



Title	Rhodium carbene complexes as versatile catalyst precursors for Si–H bond activation
Authors(s)	Krüger, Anneke, Albrecht, Martin
Publication date	2012-01-09
Publication information	Krüger, Anneke, and Martin Albrecht. "Rhodium Carbene Complexes as Versatile Catalyst Precursors for Si–H Bond Activation." Wiley-VCH, January 9, 2012. https://doi.org/10.1002/chem.201102197 .
Publisher	Wiley-VCH
Item record/more information	http://hdl.handle.net/10197/3649
Publisher's statement	This is the author's version of the following article: Krüger, Anneke; Albrecht, Martin (2012) "Rhodium Carbene Complexes as Versatile Catalyst Precursors for Si–H Bond Activation". Chemistry - A European Journal: Volume 18, Issue 2, pages 652–658, which has been published in final form at http://dx.doi.org/10.1002/chem.201102197
Publisher's version (DOI)	10.1002/chem.201102197

Downloaded 2026-05-01 23:45:10

The UCD community has made this article openly available. Please share how this access benefits you. Your story matters! (@ucd_oa)



© Some rights reserved. For more information

Rhodium Carbene Complexes as Versatile Catalyst Precursors for Si–H Bond Activation

Anneke Krüger and Martin Albrecht*

Abstract: Rhodium(III) complexes comprising monoanionic *C,C,C*-tridentate dicarbene ligands activate Si–H bonds and catalyse the hydrolysis of hydrosilanes to form silanols and siloxanes with concomitant release of H₂. In dry MeNO₂, selective formation of siloxanes takes place, while changing conditions to wet THF produces silanols exclusively.

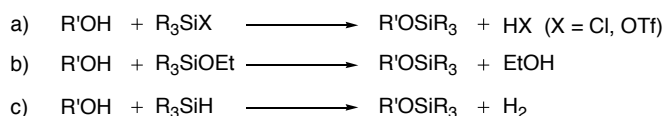
Silylethers are formed when ROH is used as substrate, thus providing a mild route towards the protection of alcohols with H₂ as the only by-product. With alkynes, comparably fast hydrosilylation takes place, while carbonyl groups are unaffected. Further expansion of the Si–H bond activation to dihydrosilanes afforded siloxanes and polysilylethers. Mechanistic

investigations using deuterated silane revealed deuterium incorporation into the abnormal carbene ligand and hence suggests a ligand-assisted mechanism involving heterolytic Si–H bond cleavage.

Keywords: rhodium · silane activation · siloxanes · mesoionic complexes · ligand cooperativity

Introduction

The silicon-oxygen linkage is a useful synthon that has found widespread application in silicon-based polymers (*e.g.* in silicones)^[1] and in organic synthesis (*e.g.* as silyl ethers).^[2] Formation of the Si–O bond has been well established and classical synthetic routes use either silyl chlorides, silyl triflates (OTf), or alkoxysilanes as starting materials (Scheme 1a and 1b).^[3] Common to all these routes is the high reactivity of the precursor, requiring rigidly anhydrous conditions. In addition the formed HCl or HOTf has to be scavenged by a base, thus inevitably producing stoichiometric amounts of an undesired salt. The catalytic activation of air-stable and moisture-insensitive hydrosilanes *via* Si–H bond cleavage offers an attractive method to circumvent the use of sensitive presursors and to perform the reaction with high atom economy (Scheme 1c).



Scheme 1. Generic methods for the formation of siloxanes.

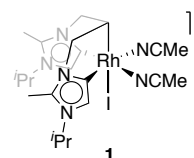


Figure 1. Dicarbene rhodium(III) complex **1**, comprising a facially coordinating formally monoanionic ligand that is isolobal to Cp-type ligands.

Results and Discussion

Silanol vs siloxane formation. The activity of complex **1** in Si–H bond activation was probed by using PhMe₂SiH as a model

[*] A. Krüger, Prof. Dr. M. Albrecht
School of Chemistry & Chemical Biology
University College Dublin
Belfield, Dublin 4, Ireland
Fax: (+)353 1716 2501
E-mail: martin.albrecht@ucd.ie

substrate. Initial runs in MeNO₂ revealed mixtures of silanol and siloxane,^[12] and concomitant formation of H₂, indicated by the evolution of gas. Dihydrogen generation was confirmed by catalytic runs in deuterated CD₃NO₂ and subsequent ¹H NMR spectroscopic analysis, which revealed a diagnostic singlet at δ_H 4.53. Table 1 summarises the results obtained in the oxidation of dimethylphenylsilane catalysed by complex 1.

