

Using NMR and ESI-MS to Probe the Mechanism of Silane Dehydrocoupling Catalyzed by Wilkinson's Catalyst

Sarah M. Jackson,^[a] Danielle M. Chisholm,^[a] J. Scott McIndoe,^{*[a]} and Lisa Rosenberg^{*[a]}

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The reaction of Wilkinson's catalyst $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (**1**) with 1–2 equiv. of di-*n*-hexylsilane gives rise to a complex mixture of products, which has been analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR and shown to include the hydrido complex $\text{Rh}(\text{PPh}_3)_3\text{H}$ (**3**). Continuous sampling of the 1:1 reaction mixture by ESI-MS provided time-dependent speciation that tracks the formation of **3** at the expense of the initial silane oxidative addition prod-

uct $[\text{Rh}(\text{PPh}_3)_2(\text{Cl})(\text{H})\{\text{Si}(n\text{Hex})_2\text{H}\}]$ (**2**), the subsequent 1st order disappearance of **3**, and the formation of other, minor side-products. Our results provide insight into established activity of **1** for catalytic dehydrocoupling of di-*n*-hexylsilane, and implicate complex **3** as the active species in this catalysis.

The stoichiometric activation of Si–H bonds in tertiary silanes by Wilkinson's catalyst, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (**1**) was first reported in the late 1960s,^[1] and not long afterwards, the activity of this Rh^{I} phosphane chloride complex for the dehydrogenative coupling of secondary silanes to give di- and trisilanes was discovered.^[2] This initial communication, and most subsequent reports of the activity of rhodium complexes for silane dehydrocoupling,^[3] noted the propensity of the system to give competing redistribution of substituents at silicon, which fueled a debate on the nature of both the Si–Si bond-forming step and the apparent Si–C bond activation by late-metal complexes.^[4] Our previous examinations of this system demonstrated the high selectivity for coupling over redistribution reactions of diphenylsilane under conditions in which hydrogen is removed rapidly,^[5a] as well as the redistribution-free coupling of primary alkylsilanes to longer oligosilane chains,^[5b] and a survey of the relative activities of a series of related Rh^{I} bis(phosphane) catalyst precursors for the redistribution-free coupling of di-*n*-hexylsilane.^[5c] However, the actual mechanism of coupling mediated by this system is still not well understood. We present here NMR and electrospray ionization mass spectrometry (ESI-MS) analysis of the reaction of Wilkinson's catalyst with stoichiometric amounts of di-*n*-hexylsilane. These results shed light on the catalyst initiation step and point to a rhodium hydride complex as the active species in the coupling reaction. They also highlight the complementarity of these two analytical techniques and demonstrate highly resolved time-dependent speciation possible using ESI-MS.

We have carried out a number of NMR experiments to identify the Rh-containing products resulting from the addition of di-*n*-hexylsilane to **1**. Although the anticipated 1:1 oxidative addition product, $[\text{Rh}(\text{PPh}_3)_2(\text{Cl})(\text{H})\{\text{Si}(n\text{Hex})_2\text{H}\}]$ (**2**)^[5c] does form, it is unstable and rapidly decomposes to give a mixture of products. For example, when the 1:1 reaction of **1** and di-*n*-hexylsilane is carried out in $[\text{D}_6]$ -benzene in an NMR tube, monitoring by $^{31}\text{P}\{^1\text{H}\}$ NMR shows that signals due to **2** diminish (over ca. 1 h) relative to a very broad signal consistent with one or more species undergoing phosphane exchange, and the corresponding ^1H NMR spectra indicate the formation of several different hydride-containing species (see Supporting Information). More detailed NMR assignments have come from 1:1 or 1:2 reactions carried out in toluene, from which we have attempted to precipitate and isolate the Rh-containing products. These reactions consistently yield a bright yellow solid that, when dissolved in deuterated benzene or toluene, shows the presence of multiple species by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Figure 1 shows the variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR of one such solid, along with assignments that were confirmed by low-temperature $^{31}\text{P}\{^1\text{H}\}$ COSY and ^1H experiments. The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (lower trace) shows peaks due to **1**,^[6] **2**,^[5c] $[\text{Rh}(\text{PPh}_3)_3\text{H}]$ (**3**)^[7] and $[\text{Rh}(\text{PPh}_3)_3(\text{Cl})(\text{H})_2]$ (**4**)^[8] along with signals due to several other, unidentified products, including a broad signal almost lost in the baseline that corresponds to one or more species undergoing phosphane exchange. At 210 K (upper trace) the exchange is sufficiently slow to allow identification of $[\text{Rh}(\text{PPh}_3)_4\text{H}]$ (**5**),^[9,10] the PPh_3 adduct of **3**; and the peaks due to the inequivalent phosphanes in **3** and **4** are better resolved. This “snapshot” of the reaction mixture shows that the major Rh containing products are the hydrido complexes **3** and **5**, which are in equilibrium in the presence of excess PPh_3 .^[11] The obvious source of the hydride ligand in **3** and **5** is the silane: in

