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Nonclassical Ruthenium Silyl Dihydride Complexes $TpRu(PPh_3)(\eta^3-HSiR_3H)$ [Tp = Hydridotris(pyrazolyl)borate]: Catalytic Hydrolytic Oxidation of Organosilanes to Silanols with TpRu(PPh_3)(\eta^3-HSiR_3H)

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An X-ray crystallographic study showed that it is more appropriate to describe the complexes $TpRu(PPh_3)$ "H₂SiR₃" as TpRu(PPh₃)(η^3 -HSiR₃H), a static structure containing H...Si...H bonding rather than a highly fluxional pair of σ -silane hydride species TpRu(PPh₃)(H_a)(η^2 -H_bSiR₃) \rightleftharpoons TpRu(PPh₃)(H_b)(η^2 -H_aSiR₃). One of the complexes was used

for the catalytic hydrolytic oxidation of organosilanes to silanols. A mechanism, which does not involve the usual oxidative addition of silane to the metal center to form the silyl hydride species, is proposed, which is supported by theoretical calculations.

Introduction

By virtue of the hypervalency around the Si center, a nonclassical interligand interaction might be present in complexes containing a silyl group and two or more hydride ligands. For example, a silvl group in a complex could simultaneously interact with two hydrides and generate a structure with H···Si···H bonding. Crabtree and co-workers first suggested an $M(\eta^3-H_2SiR_3)$ arrangement in the silvl polyhydride complex [Re(PPh₃)₂H₆(SiPh₃)] based on the close contacts between the Si atom and two of the hydride ligands disclosed in the X-ray crystallography study; the hydride positions in the structure are, however, only a working hypothesis.^[1] The complex $RuH_2(\eta^2-H_2)(\eta^2-HSiPh_3)$ - $(PCy_3)_2$ (Cy = cyclohexyl), originally formulated as a dihydrogen σ -silane complex, in fact contains the [H₂SiPh₃]⁻ moiety where the Si atom is almost symmetrically bonded to two hydrogen atoms with the two Si-H bond lengths measuring 1.72 and 1.83 Å.^[2] Nikonov and co-workers have recently provided evidence from X-ray and DFT studies for the existence of H···Si···H bonding in the complex resulting

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from silane activation on the CpFe(iPr_2MeP)H moiety; the complex is most appropriately formulated as CpFe- $(iPr_2MeP)(\eta^3-H_2SiR_3)$ (Figure 1).^[3]



Figure 1. Structure of CpFe(*i*Pr₂MeP)(η³-H₂SiR₃).

Several years ago, we synthesized a series of ruthenium complexes TpRu(PPh₃)"H₂SiR₃" [Tp = hydridotris(pyrazolyl)borate]. On the basis of NMR and DFT studies, we formulated these complexes as σ -silane hydride species, which rapidly exchange between two forms: TpRu(PPh₃)-(H_a)(η^2 -H_bSiR₃) \Rightarrow TpRu(PPh₃)(H_b)(η^2 -H_aSiR₃).^[4] We have now successfully obtained single crystals of three complexes of this type and carried out X-ray crystallographic studies, the results of which are more consistent with a static structure TpRu(PPh₃)(η^3 -HSiR₃H) containing H···Si···H bonding. In addition to the X-ray structures of three Ru(η^3 -HSiR₃H) complexes, we report catalytic hydrolytic oxidation of organosilanes to silanols with one of these complexes.

Silanols are widely utilized as building blocks for siliconbased polymeric materials^[5] and as the nucleophilic partners in cross-coupling reactions.^[6] Well-known preparative methods for silanols include hydrolysis of chlorosilanes,^[7] oxidation of organosilanes with stoichiometric amounts of oxidants,^[8] and reactions of siloxanes with alkali reagents.^[9] The obvious shortcoming of these methods is the genera-

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tion of large amounts of environmentally damaging waste. Moreover, these methods have limited scopes. Highly efficient and environmentally more friendly synthetic methods for the conversion of readily available organosilanes to silanols are therefore highly desirable, and some promising homogeneous^[10] and heterogeneous^[11] systems that catalyze the conversion with the use of water as an oxygen source have recently been reported.

Results and Discussion

Synthesis and X-ray Crystallographic Study of TpRu(PPh₃)"H₂SiR₃"

The complex TpRu(PPh₃)"H₂SiPh₃" (1a) is one of the members of the series of complexes TpRu(PPh₃)"H₂SiR₃", which we have previously reported.^[4] Complexes TpRu-(PPh₃)"H₂SiPh₂Me" (1b) and TpRu(PPh₃)"H₂SiPhMe₂" (1c) are new members of the series synthesized according to our previously reported procedure, i.e. by treating the solvento hydride precursor TpRu(PPh₃)(CH₃CN)H with the corresponding organosilanes [Equation (1)]. Similar to those of other complexes in the series, the ¹H NMR spectra of 1b and 1c each show a doublet hydride signal in the upfield region, which integrates for two hydrogen atoms and does not show decoalescence down to $-100 \,^{\circ}\text{C}$ [1b: $\delta =$ -9.93 ppm, J(HP) = 22.6 Hz; 1c: $\delta = -11.06$ ppm, J(HP) =22.8 Hz]. The hydride signals of 1b and 1c are flanked by 29 Si satellites, and the observed J(SiH) values are 25.0 and 19.2 Hz for 1b and 1c, respectively. These values are comparable to those of other complexes in the series.

