless stated otherwise. Chemical shifts for ¹H and ¹³C{¹H} were referenced with respect to the residual resonances of the respective deuterated solvents. Infrared spectra were recorded on a Bruker Alpha FT-IR spectrometer in a IR cell with NaCl windows and a path length of 0.1 mm at a resolution of 2 cm⁻¹. Elemental analyses were performed on PerkinElmer 2400 Series II CHN/O Elemental Analyzer in house.

General procedure for the silane hydrolysis. A sample of organosilane (0.4 mmol) was added into an acetonitrile (2 mL) solution containing the catalyst **1** (3 mol%) and excess H₂O (4 mmol, 0.07 mL) at 25 °C. An immediate evolution of gas was observed which was collected and measured using an upward delivery tube set up with an inverted measuring cylinder filled with water.^{22,23} Removal of solvent afforded the organosilanol which was identified by comparison of the NMR spectral data with the literature values: Phenylsilanetriol,⁵² Diphenylsilanediol,²⁰ Dimethylphenylsilanol,²⁰ Triethylsilanol.²⁰ TOF for hydrolysis of phenylsilane was calculated with respect to the mole of phenylsilane consumed. Five consecutive recyclability experiments have been carried out in a same mixture of **1** (3 mol%) and water (4 mmol) in acetonitrile (2 mL) by consecutive addition of phenylsilane (0.4 mmol).

General procedure for the preparation of **2.** In a typical reaction, PMe₃ (0.05 mmol) was added into a solution of **1** (0.05 mmol) in acetonitrile (5 mL). The resulting mixture was then stirred for 30 min at ambient temperature. Slow evaporation of the solvent at room temperature afforded **2** as white crystals after 2 d (see ESI).

Crystallographic studies. Diffraction-quality crystals were grown from acetonitrile (**2**) mounted on quartz fibers. X-ray diffraction data were collected at 103(2) K on a Bruker X8 APEX system, using Mo K α radiation, with the SMART suite of programs.⁵³ Data processing and correction were made for Lorentz and polarization effects with SAINT,⁵⁴ and for adsorption effects with SADABS.⁵⁵ Structural solution and refinement were carried out with the SHELXTL suite of programs.⁵⁶ The structures were solved by direct methods to locate the heavy atoms, followed by successive difference maps for the light, non-hydrogen atoms. Appropriate restraints were placed on all disordered parts. All non-hydrogen atoms were refined with anisotropic displacement parameters in the final model. All the organic hydrogen atoms were placed in calculated positions and refined with a riding model. The crystallographic data are summarized in Table S5.

Computational studies. The computational studies were carried out using density function theory (DFT), utilizing the hybrid functional of Truhlar and Zhao (M06).⁵⁷ The basis set used was def2TZVP,⁵⁸ for the transition metals, and 6-311+G(2d,p) for the light atoms. The polarized continuum model (PCM) was employed to describe the solvated species. Spin-restricted calculations were used for structural optimization, harmonic frequency calculations and to evaluate zero-point energy (ZPE) corrections. Optimized geometries were characterized as equilibrium structures with all real frequencies. All calculations were performed using the Gaussian 09 suite of programs.⁵⁹

ASSOCIATED CONTENT

Supporting Information

CCDC 1820444 (**2b**), 1820445 (**2a**) and 1852148 (**2c**) contain the supplementary crystallographic data for the structures reported. These are available from the Cambridge Crystallographic Data Centre. Optimization of the catalytic reaction, crystallographic tables, and optimized geometry of computed structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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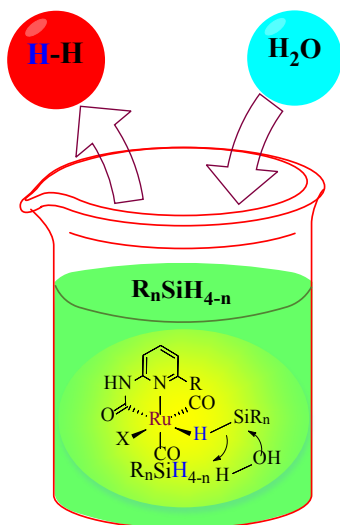
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Graphic



R = H, Me; X = Br, SC₆H₃-*o,o*-Me₂

Synopsis

The ruthenacyclic carbamoyl complexes [RuX(2-NHC(O)C₅H₃NR)(CO)₂(NCMe)] (R = H and Me; X = Br and SC₆H₃-*o,o*-Me₂) are excellent catalysts for the hydrolysis of organosilanes, particularly towards primary silanes, generating hydrogen under ambient conditions within seconds. These complexes are structural mimics of the [Fe]-hydrogenase cofactor; a labile ligand at the sixth coordination site is essential to the catalytic activity.