[a] Department of Chemistry, University of Victoria, P. O. Box 3065, Victoria, BC V8W3V6, Canada
Fax: +1-250-721-7147
E-mail: mcindoe@uvic.ca
lisarose@uvic.ca

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particular, **3** probably results from the reductive elimination of $(n\text{Hex})_2\text{Si}(\text{H})(\text{Cl})$ from **2**, along with re-association of the third phosphane ligand (Scheme 1, below).^[12] $^{29}\text{Si}\{^1\text{H}\}$ NMR of the supernatant from these reactions showed the product chlorosilane at $\delta = 14.1$ ppm, along with the disiloxane $\{(n\text{Hex})_2\text{SiH}\}_2\text{O}$ ($\delta = -1.6$ ppm),^[5c] a condensation product associated with hydrolysis of the Si–Cl bond in $(n\text{Hex})_2\text{Si}(\text{H})(\text{Cl})$, and a third species tentatively assigned as the corresponding disilanol $(n\text{Hex})_2\text{Si}(\text{OH})_2$ at $\delta = -6.9$ ppm.

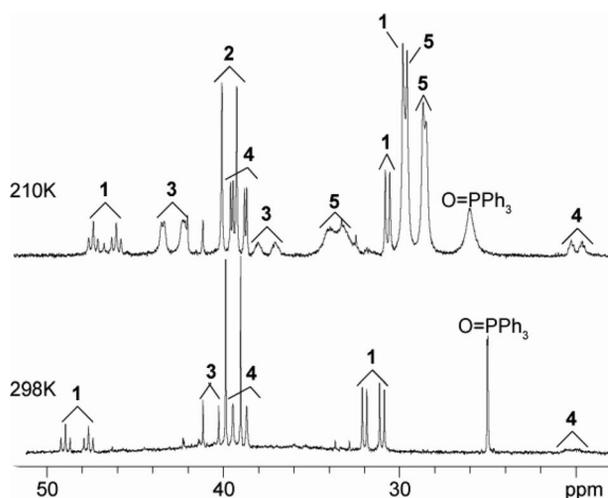
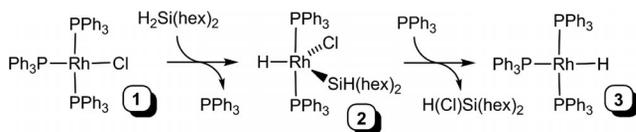


Figure 1. Variable temperature 145.8 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the yellow solid isolated from a 1:2 reaction of Wilkinson's catalyst with di-*n*-hexylsilane, in $[\text{D}_8]$ toluene. The lower trace is typical of the room temperature spectra obtained for solids isolated from either 1:1 or 1:2 reactions.



Scheme 1. Principal mode of decomposition of **2** following the oxidative addition of silane to **1**, based on NMR analysis.

The NMR spectra left us with a number of unanswered questions. In particular, we observed small peaks due to unidentified rhodium complexes. Also, we observed (apparently unreacted) **1** and its dihydrogen adduct **4**, which suggested that Si–Si bond formation (producing hydrogen) was occurring far more rapidly than the initial Si–H oxidative addition reaction, even though we had not detected any of the product disilane or trisilane by ^{29}Si NMR spectroscopy. We turned to ESI-MS to gain more information on the elemental composition of the species being formed in this reaction, both to confirm our NMR assignments and to shed light on the structures of the unidentified species. Catalytic reactions involving complexes with labile phosphane ligands can be monitored by ESI-MS^[13] by the simple expedient of doping in a charged phosphane ligand: we previously demonstrated the validity of this ESI-MS approach in the study of olefin hydrogenation catalyzed by **1**, for which we were able to spot simultaneously intermediates, catalyst resting states, off-cycle species and catalyst poi-

sons.^[14] Here we extend this approach to tracking the dynamics of the solution reaction of **1** with di-*n*-hexylsilane, by monitoring the stoichiometric reaction continuously over a period of 48 minutes. The cationic dopant ligand used was $[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2(\text{CH}_2\text{Ph})]^+\text{BF}_4^-$ (**6**). A typical spectrum of a mixture of **1** + 30% **6** + $(n\text{Hex})_2\text{SiH}_2$ appears in Figure 2.