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 $TpRu(PPh_3)(CH_3CN)H + R_3Si-H$

Crystals of 1a-c suitable for X-ray crystallographic studies were obtained by layering *n*-hexane on dichloromethane solutions of the complexes. The molecular structures of 1ac are shown in Figures 2, 3, and 4, respectively. The crystal data and refinement details are given in Table 1. Selected bond lengths and angles are listed in Table 2. It is worth noting that the two hydrogen atoms HM1 and HM2 in each of the structures were located and refined. A common feature of the structures of **1a-c** is that the silicon atom interacts almost symmetrically with the two hydrogen atoms HM1 and HM2; the Si-H bond lengths lie at the long end of the 2 Å limit normally observed for σ -Si–H bonds.^[12] The ruthenium-hydrogen (Ru-HM1 and Ru-HM2) bond lengths (1.49–1.568 Å) are within the normal range of classical ruthenium-hydride bond lengths. In addition, the two H-Ru-Si angles in each of the complexes are very close to each other (53.9° and 57.3° in 1a; 52.6° and 54.8° in 1b; 53.9° and 54.8° in 1c). The X-ray structures of 1a-c reveal that these complexes are more appropriately formulated as $TpRu(PPh_3)(\eta^3-HSiR_3H)$ containing a nearly symmetrical H···Si···H bonding in the $[HSiR_3H]^-$ moiety. On the basis of the model previously used in the B3LYP calculations, it was shown that the rapidly interchanging σ -silane hydride enantiomeric pair TpRu(PPh₃)(H_a)(η^2 -H_bSiR₃) \rightleftharpoons TpRu- $(PPh_3)(H_b)(\eta^2-H_aSiR_3)$ is slightly lower in energy



Figure 2. ORTEP view (30% probability) of TpRu(PPh₃)(η^3 -HSiPh₃H) (1a) showing the atom-labeling scheme.



Figure 3. ORTEP view (30% probability) of TpRu(PPh₃)(η^3 -HSiPh₂MeH) (**1b**) showing the atom-labeling scheme.



Figure 4. ORTEP view (30% probability) of TpRu(PPh₃)(η³-HSiPhMe₂H) (1c) showing the atom-labeling scheme.

(2.1 kJ mol⁻¹) than the corresponding symmetrical structure, which was regarded as the transition state for the interchange of the enantiomeric pairs. The B3LYP calculation was performed on a model complex in which the Tp, PPh₃, and SiR₃ moieties were replaced by (H₂C=NNH)₃BH, PH₃, and SiH₃, respectively.

Table 1.	Crystal	and	structure	refinement	data	for	1a,	1b,	and	1c.
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	1a	1b	1c·3CH ₂ Cl ₂
Empirical formula	C45H42BN6PRuSi	C40H40BN6PRuSi	C ₃₈ H ₄₄ BCl ₆ N ₆ PRuSi
Formula mass	837.79	775.72	968.43
<i>T</i> [K]	296(2)	296(2)	296(2)
λ[Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_{1}/c$	<i>P</i> 1	P1
Unit cell dimensions:			
<i>a</i> [Å]	16.1421(3)	10.4776(2)	10.8951(2)
b Å	12.2111(2)	11.3027(2)	12.6105(2)
	21.2219(4)	11.1167(4)	17.6399(3)
	90	77.8800(10)	87.5410(10)
β ^[°]	105.2180(10)	74.1180(10)	79.7450(10)
v [°]	90	72.9730(10)	69.5820(10)
V[Å ³]	4036.42(13)	1845.54(6)	2234.56(7)
Z	4	2	2
Density (calcd.) [gcm ⁻³]	1.379	1.396	1.439
$\mu [\mathrm{mm}^{-1}]$	0.498	0.539	0.807
F(000)	1728	800	988
Crystal size [mm]	$0.32 \times 0.3 \times 0.28$	$0.50 \times 0.48 \times 0.32$	$0.42 \times 0.36 \times 0.30$
θ range for data collection [°]	1.94 to 27.39	2.09 to 27.33	1.17 to 27.46
Index ranges [°]	$-20 \le h \le 20$	$-13 \le h \le 13$	$-14 \le h \le 14$
0 11	$-15 \le k \le 15$	$-14 \le k \le 14$	$-16 \le k \le 16$
	$-27 \le l \le 27$	$-22 \le l \le 21$	$-22 \le l \le 22$
Reflection collected	87540	25782	48788
Independent reflections	9136 [R(int) = 0.3921]	8282 [R(int) = 0.0347]	10102 [R(int) = 0.0558]
Completeness to $\theta = 27.39^{\circ}$ [%]	99.8	99.1	98.8
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Max. transmission	1.000	1.000	1.000
Min. transmission	0.840	0.819	0.805
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	9136/0/508	8282/0/459	10102/499
Goodness-of-fit on F^2	0.735	1.004	1.004
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0335, wR_2 = 0.0528$	$R_1 = 0.0320, wR_2 = 0.0758$	$R_1 = 0.0437, wR_2 = 0.1069$
R indices (all data)	$R_1 = 0.2735, wR_2 = 0.0645$	$R_1 = 0.0416, wR_2 = 0.0812$	$R_1 = 0.0649, wR_2 = 0.1181$
Largest difference peak/hole [eÅ-3]	0.409/-0.303	0.505/-0.525	0.695/-0.609