Table 1. Hydrolytic oxidation of dimethylphenylsilane to siloxane and silanol.^[a]

$\text{PhMe}_2\text{Si-H} + \text{H}_2\text{O} \xrightarrow[\text{solvent}]{\text{cat 1}} \text{PhMe}_2\text{Si-O-SiMe}_2\text{Ph} + \text{PhMe}_2\text{Si-OH}$						
entry	solvent	H ₂ O ^[b] /mmol	T /°C	time /h	conversion /%	siloxane:silanol
1 ^[c]	MeNO ₂	---	103	2	0	----
2	MeNO ₂	---	103	0.5 / 2	88/>99	>99:1/>99:1
3 ^[d]	MeNO ₂	---	103	2 / 27	1/79	>99:1/>99:1
4	MeNO ₂	---	80	2 / 5	29/>99	88:12/68:32
5	MeNO ₂	6.4	103	0.5 / 1	95/98	8:92/10:90
6	MeNO ₂	6.4	25	2 / 24	31/>99	6:94/12:88
7	MeCN	2.0	80	2 / 16	50/>99	12:88/13:87
8	MeCN	2.0	25	2 / 24	37/>99	3:97/2:98
9	THF	2.0	65	0.5 / 2	24/97	<1:99/<1:99
10	THF	---	65	0.5 / 5	3/38	17:83/84:16

[a] Conditions unless otherwise stated: silane (1.0 mmol) and catalyst (1 mol%) in the corresponding solvent (5 mL) using mesitylene as internal standard; product mixtures analysed by GC-MS. [b] extraneous water. [c] Control experiment without the addition of catalyst. [d] 0.1 mol% catalyst used.

When using essentially dry MeNO₂ at reflux temperature, full conversion of the hydrosilane selectively to the corresponding siloxane PhMe₂Si-O-SiPhMe₂ was reached within 2 h (entry 2).^[13] Reducing the catalyst loading from 1 mol% to 0.1 mol% decreased the reaction rate significantly (79% after >24 h), even though the selectivity remained high (entry 3). The reaction temperature affected both the reaction rate and the selectivity. At 80 °C, only 29% conversion was reached after 2 h (entry 4, cf full conversion at reflux) and 5 h were required to achieve complete silane oxidation. In addition, the selectivity dropped markedly, yielding a 2:1 ratio of siloxane and silanol. In an attempt to promote silanol formation, the water content in the solvent was increased. Upon addition of extraneous H₂O (~6 mmol), Si-OH bond formation was dominant, though not exclusive (entry 5). Moreover, faster reaction rates were observed, leading to full conversion within 1 h. Upon lowering the temperature to RT, again a loss of activity was observed though the siloxane/silanol ratio did not change significantly compared to the high temperature reaction (entry 6), suggesting that the quantities of water affect the selectivity substantially stronger than the reaction temperature. Higher ratios of silanol were obtained upon changing the solvent. In wet MeCN, silanol formation was largely dominant (87:13 and 98:2 ratio, entries 7 and 8), though prolonged reaction times were required. When using wet THF, full conversion exclusively towards the silanol product was observed within 2 h (entry 9). In the absence of extraneous H₂O, both the rate of the reaction and the selectivity dropped (entry 10). While initially, silanol is preferentially produced under these conditions, the siloxane is the predominant product at elevated conversion. Hence, the catalytic oxidation of silanes can be effectively switched by changing the solvent between dry MeNO₂ and wet THF, affording either pure siloxane or the silanol product exclusively,^[14] without derogating reaction rates.

Time-dependent monitoring of the reaction (Fig. 2) did not reveal any induction period and the kinetic reaction profile was fully

reproducible, which is indicative of homogeneous catalysis. In support of this notion, catalyst recycling was demonstrated by repetitive addition of a second and third equivalent of substrate after 20 and 45 minutes, respectively, *i.e.* at time intervals where conversions were not yet complete. This cumulative run reached 67% overall conversion 20 min after addition of the last batch and 85% overall conversion (255 TON) after 2.5 h, demonstrating the living nature of the catalytically active species.