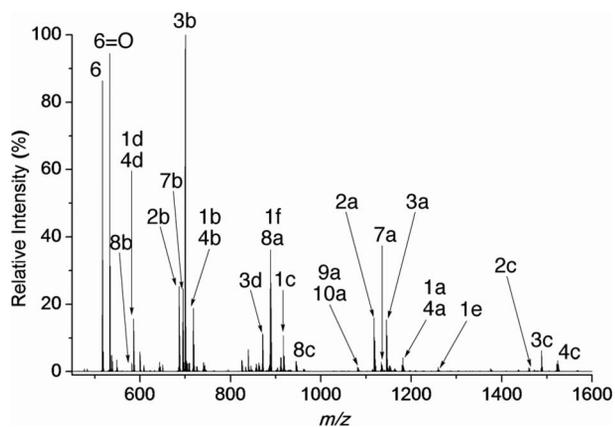


Figure 2. Positive-ion ESI-MS of $\text{Rh}(\text{PPh}_3)_3\text{Cl} + 0.36 \mathbf{6} + (n\text{Hex})_2\text{SiH}_2$ in fluorobenzene, obtained at $t =$ five min.

The apparent complexity of the spectrum is made tractable by the fact that essentially the same species is represented by more than one ion. Wilkinson's catalyst itself, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (**1**), is represented by the ions $[\text{Rh}(\text{PPh}_3)_2\text{Cl}(\mathbf{6})]^+$ (1179.2 m/z , **1a**), $[\text{Rh}(\text{PPh}_3)\text{Cl}(\mathbf{6})_2]^{2+}$ (717.2 m/z , **1b**), $[\text{Rh}(\text{PPh}_3)\text{Cl}(\mathbf{6})]^+$ (917.2 m/z , **1c**), $[\text{RhCl}(\mathbf{6})_2]^{2+}$ (586.2 m/z , **1d**) and even $[\text{RhCl}(\mathbf{6})_2(\text{BF}_4)]^+$ (1260.3 m/z , **1e**), $[\text{RhCl}(\mathbf{6})_3 + \text{BF}_4]^{2+}$ (888.8 m/z , **1f**) and $[\text{Rh}(\mathbf{6})_3 + 2(\text{BF}_4)]^+$ (1865.6 m/z , **1g**).^[15] By combining these species together as a single entity "Rh(PR₃)₃Cl" and repeating for all similarly-duplicated ions, a seeming forest of peaks is rendered down to 10 chemically distinct compounds. The identities of each can be established by a combination of m/z value, isotope pattern and product ion MS/MS (see Supporting Information). Key species observed by ESI-MS that were also observed by NMR include: $\text{Rh}(\text{PR}_3)_3\text{Cl}$ (**1**), $[\text{Rh}(\text{PR}_3)_2(\text{Cl})(\text{H})\{\text{Si}(n\text{Hex})_2\text{H}\}]$ (**2**), $\text{Rh}(\text{PR}_3)_3\text{H}$ (**3**), and $\text{Rh}(\text{PPh}_3)_3(\text{Cl})(\text{H})_2$ (**4**), along with PR_3 , and $\text{O}=\text{PR}_3$. We did not observe peaks due to $\text{Rh}(\text{PR}_3)_3\text{H}$ (**5**), even when this compound was prepared and analyzed individually by ESI-MS under identical conditions: this complex loses PPh_3 even in extremely soft ionization conditions to show only peaks due to **3**. The complex is similarly labile in solutions studied by NMR, as evidenced by the phosphane exchange occurring on the NMR timescale, but evidently the equilibrium between (**3** + PPh_3) and **5** lies toward **5** at NMR concentrations. Species observed by ESI-MS that had *not* previously been identified by NMR include $[\text{Rh}(\text{PR}_3)_2(\text{Cl})(\text{H})\{\text{Si}(n\text{Hex})_2(\text{OH})\}]$ (**7**), $[\text{Rh}(\text{PR}_3)_3]^+$ (**8**), $[\text{Rh}(\text{PR}_3)_2\{\text{Si}(n\text{Hex})_2\text{H}\}]$ (**9**), and $[\text{Rh}(\text{PR}_3)_2(\text{H})_2\{\text{Si}(n\text{Hex})_2\text{H}\}]$ (**10**).