Table 2. Selected bond lengths [Å] and angles [°] for $1a,\,1b,\,and\,1c.$

	1a	1b	$1c \cdot 3CH_2Cl_2$
Ru–HM(1)	1.491(15)	1.568(16)	1.49(2)
Ru-HM(2)	1.502(15)	1.492(16)	1.49(2)
Si(1)-HM(1)	2.016(14)	1.903(15)	1.94(2)
Si(1)-HM(2)	1.928(14)	1.955(16)	1.965(18)
Ru–Si(1)	2.3816(5)	2.3905(4)	2.4006(5)
HM(1)– Ru – $Si(1)$	57.3	52.6	53.9
HM(2)-Ru-Si(1)	53.9	54.8	54.8
HM(1)-Si(1)-Ru	38.5	40.9	38.2
HM(2)-Si(1)-Ru	39.0	38.5	38.3

Catalytic Hydrolytic Oxidation of Organosilanes to Silanols with $TpRu(PPh_3)(\eta^3-HSiPhMe_2H)$ (1c)

Complexes **1a–1c** are readily synthesized, and we suspect that it would make no difference using any one of them for the catalytic hydrolytic oxidation of silanes [Equation (2)].

$$R_3SiH + H_2O \xrightarrow{cat.} R_3SiOH + H_2$$
 (2)

Table 3 shows the results of the hydrolytic oxidation of silanes to silanols catalyzed by **1c**. The reactions did not proceed at room temperature and were performed at 90 °C. Trialkylsilanes (Entries 4–9) were oxidized more readily than the silanes bearing aryl substituents (Entries 1–3 and 10). In all the reactions reported, disiloxanes resulting from con-

Table 3. Hydrolytic oxidation of organosilanes to silanols with 1c.[a]

Entry	Silane	Time [h]	Conversion [%] ^[b]
1	Ph ₃ SiH	24	84
2	Ph ₂ MeSiH	24	99
3	PhMe ₂ SiH	20	96
4	tBuMe ₂ SiH	4	96
5	EtMe ₂ SiH	2	97
6	CyMe ₂ SiH	2	94
7	CH ₃ (CH ₂) ₁₆ CH ₂ Me ₂ SiH	4	94
8	Et ₃ SiH	4	97
9	Et ₂ MeSiH	4	85
10	1,4-(SiMe ₂ H)C ₆ H ₄	24	65
11	(+)-(R)-Me(a-Np)PhSiH	24	91 ^[c]

[a] Reaction conditions: silane (0.5 mmol), H₂O (40 equiv.), **1c** (10 μ mol, 2 mol-% with respect to silane), 1,4-dioxane (2 mL), 90 °C, under nitrogen flow. [b] Determined by ¹H NMR spectroscopy. [c] Product: (+)-(S)-Me(α -Np)PhSiOH, isolated yield, 90% *ee*.



Figure 5. NMR study of the hydrolysis of PhMe₂SiH to PhMe₂SiOH catalyzed by 1c.

densation of silanols were not detected (see Supporting Information). It is important to note that the optically active silane (+)-(R)-Me(α -Np)PhSiH (98% *ee*) was hydrolyzed to yield (+)-(S)-Me(α -Np)PhSiOH with retention (Entry 11).

NMR Monitoring of the Hydrolytic Oxidation of PhMe₂SiH to PhMe₂SiOH Catalyzed by 1c

PhMe₂SiH (5 equiv.) and water (200 equiv.) were added to a $[D_8]$ -1,4-dioxane solution of 1c in a J. Young valved NMR tube, which was heated in an oil bath at 90 °C. Figure 5 shows the ${}^{31}P{}^{1}H$ and ${}^{1}H$ NMR spectra of the solution measured at different times; the column on the far right shows the percentage conversions to the products (estimated from the integrations of the methyl peaks of the PhMe₂SiH and PhMe₂SiOH in the ¹H NMR spectra). The ${}^{31}P{}^{1}H$ NMR spectrum of the solution taken after 10 min of heating showed that **1c** was present as the overwhelming species; around 2% of the dihydrogen hydride complex $TpRu(PPh_3)(H_2)H(2)^{[13]}$ was also formed. As the reaction proceeded, the amount of 2 increased at the expense of that of 1c, and at the end of the reaction, 1c was nearly all converted to 2. The presence of 1c and 2 and the variation of their amounts at different times were corroborated by ¹H NMR spectra of the solution, which showed the hydride signals of 1c and 2 in the upfield region. It should be pointed out that in this experiment the H₂ by-product was trapped in the NMR tube.

