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Silane Deuteration Catalyzed by Ruthenium Bis(dihydrogen) Complexes or Simple Metal Salts

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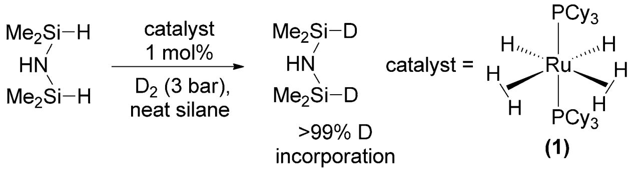
Abstract: The deuteration of a diverse group of silanes: alkyl-, aryl-, alkoxy- and chlorosilanes, siloxane and silazane, under an atmosphere of dideuterium (D_2) was explored with ruthenium bis(dihydrogen) dihydride complexes and hydrated metal salts. Deuterium incorporation of greater than 97% for the silanes $O(SiMe_2H)_2$, Et_3SiH, $(EtO)_3SiH$ and Me_2ClSiH was possible with 0.1 mol% of the ruthenium complex $[RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2]$ [0.05 mol% for $O(SiMe_2H)_2$] when catalysis was conducted in the neat silane at 30 °C under 1 bar of D_2 for 3.5 h. The air-stable ruthenium trichloride salt $RuCl_3{\cdot}xH_2O$ was also an efficient catalyst for the deuteration of $O(SiMe_2H)_2$ and Et_3SiH; deuterium incorporations for the two silanes of 93% and 90%, respectively, were possible under the same conditions as for $[RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2]$ with 0.1% catalyst loading. Hydrogen–deuterium exchange of $O(SiMe_2H)_2$ catalyzed by the rhodium trichloride ($RhCl_3{\cdot}xH_2O$) and iridium trichloride ($IrCl_3{\cdot}xH_2O$) was similarly efficient as with $RuCl_3{\cdot}xH_2O$ although catalytic alacrity dropped for Et_3SiH.

Keywords: catalysis; deuterium; hydrides; silicon; transition metals

The incorporation of isotopic labels into chemical compounds is a simple yet powerful technique for probing molecular transformations, enhancing spectroscopic studies and obtaining revealing kinetic parameters.[1] Methods for selective H/D exchange are valuable to develop considering the profundity of reactions proceeding by hydrogen transfer and the omnipresence of ^1H NMR spectroscopy. Common methods for the addition of deuterium to molecules exploit well-established routes modified by the use of deuterated reagents. Homogenous metal catalysis is an invaluable tool for deuteration, greatly enhancing the scope of E−H (E = H, C, Si) bonds which may be successfully transformed into E−D bonds.

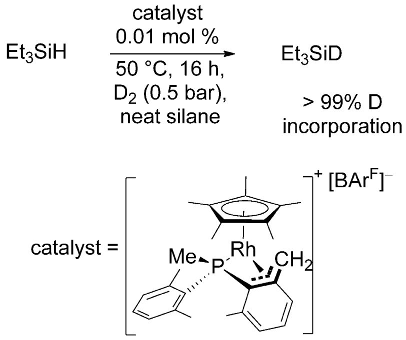
Hydrosilylation is a common route for the reduction of unsaturated groups and could be exploited for the addition of deuterium to an organic substrate.[2] Hydridosilanes are also useful for the reduction of carbon-halogen bonds including hydrodefluorination.[3] Deuterosilane could therefore be used to bring about labeling in a highly selective manner in a variety of molecules. The standard method for silane deuteration is the reduction of a silicon-halogen bond by $NaBD_4$ or $LiAlD_4$.[4] An effective route bypassing the stoichiometric generation of a halide salt would be highly beneficial. An early example of catalytic Si−H exchange with an external deuterium source was given by Curtis and co-workers.[5] The first study into the catalytic deuteration of hydridosilanes with D_2 by the rhodium dimer $[RhH(dipe)]_2$ was reported by Fryzuk and co-workers in 1991 although no details of the catalyst loading or D incorporation were provided.[6]