As shown in Figure 3 for the six most abundant compounds, tracking the evolution of each species over time generates a revealing reaction profile.^[16] Similar to what was observed by NMR, the Si–H oxidative addition prod-

uct $[\text{Rh}(\text{PR}_3)_2(\text{Cl})(\text{H})\{\text{Si}(n\text{Hex})_2\text{H}\}]$ (**2**) is 25% abundant initially but decays to 0% after 20 min. $\text{Rh}(\text{PR}_3)_3\text{H}$ (**3**) grows in rapidly at the start of the reaction at the expense of **2** to peak at 27%, then decays away following first order kinetics ($t_{1/2} = 8.8$ min, see inset in Figure 3). This behaviour is consistent with the production of **3** directly from **2**, by reductive elimination of $(n\text{Hex})_2\text{Si}(\text{H})(\text{Cl})$, followed by the consumption of **3** in some slower reaction step. $\text{Rh}(\text{PR}_3)_3\text{Cl}$ (**1**) drops from 13% to 5% after 5 minutes, then slowly grows back in over the next 40 minutes to about 8%. This unexpected re-emergence of **1** is mimicked almost perfectly by $\text{Rh}(\text{PPh}_3)_3(\text{Cl})(\text{H})_2$ (**4**) and $[\text{Rh}(\text{PR}_3)_2(\text{Cl})(\text{H})\{\text{Si}(n\text{Hex})_2(\text{OH})\}]$ (**7**), though with different starting values (4% and 0%, respectively). Qualitatively, the analogous slopes of these traces suggest that increasing concentrations of **1**, **4** and **7** derive from a common reaction step. A straightforward explanation is that the chlorosilane $(n\text{Hex})_2\text{Si}(\text{H})(\text{Cl})$ is slowly being hydrolysed by trace water to produce HCl and $(n\text{Hex})_2\text{Si}(\text{H})(\text{OH})$. The reaction of **3** with HCl would generate complex **4**, which could then reductively eliminate H_2 to give **1**. Observation of complex **7**, resulting from the oxidative addition of $(n\text{Hex})_2\text{Si}(\text{H})(\text{OH})$ to **1**, represents the first evidence we have obtained for the interaction of rhodium in this system with silane hydrolysis products, despite the fact that the disiloxane $\{(n\text{Hex})_2\text{SiH}\}_2\text{O}$ was prepared from the reaction of $(n\text{Hex})_2\text{SiH}_2$ with H_2O in the presence of **1**.^[5c,17]

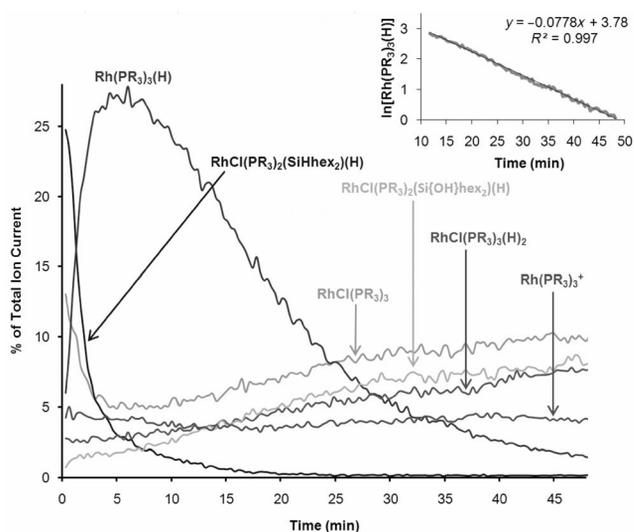
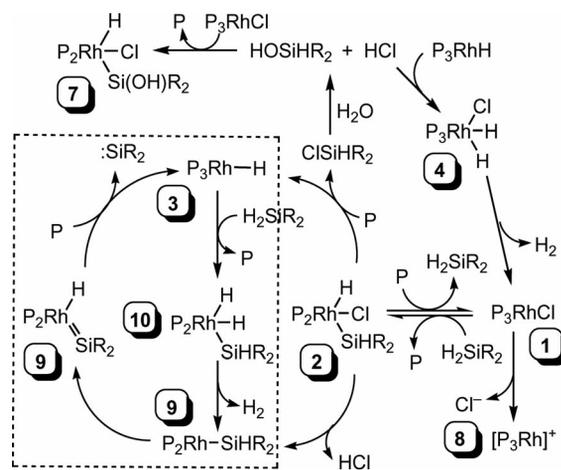