Relative Stability of 1c and TpRu(PPh₃)(η^3 -HSiEtMe₂H) (1d)

In the course of growing single crystals for X-ray crystallographic studies, we learned that complexes containing trialkylsilanes are less stable than those containing silanes with aryl groups. The trialkylsilane complexes undergo decomposition more readily, and we have been unable to obtain single crystals of them. We therefore carried out ligand substitution of 1c with HSiEtMe₂ [Equation (3)] to gain a more quantitative comparison of the thermal stability of 1c and 1d. It was learned that after heating a $[D_8]$ -1,4-dioxane solution of 1c in the presence of HSiEtMe₂ (5 equiv.) at 90 °C for 3 h, the relative equilibrium concentrations of 1c/ 1d was ca. 50:50, and the equilibrium constant K_{eq} was estimated to be 1.1×10^{-1} . This experiment shows that the thermal stability of 1c is about nine times that of 1d. The $[H_2SiR_3]$ moiety, in bonding to the metal fragment, transfers electron density from the occupied orbitals ψ_1 and ψ_2 to the metal center orbitals; on the other hand, the metal back-donates a lone pair into the empty ψ_3 orbital of $[H_2SiR_3]^{-,[14]}$ Here, ψ_1 is the all-in-phase combination of the two H 1s orbitals and the SiR₃ sp³-hybridized orbital, ψ_2 is the out-of-phase combination of the two H 1s orbitals only, and ψ_3 is the all-out-of-phase combination of the two H 1s orbitals and the SiR₃ sp³-hybridized orbital. The higher stability of 1c vs. 1d is probably due to the phenyl group of the silane ligand in the former being able to invite more back-donation from the metal atom.



Proposed Mechanism for the Catalytic Hydrolytic Oxidation of Silanes to Silanols

The NMR monitoring experiment above shows that in the course of catalysis, 1c and 2 were the only detectable organometallic complexes, and these two complexes are interconvertable by ligand exchange. We believe that 1c is the key species reacting directly with water to generate the silanol. The fact that hydrolytic oxidation of the chiral silane (+)-(R)-Me(α -Np)PhSiH to give the silanol product (+)-(S)- $Me(\alpha-Np)PhSiOH$ with retention is a strong indication that the water molecule attacks the silicon center in the manner shown in Scheme 1. A dihydrogen bonding interaction between the proton of the attacking water molecule and the hydride of the $[H_2Si(Me)(\alpha-Np)Ph]^-$ moiety is expected to be present. We have reported a similar dihydrogen bonding interaction between the hydride ligand and the proton of the attacking water molecule in hydration of nitriles catalyzed by Ru-H complexes.[15,16]





Scheme 2 shows a possible mechanism for the hydrolytic oxidation of silanes to silanols. We propose the existence of a dihydrogen bonding interaction between one of the hydrides of the [H₂SiR₃]⁻ moiety and a water proton during nucleophilic attack of the water molecule at the silicon center. Several studies of metal-silane interactions indicate that silane is a strong σ^* -accepting ligand because of the weaker H–Si σ -bonding. The metal ($d\pi$)-to-silane (σ^*) back-bonding is deemed very important for the metal-(η^2 -silane) interaction.^[17] The lower activity of the arylsilanes in comparison to the trialkylsilanes in hydrolytic oxidation reactions can be explained in terms of the diminished electrophilicity of the silicon center resulting from more backbonding from the metal atom and the stronger Ru-Si bond in A (Scheme 2) when R_3 contains one or more phenyl groups. The lower electrophilicity at the silicon center renders nucleophilic attack by the water more sluggish, and the strong Ru-Si bond would slow down the extrusion of the silanol product from the metal center.



Scheme 2.

To study the feasibility of the proposed reaction mechanism shown in Scheme 2 for the catalytic hydrolytic oxidation of silanes, DFT calculations were performed to examine the catalytic cycle by using TpRu(PMe₃)(η³-HSiH- Me_2H) (1A) as the model catalyst. The potential energy profile is shown in Figure 6 with the calculated relative electronic energies. The reaction of 1A with water occurs by a nucleophilic attack of the water oxygen atom on the silicon center of the η^2 -silane ligand in a six-membered-ring transition state to give silanol and the dihydrogen complex 2A. From the dihydrogen complex 2A, ligand substitution with silane occurs to regenerate 1A and to release a dihydrogen molecule, completing the catalytic cycle. The overall reaction barrier shown in Figure 5 is 90.0 kJ mol⁻¹ and the hydrolysis reaction is thermodynamically favorable. These results support the proposed mechanism discussed above.

Figure 7 presents the optimized structures with selected structural parameters for the species shown in Figure 5. The bond lengths calculated for the Ru–Si, Si–H, and Ru–H bonds in **1A** are similar to those determined experimentally in TpRu(PPh₃)(η^3 -HSiR₃H). In **1A**, both hydride ligands maintain strong interactions with the silicon center of the silyl ligand, indicating the hypervalency around the silicon center.^[12b] The double silyl–hydrido interactions have been also found in Cp(*i*Pr₂MeP)FeH₂SiR₃ reported recently.^[3] **2A** is a dihydrogen complex with an H–H distance of 0.90 Å. The transition structure **TS**_{A(1-2)} displays a strong dihydrogen bonding with an H···H distance of 1.29 Å.