The selective deuteration of the Si−H bonds of 1,1,3,3-tetramethyldisilazane, $HN(SiMe_2H)_2$, catalyzed by the bis(dihydrogen) ruthenium complex $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$, **1**, (Cy = cyclohexyl) was investigated by our group in 2005 (Scheme 1).[7] The deutero product $HN(SiMe_2D)_2$ was subsequently employed for a solid-state ^2H NMR spectroscopy study of the molecular dynamics of the $-SiMe_2D$ moiety grafted to various forms of silica.[8] In 2010, Carmona and co-workers reported a highly efficient rhodium-catalyzed preparation of deuterated and even tritiated silanes under an atmosphere of D_2 or T_2.[2b,9] It was possible to prepare



(1)

Scheme 1. Deuteration of $HN(SiMe_2H)_2$ by D_2 with **1**.[7]



Scheme 2. Deuteration of Et_3SiH catalyzed by a Rh(III) complex.[9a]

Et_3SiD, Me_2PhSiD and Ph_2SiD_2 on a scale of several grams with very low catalyst loading (for example: 0.01% catalyst in neat Et_3SiH at 50 °C, 0.5 bar D_2, >99% D incorporation) (Scheme 2). The alacrity of Si–H/D exchange is accounted for by the facility of H/D-exchange observed for *sp*^{3}-hybridized C–H groups of the phosphine xylyl groups of the rhodium complex.[9a] In 2011, Nolan and co-workers found that the iridium-N-heterocyclic carbene complex, [IrCl(I-*t*-Bu′)$_2$], was a more efficient catalyst than the analogous rhodium complex, and 94% deuterium incorporation for Et_3SiH with a low catalyst loading of 0.01 mol% was achieved (CD_2Cl_2, 0.5 atm D_2, 3 h).[10]

Following our initial investigation of the deuteration of 1,1,3,3-tetramethyldisilazane and with impetus provided by the more recent results in this area, we decided to study silane deuteration with $[RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2]$, **2**, (Cyp = cyclopentyl) the tricyclopentylphosphine analogue of **1**. The two complexes exhibit distinct behavior due to the different sizes of the cycloalkyl rings.[11] A thorough study of the deuteration processes of **2** has recently been presented.[12] Combining neutron diffraction and ^{2}H NMR, it was possible to demonstrate that together with exchange of the hydride and dihydrogen ligands with deuterium, C–H/D exchange at the cyclopentyl ligand could be achieved depending on the conditions. We now present the catalytic deuteration of a range of silanes by the dihydride bis(dihydrogen) ruthenium complexes **1** and **2**, and disclose the ability of the hydrated salts $MCl_3{\cdot}xH_2O$ (M = Ru, Rh, Ir) to also act as catalyst precursors under very mild conditions.

Initial testing of the feasibility of Si–H/D exchange for Et_3SiH catalyzed by **2** was carried out with 1 mol% catalyst loading in C_6D_6, under an atmosphere of D_2 (1 bar). The reaction mixture was stirred vigorously at 30 °C to promote solution homogeneity and convection of reagents. To favor the equilibrium between protio- and deuterosilane, the reaction mixture was frozen and the atmosphere of D_2 refreshed by evacuation followed by reapplication of the gas (see the Experimental Section). Deuterium incorporation of 92% was gauged after a reaction time of 3.5 h from ^{1}H NMR spectroscopy by integration of the residual Si–H signal and the ethyl groups. Additional characterization by ^{2}H and ^{29}Si NMR together with IR spectroscopic analyses was conducted. The effect of changing the pressure of D_2 and the catalyst loading was investigated and Table 1 displays the incorporation of deuterium into the silane.