Figure 3. Reaction profile showing the evolution of the six most abundant Rh-containing species observed over time by ESI-MS. Each trace is generated by summing the intensities of all related entities and normalizing to the total ion current. Inset: $\ln[\text{Rh}(\text{PR}_3)_3(\text{H})]$ vs. time for the decay of this species, demonstrating first-order behavior.

Scheme 2 presents a series of reactions that rationalize the intermediates we see both by NMR and by MS, and that correlate well with the time-dependent speciation we have been able to observe by ESI-MS. The cation **8** is a prominent peak in all the mass spectra collected, although its intensity relative to the total ion current changes little over time (see Figure 3), suggesting that it does not partici-

pate in the overall reaction with silane.^[18] The relative abundance of complexes **9** and **10** (not shown in Figure 3) is low throughout ($\leq 1\%$, see Supporting Information), but these Si-containing species are relevant: **9** represents the loss of HCl , as opposed to $(n\text{Hex})_2\text{Si}(\text{H})(\text{Cl})$, from complex **2**, or the loss of H_2 from **10**, while **10** would result from the addition of silane to complex **3**. Also, preliminary ESI-MS data collected for a mixture of independently synthesized **3** and the silane show compounds **9** and **10** in low abundance. Highlighted in the dotted box in Scheme 2 is a proposed catalytic cycle for silane dehydrocoupling that relies on the formation and loss of a silylene ligand. There is literature precedent for the α -elimination reaction at Rh-silyl complexes such as **9** to generate reactive silylene intermediates (**9'**, for instance),^[3c,19] and these have long been postulated as key intermediates in these Rh-catalyzed coupling reactions.^[2] Some evidence for α -elimination chemistry in this system comes from MS/MS experiments on **2**, which show the loss of H_2 (see Supporting Information). However, it is certainly possible to replace this portion of the cycle with the oxidative addition of silane to **9**, followed by reductive elimination of a Si-Si bond.^[20]



Scheme 2. Reactions illustrating the activation of $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (**1**) by dialkylsilane, the possible silane dehydrocoupling activity of the resulting rhodium hydride complex **3**, and the competing decomposition resulting from the action of trace water in the reaction mixture.

In conclusion, we have obtained new insight into the early time regime of the reaction of Wilkinson's catalyst with a dialkylsilane, using time-averaged structural information from NMR and fast sampling and rapid data collection by ESI-MS. These results demonstrate the sensitivity of this late metal halide catalyst system to steady, indirect degradation by trace water,^[21] and the probable importance of rhodium hydride intermediates in the dehydrocoupling reaction. In keeping with this latter result, we find that the hydride complexes **3** and **5** do indeed catalyze the dehydrocoupling of di-*n*-hexylsilane, with activities comparable to and higher than **1** (see Supporting Information). Currently we are extending these studies to the examination and correlation of NMR and ESI-MS data for actual cata-

lytic mixtures, and we will report on this work in due course.

Experimental Section

NMR analysis of the stoichiometric reaction of **1** with silane: (a) To solid complex **1** (0.026 g, 0.028 mmol) in an NMR tube was added di-*n*-hexylsilane as a standard solution (20 mg/mL) in [D₆]benzene (0.3 mL, 0.006 g, 0.03 mmol). Another 0.2 mL of [D₆]benzene was added, and the tube was capped and sealed with parafilm. The solid **1** took about 15 min to completely dissolve, giving a light orange solution. (b) Complex **1** (101 mg, 0.109 mmol) was dissolved in toluene (18 mL). Di-*n*-hexylsilane (0.050 g, 0.249 mmol) in toluene was added, and the solution was stirred for 1 h (solid red complex took ca. 5 min to dissolve completely, giving a clear, light orange-yellow solution). The toluene was removed under vacuum, leaving a yellow residue. The addition of pentane (10 mL) gave a suspension of a fine yellow powder and a yellow supernatant solution. The yellow solid was isolated by cannula filtration, dried under vacuum, and 19 mg were used to prepare a sealed NMR sample in [D₈]toluene.