An alternative mechanism for the hydrolytic oxidation of silanes catalyzed by 1 is shown in Scheme 3. The cycle begins with the generation of the aqua hydride complex 3 by H_2O /silane exchange, 3 then generates the hydroxido species 4 probably through σ -bond metathesis.^[18] Displacement of the dihydrogen ligand in 4 by silane and subsequent intramolecular hydroxylation of the silane ligand yields the product and metal hydride. Although we have not observed the aqua hydride complex 3 in the NMR monitoring experiment, we cannot, however, exclude the possibility that it might be present in trace amounts, which eludes NMR detection.

Our theoretical calculations show that the replacement of $HSiHMe_2$ by a water molecule is endothermic [Equation (4)]; **3A** is less stable than **1A** by 36.4 kJ mol⁻¹, consis-



Figure 6. Energy profile calculated for the hydrolysis reaction of HSiHMe₂ catalyzed by $TpRu(PMe_3)(\eta^3$ -HSiHMe₂H) (1A). The calculated relative electronic energies are given in kJ mol⁻¹.



Figure 7. Optimized structures for the species involved in the hydrolysis reaction of HSiHMe₂ catalyzed by $TpRu(PMe_3)(\eta^3-HSiHMe_2H)$ (1A) (Figure 5). Bond lengths are given in Å.



Scheme 3.

tent with the experimental results that the aqua hydride complex **3A** was not observed. The energy required to dissociate a silane molecule from **1A** was estimated to be $124.3 \text{ kJ} \text{ mol}^{-1}$, indicating that the replacement of water by silane is relatively difficult to achieve.



Conclusions

Based on the X-ray crystallographic structures of 1a-c, it is more appropriate to describe this class of Ru-silane complexes TpRu(PPh3)"H2SiR3" as having a static structure TpRu(PPh₃)(η³-HSiR₃H) containing H···Si···H bonding, rather than a highly fluxional pair of σ -silane hydride complexes $TpRu(PPh_3)(H_a)(\eta^2-H_bSiR_3) \Rightarrow TpRu(PPh_3) (H_b)(H_aSiR_3)$. The complex TpRu(PPh₃)(η^3 -HSiPhMe₂H) (1c) was used to catalyze the hydrolytic oxidation of silanes to silanols. Although the catalytic activity of **1c** might not be as high as that of some of the catalytic systems reported by others, we have, however, been able to present a much clearer picture of the mechanistic aspects of the reaction. More importantly, this is a rare example of employing a complex containing the $[H_2SiR_3]^-$ moiety for a catalytic study. The reaction mechanisms of most of the previously studied catalytic systems have not been studied in detail. It was generally suggested that the catalysis involves oxidative addition of the silane molecule to the metal atom to form the silvl hydride species. From our study, a new mechanism was proposed. Theoretical calculations show that the crucial step of the catalytic process is the nucleophilic attack of the water oxygen atom at the silicon center of the $[H_2SiR_3]^$ moiety; a strong dihydrogen bonding interaction between one of the hydrides of $[H_2SiR_3]^-$ and a water proton is present in the transition state. This work provides experiental evidence, which is scarce, for the presence of the $[H_2SiR_3]^$ ligand and establishes a unique mechanism for the transition metal catalyzed hydrolytic oxidation of silanes to silanols. An alternative mechanism, which involves intramolecular hydroxido attack at the silane ligand is also proposed. However, theoretical calculations indicate that this alternative mechanism is less favorable.