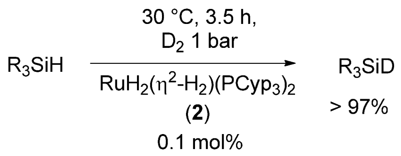
When the amount of catalyst was halved to 0.5 mol% and the reaction time doubled to 6.5 h, 95% deuterium incorporation was achieved (entry 2, Table 1). Increasing the pressure of deuterium from 1 to 3 bar had essentially no effect on the deuterium incorporation (entry 3, Table 1). When the experiment was conducted in the absence of D_2, C_6D_6 was able to act as a deuterium source, 12% deuterium incorporation was observed (entry 4, Table 1). Considering that C–D activation of C_6D_6 by **2** has previously been demonstrated, it is possible to account for the minor conversion of Si–H to Si–D.[12] When D_2 (1 bar) was applied to a mixture of Et_3SiH and C_6D_6 in the absence of a catalyst, no deuterium incorporation was observed (entry 5, Table 1).

The deuteration of five other silanes $HN(Me_2SiH)_2$, $O(SiMe_2H)_2$, $(i\text{-}Pr)_2ClSiH$, $(EtO)_3SiH$ and Me_2ClSiH, was also investigated. The same experimental procedure was followed as outlined for Et_3SiH. Deuterium incorporation greater than 95% was achieved with 0.1 or 0.05 mol% **2** (entries 6–9, Table 1). As previously reported, in the case of $HN(Me_2SiH)_2$, very selective

Table 1. Deuteration of silanes in C_6D_6 with **2** after 3.5 h at 30 °C.

Entry	Silane	D_2 [bar]	Catalyst [mol%]	D_{incorp} [%]
1	Et_3SiH	1	1.0	92
2	Et_3SiH	1	0.5[a]	95
3	Et_3SiH	3	1.0	93
4	Et_3SiH	0	1.0	12
5	Et_3SiH	1	0	0
6	$HN(Me_2SiH)_2$	1	0.05	98
7	$O(SiMe_2H)_2$	1	0.05	97
8	$(i\text{-}Pr)_2ClSiH$	1	0.10	95
9	$(EtO)_3SiH$	1	0.10	99
10	Ph_3SiH	1	1.0	99

[a] Reaction time 6.5 h.



Scheme 3. Procedure for the catalytic deuteration of neat silanes with **2** under an atmosphere of D_2.

D-incorporation was achieved with no H/D exchange at the NH site.[7] The silane deuteration study conducted by Nolan and co-workers reports 98% deuterium incorporation for triethoxysilane with 1 mol% $[IrCl(I\text{-}t\text{-}Bu')_2]$ loading and a reaction time of three hours although under the same conditions, only 48% deuterium incorporation was achieved for diisopropylchlorosilane.[10] We also tested $H_2SiPhMe$ which led to complete H/D exchange but with extensive redistribution reactions as already observed when exposing such a secondary silane to a bis(dihydrogen) ruthenium complex.[13] $D_2SiPhMe$, $DSiPh_2Me$ and $DSiMe_2Ph$ were obtained in a 3:1:0.1 ratio. Finally, excellent deuterium incorporation was also achieved in the case of the arylsilane $HSiPh_3$ (entry 10, Table 1).

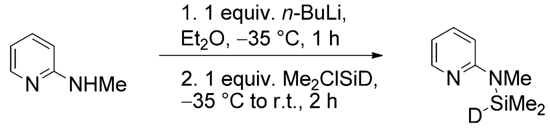
Considering that many silanes are liquids, the feasibility of solvent-less Si–H/D exchange was investigated (Scheme 3). Eliminating the need for solvent would substantially reduce the cost of the process if it were conducted on a large scale. Furthermore, the isolation of the deuterated silanes is more facile in the absence of a solvent. As for the reactions carried out in C_6D_6, the homogenous solution of silane and **2** was frozen in the Fischer–Porter vessel and the atmosphere of argon removed under vacuum. The mixture was allowed to melt and D_2 (1 bar) was applied to the stirred solution at 30 °C. The atmosphere inside the vessel was refreshed three times during the reaction. The silane and catalyst were stirred together at 30 °C under an atmosphere of D_2 for a total time of 3.5 h. The results are presented in Table 2.