ESI-MS analysis of the stoichiometric reaction of **1** with silane: All mass spectrometric analyses were performed on a Micromass QToF *micro* hybrid quadrupole/time-of-flight mass spectrometer in positive ion mode using pneumatically-assisted electrospray ionization with a cone voltage of 10 V, capillary voltage of 3100 V, source temperature of 120 °C and desolvation temperature of 150 °C. Solutions were run in fluorobenzene and introduced to the mass spectrometer by a syringe pump at a rate of 10 μL min⁻¹. ESI-MS spectra of the catalyst mixture were obtained by adding to 12 mL of fluorobenzene RhCl(PPh₃)₃ (11 mg, 0.012 mmol, 0.96 mmol L⁻¹) and [6]⁺BF₄⁻ (2 mg, 0.003 mmol, 0.28 mmol L⁻¹) to give a bright orange solution. To this solution was added (*n*Hex)₂SiH₂ (2 mg, 0.012 mmol) to give a bright yellow solution within seconds.

Supporting Information (see also the footnote on the first page of this article): additional NMR and ESI-MS data, experimental details for dehydrocoupling catalysed by **1**, **3**, and **5**.

Acknowledgments

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[10] Orange crystals of **5** were obtained independently via slow evaporation from a [D₆]benzene solution of the yellow solid isolated from a 1:1 reaction of **1** with di-*n*-hexylsilane, as determined by comparison of X-ray crystallographic data with that previously reported; a) R. McDonald, personal communication; b) R. W. Baker, P. Pauling, *J. Chem. Soc. C* **1969**, 1495.
[11] The free PPh₃ results from the initial oxidative addition reaction generating the bis(phosphane) complex **2** from the tris(phosphane) complex **1**. We presume the mass balance between residual **2** and complex **5** is skewed in Figure 1 because of the selective precipitation used to obtain the sample: either PPh₃ and/or complex **5** is less soluble than complex **2**.
[12] Precedent for the transformation of Rh^I phosphane chloride complexes into rhodium hydride complexes in the presence of hydrosilane reagents includes ref.^[8a,8b] and a) K. Osakada, *J. Organomet. Chem.* **2000**, 611, 323.
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[15] The bis(phosphane) ions **1c–e** are included in the speciation of “P₂RhCl” because previous studies (ref.^[14]) showed them to result directly from **1** as a consequence of the cone voltage required to obtain acceptable spectra of the solution.
[16] The first 30 seconds or so of reactivity is lost because it takes approximately that long to mix the reactants, transfer to a gas-tight syringe and inject into the mass spectrometer.
[17] Neither di-*n*-hexylsilane, nor the di- and trisilanes resulting from its homodehydrocoupling reactions, react with water in the absence of Rh.
[18] Loss of halide ligands to generate such ions is commonly observed in ESI-MS of metal halide complexes. See, for example: a) A. O. Aliprantis, J. W. Canary, *J. Am. Chem. Soc.* **1994**, 116, 6985; b) C. Decker, W. Henderson, B. K. Nicholson, *J. Chem. Soc., Dalton Trans.* **1999**, 3507; c) W. Henderson, C. Evans, *Inorg. Chim. Acta* **1999**, 294, 183; d) C. Vicent, M. Viciano, E. Mas-Marza, M. Sanau, E. Peris, *Organometallics* **2006**, 25, 3713; e) L. S. Santos, G. B. Rosso, R. A. Pilli, M. N. Eberlin, *J. Org. Chem.* **2007**, 72, 5809.
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[20] If the catalytic cycle relies on reductive elimination of disilane from a bis(silyl) complex, the fact that we do not observe a Rh(Si)₂ species by MS suggests that this elimination step is not rate-determining.
[21] Preliminary ESI-MS data for the mixture of complex **3** with silane do not show any O-containing Rh complexes similar to complex **7**.

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