Experimental Section

General: All manipulations were carried out under nitrogen by using standard Schlenk techniques. Solvents were dried, degassed, and distilled prior to use: THF, 1,4-dioxane, and diethyl ether from Na benzophenone ketyl; n-hexane and toluene from Na; acetonitrile and dichloromethane from CaH2. All chemicals were commercially available (Aldrich, Acros, Strem, and International Laboratory) and used without further purification. The chiral silane (+)-(*R*)-Me(α -Np)PhSiH (98% *ee*)^[19] and the complexes TpRu(PPh₃)-(CH₃CN)H^[13] and TpRu(PPh₃)(η³-HSiPh₃H)^[4] (1a) were prepared according to literature methods. Deuterated NMR solvents, purchased from Armar and Cambridge Isotope Laboratories, were dried with P₂O₅ prior to use. ¹H NMR spectra were obtained with Varian (500 MHz) or Bruker DPX (400 MHz) spectrometers, and chemical shifts are reported relative to residual protons of the deuterated solvents. ¹³C NMR spectra were recorded with a Bruker DPX 400 spectrometer at 100.61 MHz, and chemical shifts are referenced to internal CD₂Cl₂ (δ = 53.8 ppm). ³¹P NMR spectra were recorded with a Bruker DPX 400 spectrometer at 161.70 Mz, and chemical shifts are referenced to external 85% H₃PO₄ in D₂O (δ = 0.00 ppm). ²⁹Si NMR spectra were obtained with a Bruker DPX 400 spectrometer at 79.50 MHz, and chemical shifts are referenced to external Me₄Si in CDCl₃ ($\delta = 0.00$ ppm). IR spectra were obtained with a Bruker Vector 22 FTIR spectrophotomer. Optical rotations were recorded with a Perkin-Elmer 341 polarimeter in a 10 cm cell. Electrospray ionization mass spectrometry was carried out with a Finnigan MAT 95S mass spectrometer with the samples dissolved in dichloromethane. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Synthesis of TpRu(PPh₃)(η³-HSiPh₂MeH) (1b): TpRu(PPh₃)-(CH₃CN)H (0.20 g, 0.32 mmol) was loaded into a 50 mL twonecked pear-shaped flask, which was evacuated and filled with nitrogen for four cycles. Freshly distilled toluene (10 mL) and Ph₂Me-SiH (0.8 mL, 4 mmol) were then added by syringe into the flask, and the resulting solution was heated at 90 °C with stirring for 4 h. The solution was cooled to room temperature, and the volume was reduced to 1 mL in vacuo before cooled hexane (10 mL) was added to precipitate the product as orange solid. The solid was collected, washed with cooled hexane (5 mL) and dried under vacuum. Yield: 0.14 g (55%). C₄₀H₄₀BN₆PRuSi (775.73): C 61.93, H 5.20, N 10.83; found C 61.93, H 5.25, N 10.85. IR (KBr): v = 1942 [m, v(Ru-H)], 2468 [m, v(B–H)]. ¹H NMR (400.13 MHz, CD₂Cl₂, 25 °C): δ = -9.93 (d, ${}^{1}J_{SiH} = 25.0$, ${}^{2}J_{HP} = 22.6$ Hz, 2 H, RuH); 0.70 (s, 3 H, Si-CH₃), 5.48 (t, 1 H of Tp), 5.77 (t, 2 H of Tp), 7.52 (d, 1 H of Tp), 7.68 (d, 2 H of Tp), 7.82 (d, 1 H of Tp), 8.35 (d, 2 H of Tp), 6.93–7.60 (m, 25 H of Ph) ppm. ¹³C{¹H} NMR (100.61 MHz, CD_2Cl_2 , 25 °C): $\delta = 9.49$ (s, SiCH₃) ppm. ³¹P{¹H} NMR



(161.7 MHz, CD₂Cl₂, 25 °C): δ = 70.3 ppm. ²⁹Si{¹H} NMR (79.50 MHz, CD₂Cl₂, 25 °C): δ = 16.8 (s) ppm. ESI-MS: m/z = 576 [M–Ph₂MeSiH]⁺.

Synthesis of TpRu(PPh₃)(η³-HSiPhMe₂H) (1c): This complex was synthesized by using the same procedure as described above for **1b**, except that PhMe₂SiH was used in place of Ph₂MeSiH. Yield: 0.11 g (48%). C₃₅H₃₈BN₆PRuSi (713.66): C 58.90, H 5.37, N 11.78; found C 58.91, H 5.41, N 11.80. IR (KBr): $\tilde{v} = 2013$ [m, v(Ru–H)], 2464 [m, v(B–H)]. ¹H NMR (400.13 MHz, CD₂Cl₂, 25 °C): $\delta = -11.06$ (d, ¹*J*_{SiH} = 19.2, ²*J*_{HP} = 22.8 Hz, 2 H, Ru*H*); 0.36 [s, 6 H, Si(C*H*₃)₂]; 5.33 (t, 1 H of Tp), 5.77 (t, 2 H of Tp), 5.88 (d, 1 H of Tp), 7.58 (d, 2 H of Tp), 7.66 (d, 1 H of Tp), 7.93 (d, 2 H of Tp), 6.03–7.30 (m, 20 H of Ph) ppm. ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂, 25 °C): $\delta = 13.05$ [s, Si(*CH*₃)₂] ppm. ³¹P{¹H} NMR (161.7 MHz, CD₂Cl₂, 25 °C): $\delta = 15.1$ (s) ppm. ESI-MS: *m*/*z* = 576 [M–PhMe₂SiH]⁺.

General Procedure for the Hydrolysis of Silanes Catalyzed by 1c: The catalyst 1c (7.1 mg, 0.01 mmol) was loaded into a 25 mL twonecked pear-shaped flask, which was then evacuated and flushed with nitrogen for four cycles. Silane (0.5 mmol), water (0.36 mL, 20 mmol), and 1,4-dioxane (2 mL) were then added by syringe into the flask (in the case of Ph₃SiH, the solid was loaded into the flask prior to system evacuation and nitrogen flushing), and the resulting solution was stirred under a nitrogen flow in a preheated 90 °C silicone oil bath for the predesignated times. At the end of the reaction, the flask was cooled to room temperature before a 0.1 mL aliquot of the solution was withdrawn and analyzed by ¹H NMR spectroscopy (in CD₃COCD₃ or CD₃CN). Conversions were determined by comparison of the integrations of the characteristic peaks of the product and the unreacted silane.