Table 2. Deuteration of neat silanes with **2** after 3.5 h at 30 °C.

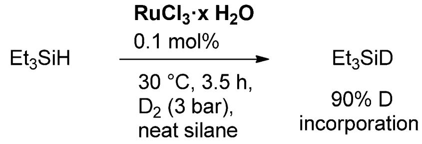
Entry	Silane	Catalyst [mol%]	D_{incorp} [%]
1	Et_3SiH	0.10	97
2	Et_3SiH	0.05	75
3	Et_3SiH	0	0
4	$O(SiMe_2H)_2$	0.0500	99
5	$O(SiMe_2H)_2$	0.0100	80
6	$O(SiMe_2H)_2$	0.0075	53
7	$O(SiMe_2H)_2$	0.005	42
8	$O(SiMe_2H)_2$	0	6
9	$(EtO)_3SiH$	0.10	> 99
10	Me_2ClSiH	0.10	> 99

The high deuterium incorporation of 97% for Et_3SiH (entry 1 Table 2) indicates that **2** is a very active catalyst for Si–H/D exchange in the absence of solvent. It is interesting that a greater extent of Et_3SiH deuteration may be achieved with lower catalyst loading when C_6D_6 is not present despite evidence that deuterium may be transferred from C_6D_6 to the silane (entry 4 Table 1). It is possible that in C_6D_6, a pathway involving C–D bond activation may compete with Si–H/D exchange. The solubility of D_2, DH and H_2 in C_6D_6 and the neat silane might also be important factors. There is essentially no difference between the deuterium incorporation for $O(SiMe_2H)_2$ obtained with and without C_6D_6, 97% (entry 7 Table 1) and 99% (entry 4 Table 2), respectively. Half the amount of catalyst, per Si–H bond, is required to bring about 99% deuteration of $O(SiMe_2H)_2$, 0.05 mol% (entry 4 Table 2), than was required for 97% deuteration of Et_3SiH, 0.1 mol% (entry 1 Table 2). $O(SiMe_2H)_2$ is distinct from Et_3SiH because it features two Si–H bonds. Perhaps a cooperative effect for deuteration of both Si–H bonds of the same $O(SiMe_2H)_2$ molecule is in operation. The siloxane complex $[RuH_2\{(\eta^2\text{-}HSiPh_2)_2O\}(PCy_3)_2]$, **3**, was reported from the reaction of **1**, with two equivalents of $O(SiMe_2H)_2$ featuring η^2-Si–H coordination of the two Si–H bonds.[14] Presumably exchange with deuterium could occur cooperatively for the coordinated Si–H bonds. Considering the similarity between **1** and **2**, it would seem rational that the complexes undergo similar reactivity with $O(SiMe_2H)_2$. Indeed, when two equivalents of $O(SiMe_2H)_2$ were added to a pentane suspension of **2**, ^1H and ^{31}P NMR spectra collected from the resulting grey powder were similar to those of **3**. A single broad singlet was observed at $\delta = -9.80$ in the hydride region of the ^1H NMR spectrum for the product of the reaction of $O(SiMe_2H)_2$ with **2** and a broad signal in the ^{31}P NMR spectrum at $\delta = 42.7$. For **3**, the corresponding data are $\delta = -9.48$ for the ^1H NMR of the hydride and $\delta = 49.9$ for the ^{31}P NMR chemical shift.[14] Further analysis of the product of the reaction of $O(SiMe_2H)_2$ with **2** is underway.