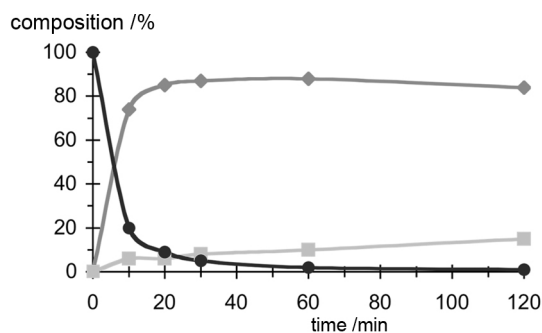


Figure 2. Reaction profile for the formation of siloxane and silanol in wet MeNO₂: ■ silanol, ◆ siloxane, ● silane (for conditions, see Table 1, entry 5); prolonged reaction times induce a gradual and partially catalysed transformation of silanol to siloxane.^[14]

Role of the catalyst. The activity of a series of related and previously described^[11,15] carbene rhodium(III) complexes 2–6 was evaluated in order to identify factors that may critically influence the catalytic performance (Fig. 3). Under standard conditions (dry MeNO₂ at reflux temperature), the related tridentate dicarbene complexes 2 and 3 comprising one or two normally bound carbene ligands, respectively, also catalysed siloxane formation with high selectivity (Table 2, entries 2 and 3). The activity of 2 was significantly lower and long reaction times were required to reach full conversion. With complex 3 containing two normally bound carbenes, rates were higher though not as high as with 1, reaching 84% conversion after 2 h. In contrast, the normal dicarbene complex 4 was essentially inactive in the same time period (entry 4). Lower activity of complex 4 may be due to the absence of a Rh-C_{alkyl} bond as potential site for 1,2-addition of the polarised Si-H substrate.^[16] Alternatively, acetate displacement in 4 may be more demanding than MeCN substitution in 1 or 3, thus hampering the activation of the catalyst precursor. The former hypothesis was probed by using complexes 5 and 6 as catalyst precursors. These complexes comprise a rigidly bidentate bonding dicarbene ligand with a methylene group rather than a trimethylene linker between the heterocycles, thus preventing ligand C-H bond activation and the formation of a Rh-C_{alkyl} bond. When employing complex 5 featuring an abnormally bound dicarbene ligand, only slightly lower performance was observed as compared to the tridentate analogue 1 (entry 5). Complex 6 comprising two normally bound carbene ligands was nearly as effective as the abnormal congener and slightly more active than the tridentate complex 3, which also contains two normally bound carbene ligands (entry 6). Apparently, the presence of a Rh-C_{alkyl} unit is not essential for Si-H bond activation and ensuing catalytic activity. Direct mechanistic conclusions are difficult to draw from this catalyst evaluation, for example because complexes 3 and 6 differ both in the formal charge at the rhodium centre as well as in the number of weakly bound solvent ligands. However, the abnormal carbene bonding mode consistently induces higher catalytic activity and better selectivity than the normal mode and the best performance was achieved with

complex **1** as catalyst precursor. Catalytic runs in the presence of PPh₃ (10 molequiv.) gave slightly lower conversions (entry 7), though the reaction solution remained clear even when all substrate was consumed. In the absence of phosphine, formation of a dark residue was observed unless further substrate was added. The hydrolytic oxidation is not affected by the presence of mercury(0).^[17] Addition of 0.5 mL (ca. 3000 molequiv) Hg⁰ to the reaction solution after 10 min (42% conversion) did not stop the reaction (entry 8), even though an instant decomposition reaction was observed, presumably due to partial rhodium(III) reduction in the presence of elemental mercury, H₂ and HSiR₃. Of note, Rh/C was significantly less active and less selective (entry 9). The combination of these results,^[18] *i.e.* reproducible kinetics, absence of induction time, insensitivity to Hg⁰, stabilisation by PPh₃, and the isolation of the rhodium complex after catalytic conversion (see below) all lend strong support to a homogeneously catalyzed process.