Monitoring of the Hydrolytic Oxidation of PhMe₂SiH to PhMe₂-SiOH Catalyzed by 1c with NMR Spectroscopy: A sample of 1c (31.2 mg) was loaded into a J. Young valved NMR tube. The tube was evacuated and filled with nitrogen for four cycles. PhMe₂SiH (33 μ L, 5 equiv.), water (157 μ L, 200 equiv.), and [D₈]-1,4-dioxane (1 mL) were added by syringe into the tube. The resulting solution was heated to 90 °C. At different time intervals, the tube was cooled to room temperature, and ¹H and ³¹P NMR spectra of the solution were measured.

Monitoring of the Reaction Between 1c and EtMe₂SiH: A sample of 1c (31.2 mg) was loaded into a J. Young valved NMR tube. The tube was evacuated and filled with nitrogen for four cycles. EtMe₂-SiH (28 μ L, 5 equiv.) and [D₈]-1,4-dioxane (1 mL) were added by syringe into the tube. The solution was heated to 90 °C for 3 h. The tube was cooled to room temperature, and ¹H and ³¹P NMR spectra of the solution were measured.

Crystallographic Structure Analysis of 1a–c: Orange crystals of **1a–c** suitable for study by X-ray diffraction were obtained by layering of *n*-hexane on a dichloromethane solution of the complexes. Suitable crystals of **1a** $(0.32 \times 0.3 \times 0.28 \text{ mm})$, **1b** $(0.50 \times 0.48 \times 0.32 \text{ mm})$, and **1c** $(0.42 \times 0.36 \times 0.30 \text{ mm})$ were mounted on a Bruker CCD area detector diffractometer and subjected to Mo- K_a radiation ($\lambda = 071073$ Å) from a generator operating at 50 kV and 30 mA. The intensity data of **1a–c** were collected in the range $\theta = 1.94-27.39^\circ$, 2.09–27.33°, and 1.17–27.46°, respectively, with oscillation frames of Ψ and ω and in the range 0–180°. A total of 1728 frames for **1a**, 800 for **1b**, and 988 for **1c** were taken in four shells. An empirical absorption correction of the SADABS (G. M. Sheldrick, 1996) program based on Fourier coefficient fitting was applied. The crystal structures were solved by Patterson function methods, expanded by difference Fourier synthesis, and

refined by full-matrix least squares on F^2 by using the Bruker smart and Bruker SHELXTL program packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as rigid atoms. The *R* and R_w values of **1a**, **1b**, and **1c** are 0.0335 and 0.0528, 0.0320 and 0.0758, and 0.0437 and 0.1069, respectively. CCDC-763941 (**1a**), -763942 (**1b**) and -763943 (**1c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Computational Details: Molecular geometries of the model complexes were optimized without constraints by DFT calculations using the mPW1K^[20] functional. Frequency calculations at the same level of theory have also been performed to identify all the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency). Transition states were located by using the Berny algorithm. Intrinsic reaction coordinates^[21] were calculated for the transition states to confirm that such structures indeed connect two relevant minima. The effective core potentials of Hay and Wadt with double-ζ valence basis sets (LanL2DZ)^[22] were used to describe Ru, P, and Si. Polarization functions were also added for Ru ($\zeta_f = 1.235$), P ($\zeta_d = 0.387$), and Si $(\zeta_d = 0.284)$.^[23] The 6-311G (d, p) Pople basis set was used for the water molecule and H atoms that were directly bonded to the metal center.^[24] The 6-311G basis set was used for all the other atoms.^[25] All of the DFT calculations were performed with the Gaussian 03 package.[26]

Supporting Information (see footnote on the first page of this article): ¹H NMR spectra of the reaction mixture of the TpRu(PPh₃)(η^3 -HSiPhMe₂H)-catalyzed hydrolytic oxidation of organosilanes to silanols and cartesian coordinates for all the complexes calculated in this study.

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- X.-L. Luo, D. Baudry, P. Boydell, P. Charpin, M. Nierlich, M. Ephritikhine, R. H. Crabtree, *Inorg. Chem.* 1990, 29, 1511.
- [2] K. Hussein, C. J. Marsden, J.-C. Barthelat, V. Rodriguez, S. Conejero, S. Sabo-Etienne, B. Donnadieu, B. Chaudret, *Chem. Commun.* **1999**, 1315.
- [3] D. V. Gutsulyak, L. G. Kuzmina, J. A. K. Howard, S. F. Vyboishchikov, G. I. Nikonov, *J. Am. Chem. Soc.* 2008, 130, 3732.
- [4] S. M. Ng, C. P. Lau, M. F. Fan, Z. Lin, Organometallics 1999, 18, 2484.
- [5] a) I. Ojima, Z. Li, J. Zhu in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Rappoport, Y. Apeloig), Wiley, New York, **1998**, chap. 29; b) E. W. Colvin, *Silicon Reagents in Organic Synthesis*, Academic Press, London, **1988**, p. 7; c) P. D. Lickiss, *Adv. Inorg. Chem.* **1995**, *42*, 147.
- [6] a) K. Hirabayashi, Y. Nishihara, A. Mori, T. Hiyama, *Tetrahedron Lett.* 1998, 39, 7893; b) K. Hirabayashi, J. Kawashima, Y. Nishihara, A. Mori, T. Hiyama, *Org. Lett.* 1999, 1, 299; c) S. E. Denmark, D. Wehrli, *Org. Lett.* 2000, 2, 565; d) K. Hirabayashi, A. Mori, J. Kawashima, M. Suguro, Y. Nishihara, T. Hiyama, J. Org. Chem. 2000, 65, 5342.
- [7] a) E. G. Rochow, W. F. Gilliam, J. Am. Chem. Soc. 1941, 63, 798; b) R. O. Sana, J. Am. Chem. Soc. 1944, 66, 1707.
- [8] W. Adam, R. Mello, R. Curci, Angew. Chem. Int. Ed. Engl. 1990, 29, 890.