When $O(SiMe_2H)_2$ was stirred under an atmosphere of D_2 in the absence of **2**, 6% deuterium incorporation was identified (entry 8, Table 2). Despite careful washing of the reaction vessel and stir bar with *aqua regia* to eliminate traces of ruthenium before each catalytic run, it appears that partial activation of Si–H occurs by some means. No deuterium incorporation was observed when Et_3SiH was stirred with 1 bar D_2 in the absence of an added catalyst, (entry 3, Table 2). Full deuteration of $(EtO)_3SiH$ (> 99%) was achieved in the neat silane with 0.10 mol% catalyst loading (entry 9 Table 2), similar to the 99% incorporation achieved in C_6D_6, (entry 9 Table 1). The deuteration of Me_2ClSiH was accomplished with 0.10 mol% loading and > 99% deuterium incorpora-



Scheme 4. Preparation of a deuterated silazane compound.



Scheme 5. Procedure for the catalytic deuteration of neat Et_3SiH with $RuCl_3{\cdot}xH_2O$ under an atmosphere of D_2.

tion (entry 10, Table 2). The reaction was conducted on a relatively large scale (7 g) to prepare Me_2ClSiD for use as a reagent in the synthesis of a deuterated silazane compound (Scheme 4).

The ability of the PCy_3 complex **1** to catalyze the deuteration in neat Et_3SiH and $O(SiMe_2H)_2$ was also investigated. For $O(SiMe_2H)_2$, deuterium incorporation of 99% was achieved with 0.05 mol% catalyst loading of **1** and **2**. When 0.01 mol% of **1** was employed, deuterium incorporation was 67% *versus* 80% in the case of **2**. In view of the relatively small differences, a fuller study with **1** was not undertaken.

The studies of silane deuteration reported by Carmona, and Nolan have featured expensive air-sensitive rhodium- or iridium-ligand complexes as catalysts.[9a,b,10] In our system, even if ruthenium can be considered as a cheaper metal, we are still faced with the sensitivity problem of **1** and **2**. The ability of the unelaborate salt $RuCl_3{\cdot}xH_2O$ to catalyze Si–H/D exchange was thus examined as a robust route for the deuteration of silanes. The reactions were carried out in the same manner as described when **1** and **2** were the catalysts. $RuCl_3{\cdot}xH_2O$ is not immediately soluble when mixed with Et_3SiH or $O(SiMe_2H)_2$ however, after stirring for *ca.* 10 min at 30 °C the black solid suspended in the colorless liquid became a dark brown solution for each silane. The deuterium incorporation percentages are presented in Table 3. It was possible to achieve high deuterium incorporation with $RuCl_3{\cdot}xH_2O$ as the catalyst for both Et_3SiH (Scheme 5) and $O(SiMe_2H)_2$. With 0.1 mol% catalyst loading, 90% of Et_3SiH (entry 1, Table 3) was deuterated and 93% of $O(SiMe_2H)_2$ (entry 3, Table 3). It is noteworthy that hydrolysis of the silanes was not observed in the presence of trace amounts of water bound to ruthenium. It might be possible to improve the deuterium incorporation values by extension of the reaction time. For the study reported by Carmona and co-workers for the deuteration of Et_3SiH, it was possible to achieve >99% deuterium incorporation with 0.01 mol% catalyst loading after 24 h at 50 °C.[9a]

Table 3. Deuteration of neat silanes with $MCl_3{\cdot}xH_2O$ (M = Ru, Rh, Ir) after 3.5 h at 30 °C.