Table 2. Hydrolytic oxidation of dimethylphenylsilane to siloxane and silanol.^[a]

entry	Rh catalyst	time /h	conversion /%	siloxane:silanol
1	1	0.5/2	88/>99	>99:1
2	2	2/22	49/96	>99:1
3	3	0.5/2	72/84	91:9/>99:1
4	4	2/22	3/70	>99:1
5	5	0.5/2	78/96	>99:1
6	6	0.5/2	73/92	91:9/>99:1
7	1 + PPh ₃	2	82	>99:1
8	1 + Hg ⁰	2	89	>99:1
9	Rh/C ^[b]	2	41	72:28

[a] General conditions: Me₂PhSiH (1.0 mmol) and rhodium complex (1 mol%) in MeNO₂ (5 mL) at reflux using mesitylene as internal standard; conversion and selectivity determined by GC-MS. [b] 21 mg of 5% Rh on C.

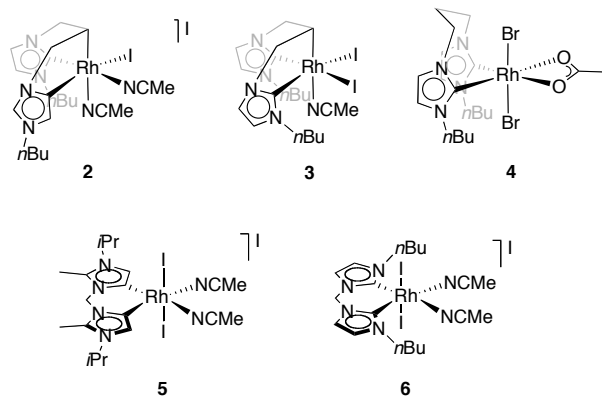
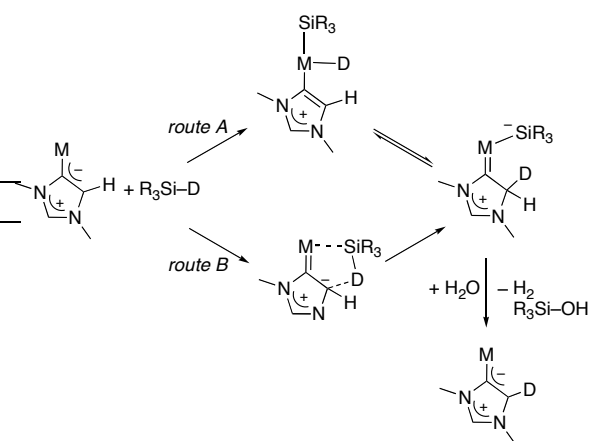


Figure 3. Catalysts employed in the hydrolytic oxidation of silanes.

Further mechanistic insights into the rhodium-mediated Si–H bond activation was obtained from experiments using the monodeuterated silane Et₃Si–D as substrate. Upon reaction with complex **1** in the presence of small quantities of H₂O, deuterium exchange into the heterocyclic C5-position of the carbene ligand was observed. The absence of a resonance in the ¹H NMR spectroscopy at δ 7.4 and the appearance of a signal in the ²H NMR spectrum exclusively at this frequency confirmed the selective and complete deuteration of the positions adjacent to the rhodium-bound carbon. This observation suggests a ligand-assisted Si–D bond cleavage process and does not support an outer sphere mechanism involving nucleophilic attack of H₂O at a Si–D σ-complex.^[19] Instead, oxidative addition of the hydrosilane to the metal centre to form a (silyl)(hydride)rhodium(V) complex may occur,^[20]

presumably facilitated by the high electron donor ability of the abnormal carbene ligands (route A, Scheme 2).^[21] Subsequent tautomerisation of the rhodium hydride to a carbene isomer would induce a sp²-to-sp³ rehybridisation of the heterocyclic C5 carbon. Alternatively, this carbene intermediate may be accessible via direct heterolytic bond cleavage of the Si–D bond in a ligand assisted process across the metalla-allyl fragment in a formally isohypsic process (route B). Hydrolysis then produces the silanol and H₂ (or HD). Both routes imply the active participation of the carbene ligand as suggested earlier for water oxidation and the reaction of abnormal carbene complexes with H⁺.^[15a,22]

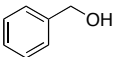
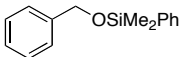
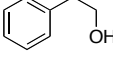
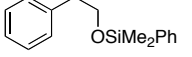
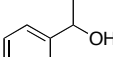
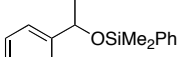
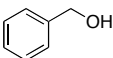
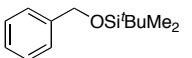
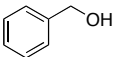
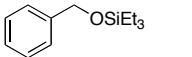
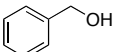
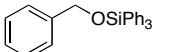


Scheme 2. Suggested pathway for deuterium incorporation into the NHC ligand involving either oxidative addition (route A) or ligand-assisted direct Si–D bond cleavage (route B).