- [9] a) S. M. Sieburth, W. Mu, J. Org. Chem. 1993, 58, 7584; b) K. Hirabayashi, A. Mori, T. Hiyama, Tetrahedron Lett. 1997, 38, 461.
- [10] a) M. Lee, S. Ko, S. Chang, J. Am. Chem. Soc. 2000, 122, 12011; b) Y. Lee, D. Seomoon, S. Kim, H. Han, S. Chang, P. H. Lee, J. Org. Chem. 2004, 69, 1741; c) E. A. Ison, R. A. Corbin, M. M. Abu-Omar, J. Am. Chem. Soc. 2005, 127, 11938.
- [11] a) K. Mori, M. Tano, T. Mizugaki, K. Ebitani, K. Kaneda, *New J. Chem.* 2002, 26, 1536; b) E. Choi, C. Lee, Y. Na, S. Chang, *Org. Lett.* 2002, 4, 2369; c) T. Mitsudome, S. Arita, H. Mori, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem. Int. Ed.* 2008, 47, 7938.
- [12] a) U. Schubert, Adv. Organomet. Chem. 1990, 30, 151; b) Z. Lin, Chem. Soc. Rev. 2002, 31, 239.
- [13] Y.-Z. Chen, W. C. Chan, C. P. Lau, H. S. Chu, H. L. Lee, G. Jia, *Organometallics* **1997**, *16*, 1241. We are not sure of the exact structure of **2**, it might be analogous to those of **1a–1c**, containing an $[\eta^3-H_3]^-$ moiety instead of the hydride and η^2-H_2 ligands.
- [14] a) S. F. Vyboischchikov, G. I. Nikonov, Chem. Eur. J. 2006, 12, 8518; b) G. I. Nikonov, Angew. Chem. Int. Ed. 2001, 40, 3353.
- [15] C. W. Leung, W. Zheng, D. Wang, S. M. Ng, C. H. Yeung, Z. Zhou, Z. Lin, C. P. Lau, *Organometallics* 2007, 26, 1924.
- [16] W. K. Fung, X. Huang, M. L. Man, S. M. Ng, M. Y. Hung, Z. Lin, C. P. Lau, J. Am. Chem. Soc. 2003, 125, 11539.
- [17] a) M.-F. Fan, G. Jia, Z. Lin, J. Am. Chem. Soc. 1996, 118, 9915; b) M.-F. Fan, Z. Lin, Organometallics 1997, 16, 494; c) M.-F. Fan, Z. Lin, Organometallics 1999, 18, 286.
- [18] a) J. F. Hartwig, S. Bhandari, P. R. Rablen, J. Am. Chem. Soc.
 1994, 116, 1839; b) J. C. Lee, E. Peris, A. L. Rheingold, R. H. Crabtree, J. Am. Chem. Soc. 1994, 116, 11014; c) M. Schlaf, R. H. Morris, J. Chem. Soc., Chem. Commun. 1995, 625; d) D. G. Musaev, A. M. Mebel, K. Morokuma, J. Am. Chem. Soc.
 1994, 116, 10693; e) P. E. M. Siegbahn, R. H. Crabtree, J. Am. Chem. Soc. 1996, 118, 4442; f) C. Hinderling, D. Feichtinger, D. A. Plattner, P. Chen, J. Am. Chem. Soc. 1997, 119, 10793; g) A. Milet, A. Dedieu, G. Kapteijin, G. van Koten, Inorg. Chem. 1997, 36, 3223.
- [19] L. H. Sommer, C. L. Frye, G. A. Parker, K. W. Michael, J. Am. Chem. Soc. 1964, 86, 3271.

- [20] B. J. Lynch, P. L. Fast, M. Harris, D. G. Truhlar, J. Phys. Chem. A 2000, 104, 4811.
- [21] a) J. Fukui, J. Phys. Chem. 1970, 74, 4161; b) K. Fukui, Acc. Chem. Res. 1981, 14, 363.
- [22] P. J. Hay, W. R. Wadt, J. Chem. Phys. 1995, 82, 299.
- [23] a) A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, 208, 111; b) A. Höllwarth, M. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, 208, 237.
- [24] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, J. Chem. Phys. 1980, 72, 650.
- [25] a) M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163; b) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213; c) R. C. Binning Jr, L. A. Curtiss, *J. Comput. Chem.* **1990**, *11*, 1206.
- [26] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven Jr, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuii, M. Hada, M. Ehara, K. Tovota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, revision B05; Gaussian, Inc., Pittsburgh, PA, 2003.

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