Entry	Silane	Catalyst	mol%	D_{incorp} [%]
1	Et_3SiH	$RuCl_3{\cdot}xH_2O$	0.10	90
2	Et_3SiH	$RuCl_3{\cdot}xH_2O$	0.05	30
3	$O(SiMe_2H)_2$	$RuCl_3{\cdot}xH_2O$	0.10	93
4	$O(SiMe_2H)_2$	$RuCl_3{\cdot}xH_2O$	0.01	52
5	$O(SiMe_2H)_2$	$RuCl_3{\cdot}xH_2O+Hg$	0.10	73
6	Me_2ClSiH	$RuCl_3{\cdot}xH_2O$	0.10	23
7	Et_3SiH	$RhCl_3{\cdot}xH_2O$	0.1	6
8	$O(SiMe_2H)_2$	$RhCl_3{\cdot}xH_2O$	0.1	85
9	Et_3SiH	$IrCl_3{\cdot}xH_2O$	0.1	0
10	$O(SiMe_2H)_2$	$IrCl_3{\cdot}xH_2O$	0.1	91

The effect of added tricyclopentylphosphine on the catalytic reaction with Et_3SiH was investigated; it was thought that the phosphine might stabilize the catalytically active species. However, the presence of two equivalents of $PCyp_3$ in the reaction vessel appears to significantly hinder Si –H/D exchange, 2% deuterium incorporation was observed. Perhaps the phosphine competes with Si–H activation through coordination to ruthenium. The reaction with $O(SiMe_2H)_2$ was conducted in the presence of a drop of mercury as a test for the homogeneity of the process.[15] Deuterium incorporation in the presence of mercury was 73% (entry 5, Table 3) which does not discount the homogenous catalytic deuteration of $O(SiMe_2H)_2$ by $RuCl_3{\cdot}xH_2O$.

The ability of $RhCl_3{\cdot}xH_2O$ and $IrCl_3{\cdot}xH_2O$ to catalyze the deuteration of silanes was also investigated and compared to the high deuterium incorporation achieved with $RuCl_3{\cdot}xH_2O$. Even if the rhodium and iridium salts display similar activity for $O(SiMe_2H)_2$ (entries 8 and 10 *versus* 3) the results are considerably different in the case of Et_3SiH with only 6% of deuterium incorporation at rhodium and no exchange at all at iridium (entries 7 and 9, respectively, Table 3).

As for **1** and **2**, the MCl_3 series have a greater ability to catalyze Si–H/D exchange in $O(SiMe_2H)_2$ than Et_3SiH. It is possible that the presence of two Si–H bonds in $O(SiMe_2H)_2$ facilitates deuterium incorporation. The Karstedt's catalyst, $[\{Pt(\eta^2\text{-}(CH_2{=}CH\text{-}SiMe_2)_2O)\}_2\mu\text{-}(CH_2{=}CHSiMe_2)_2O]$, is industrially employed for hydrosilylation and features the coordination of vinylsiloxane to Pt.[16] Perhaps $O(SiMe_2H)_2$ is a ligand at the metal center when $MCl_3{\cdot}xH_2O$ is a catalyst for deuteration and stabilizes the catalytically active species. In the ruthenium case, it is noteworthy that η^2-coordination of $O(SiMe_2H)_2$ to ruthenium was demonstrated with $[RuH_2\{(\eta^2\text{-}HSiPh_2)_2O\}(PCy_3)_2]$ **3**, and thus $O(SiMe_2H)_2$ could also behave similarly with $RuCl_3{\cdot}xH_2O$. A mechanistic investigation is in progress to explore such a pathway.

Table 4. ^{1}H and ^{29}Si NMR (C_6D_6) and ^{2}H NMR (C_6H_6) and infrared spectroscopic (neat) data for selected silanes and the deuterated isotopomers [δ (ppm), J (Hz), ν (cm^{-1})].

Silane	^{1}H (^{2}H) NMR δ_{SiH} (δ_{SiD})	^{29}Si NMR δ_{Si}	$^1J_{Si,H}$ ($^1J_{Si,D}$)	ν_{SiH} (ν_{SiD})
Et_3SiH	4.00 (3.90)	0.13 (−0.38)	178 (27)	2100 (1530)
$HN(Me_2SiH)_2$	4.82 (4.82)[7]	−11.49 (−11.83)	194 (29)	2119 (1539)[7]
$O(SiMe_2H)_2$	5.06 (4.97)	−4.61 (−5.09)	204 (31)	2128 (1548)
$(EtO)_3SiH$	4.68 (4.57)	−59.12 (−57.04)	288 (36)	2196 (1603)
Me_2ClSiH	4.92 (4.78)	11.40 (11.12)	223 (34)	2169 (1575)

In conclusion, it has been possible to achieve the catalytic deuteration of silanes with several transition metal species. It was possible to achieve 99% deuterium incorporation in neat $O(SiMe_2H)_2$ with 0.05 mol% $[RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2]$. The same deuterium incorporation for $O(SiMe_2H)_2$ was also observed with 0.05 mol% $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ although the catalyst is less efficient at low loading. It is likely that longer reaction times for the deuteration experiments would enhance deuterium incorporation although optimization has not been studied. Extensive deuterium incorporation was also possible for Et_3SiH, 97% with 0.1 mol% $[RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2]$. The deuterated silanes $(EtO_3)SiD$ and Me_2ClSiD were also generated in >80% isolated yields with deuterium incorporations of >99% following the same method on a scale of several grams. The facile route to deuterosilanes developed in this study was exploited in the preparation of a deuterated silazane from Me_2ClSiD.

The simple hydrated salts $RuCl_3{\cdot}xH_2O$, $RhCl_3{\cdot}xH_2O$ and $IrCl_3{\cdot}xH_2O$ were also proficient deuteration catalysts for $O(SiMe_2H)_2$. With 0.1 mol% $MCl_3{\cdot}xH_2O$, *ca.* 90% deuterium incorporation was possible. In the case of Et_3SiH only the ruthenium salt is a good catalyst precursor (90% D incorporation at 0.1 mol% loading *versus* 6% and 0% in the Rh and Ir cases, respectively). These preliminary results suggest that the use of sensitive and rather sophisticated transition metal complexes for silane deuteration might not always be necessary as successful catalysis can also be achieved with $MCl_3{\cdot}xH_2O$ salts (M = Ru, Rh, Ir), particularly in the case of ruthenium, the cheapest metal of the series.

Experimental Section

General Procedure for the Deuteration of Triethylsilane, 1,1,3,3-Tetramethyldisilazane, 1,1,3,3-Tetramethyldisiloxane, Diisopropylchlorosilane, and Triethoxysilane

The hydridosilane was added to a C_6D_6 (5 mL) solution of $[RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2]$ in a Fischer–Porter vessel under an atmosphere of argon. (The amounts of substrate and catalyst are reported in the Supporting Information.) The reaction mixture was frozen at −50 °C and the argon removed by application of a vacuum for 20 s. The reaction mixture was allowed to melt and the Fischer–Porter vessel placed in a thermostatically controlled water bath at 30 °C. With the reaction mixture stirring vigorously at 1300 rpm, D_2 (1 bar over the atmospheric pressure) was applied and the stirring maintained. After 1 h, the reaction mixture was again frozen at −50 °C and the atmosphere inside the Fischer–Porter vessel evacuated. After melting, returning to 30 °C, and recommencing the stirring, the D_2 (1 bar over the atmospheric pressure) atmosphere was reapplied. The procedure of freezing, evacuating and reapplication of D_2 was twice repeated, after 1 h and then after a further 45 min. After a total time of 3.5 h, ^{1}H NMR spectroscopic analysis was employed to ascertain the incorporation of deuterium. ^{29}Si{^{1}H} NMR spectra were collected for characterization of the deuterated silane products (see Table 4).

The experiments catalyzed by $[RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2]$, $IrCl_3{\cdot}xH_2O$, $RhCl_3{\cdot}xH_2O$ and $RuCl_3{\cdot}xH_2O$, conducted in the absence of C_6D_6, were conducted in the same manner as outlined above although the silanes were frozen with N_2 (liquid).

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