Silylether formation via silane alcoholysis. Reaction of PhMe₂SiH in the presence of ROH instead of extraneous H₂O cleanly afforded the corresponding silylether (Table 3).^[23] Hence, this rhodium-mediated Si–H bond activation constitutes an alternative route to silyl-protected alcohols,^[24,25] avoiding the use of moisture-sensitive R₃SiCl or R₃SiOTf as typically employed for alcohol protection.^[26] The reaction does not require any sacrificial acid or base, as H₂ is the only formed side product. In order to probe the potential of this method, a series of different alcohols and hydrosilanes were evaluated for silylether formation.

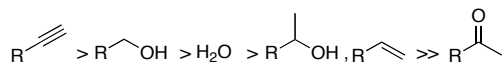
When using one equivalent of dimethylphenylsilane, primary alcohols such as benzylalcohol and 2-phenylethanol were readily silylated and after 4 hours about 85% conversion to the corresponding silylether was reached (entries 1, 2). Secondary alcohols were converted much slower (entries 3, 4) and competitive reaction with residual H₂O was deduced from the substantial amounts of siloxane and silanol detected after 4 h (GC-MS). Variation of the silane from PhMe₂SiH to *t*BuMe₂SiH gave better yields and quantitative silylether formation was achieved within 4 h (entry 5). This method thus represents an attractive substitute to the standard procedure (DMF, imidazole)^[26] for introducing the *tert*-butyldimethylsilyl (TBDMS) protecting group on primary alcohols. The acid- and base-free conditions are particularly useful for highly complex and pH-sensitive substrates. Of note, larger silyl groups are less reactive and the (triethyl)silylethers were obtained only in moderate yields (entry 6), perhaps due to sterically disfavoured nucleophilic attack at the rhodium-bound silicon centre (*cf* Si–D activation, *vide supra*).

Table 3. Protection of primary and secondary alcohols using dimethylphenylsilane.^[a]

entry	alcohol	silane	product	time /h	yield /%
1		H-SiMe ₂ Ph		1 4	59 85
2 ^[b]		H-SiMe ₂ Ph		1 3	72 83
3		H-SiMe ₂ Ph		1 3	34 66
4	^t PrOH	H-SiMe ₂ Ph	^t PrOSiMe ₂ Ph	1	37
5		H-Si ^t BuMe ₂		1 4	66 >99
6		H-SiEt ₃		1 3	17 28
7		H-SiPh ₃		1	63

[a] Conditions unless otherwise stated: silane (1.0 mmol), alcohol (1.0 mmol) and **1** (1 mol%) in MeNO₂ (5 mL) at reflux; product yield and selectivity determined by GC-MS or ¹H NMR. [b] 1.5 mmol of Me₂PhSiH used.


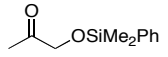

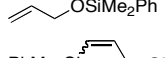

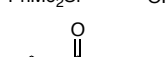

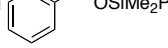
Hydrosilylation. The catalytic activity of complex **1** in Si-H bond activation was further investigated in the presence of other functional groups, in particular because of the recent success of N-heterocyclic carbene rhodium complexes as catalyst precursors in hydrosilylation reactions.^[27] Under reaction conditions as described for entry 2 (Table 1) phenylacetylene was fully hydrosilylated within 30 minutes. No siloxane and only trace amounts of silanol (<1%) were observed. Styrene hydrosilylation was considerably slower (24% after 2 h) and most hydrosilane was converted to siloxane due to competitive reaction with residual H₂O. Under the same reaction conditions no reactivity was observed towards acetophenone and siloxane was the predominant product (80% conversion after 2 h). The slightly lower rate of siloxane formation as compared to runs in the absence of ketone (*cf.* >99% conversion, entry 2, Table 1) may be attributed to the coordinating ability of acetophenone to the metal centre. No olefin or ketone reduction due to the generated H₂ was detected,^[28] which is in agreement with the previously observed low reactivity of complex **1** in hydrogenation reactions.^[11] These results together with those from alcohol silylation provide the following reactivity preference of hydrosilanes when catalysed by complex **1**:



This trend suggests the possibility to carry out selective silylations. In order to verify this hypothesis, substrates with different functional groups were reacted in the presence of stoichiometric quantities of hydrosilane and catalytic amounts of complex **1**. Substrates containing a primary alcohol and a carbonyl function gave silyl ethers selectively and did not affect the ketone moiety (Table 4, entry 1). When using an olefin-substituted alcohol such as allyl alcohol, the selectivity was slightly lower and additional hydrosilylation of the C=C double bond was observed, affording C,O-disilylated propanol as a minor side product (entry 2). In contrast, propargylic alcohol underwent selective hydrosilylation, while silyl ether formation was completely suppressed (entry 3). Benzoic acid was only poorly silylated and siloxane and silanol formation was predominant, indicating that carboxylic acids are substantially less suitable than H₂O for silan oxidation using

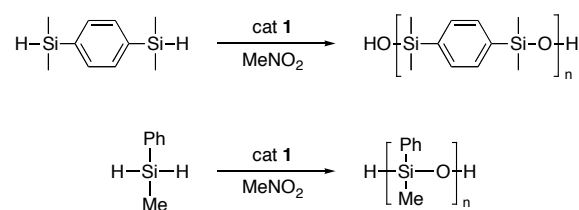
complex **1** (entry 4). Accordingly, complex **1** represents a rare^[29] catalyst precursor that allows alcohols to be selectively silylated in the presence of carbonyl groups and C=C double bonds.^[30] With functionalised alkynes, however, exclusive hydrosilylation without affecting the hydroxy-functionality was noted.^[31]

Table 4. Silylation of functionalised substrates.^[a]

entry	substrate	silylation product	time /h	yield /%	silanol, siloxane /%
1			1 2	48 57	20, 13 23, 18
2			1	75+12 ^[b]	<1, 7
3			1	100	<1, <1
4			1 3	8 13	41, 34 25, 57

[a] General conditions: Me₂PhSiH (1.0 mmol), substrate (1.0 mmol) and **1** (1 mol%) in MeNO₂ (5 mL) at 103 °C; conversion and selectivity determined by GC-MS. [b] minor product from subsequent olefin hydrosilylation (PhMe₂Si-C₃H₆-OSiMe₂Ph).

Polymerisations. Expansion of the silane substrate to silanes with two Si-H bonds provided access to polysiloxanes and silicones via mild hydrolytic oxidation. Upon using 1,4-bis(dimethylhydrosilyl)benzene as substrate, polymerisation occurred readily, indicated by the appearance of an off-white solid (31%) and a colourless oil (14%, yields based on mass balance, Scheme 3). While low solubility properties prevented any analysis of the solid fraction in solution, IR spectroscopy indicated the expected Si-O-Si stretching frequency at 1072 cm⁻¹ and also bands around 825 cm⁻¹, which were assigned to terminal Si-OH units.^[32] NMR analysis of the oil showed multiple resonances around δ 7.53 and 0.34, attributed to the phenyl and methyl protons, respectively, and also a small septet due to the silyl-bound proton (δ 4.43), pointing towards oligomeric rather than polymeric siloxane fractions.



Scheme 3. Catalytic formation of polysiloxane (top) and silicone (bottom) from hydrosilane precursors.

Complex **1** was also used to produce silicones under comparably mild conditions.^[3,33] When using MePhSiH₂ as a substrate (Scheme 3), an oily fraction was recovered in essentially quantitative yield. Analysis by NMR and IR spectroscopy revealed similar features as those described above, *i.e.* multiple resonances in the aromatic (δ 7.77–7.19) and aliphatic (δ 0.59–0.03) ¹H NMR region, and Si-O-Si stretching frequency in the 1099–1016 cm⁻¹ range. Moreover, the appearance of weak IR bands around 2171–2127 cm⁻¹ suggest the presence of terminal Si-H groups.^[32] Most instructively, ESI-MS analysis (positive mode) showed oligomeric fractions containing up to nine -SiMePhO- fragments. While larger oligomers and polymers may not be sufficiently volatile to be detected by this technique, these results unambiguously confirm the potential of

complex **1** to catalyse multiple Si–O bond formation at the same structural unit. These complexes may thus find application in silicone synthesis, in particular when acid- and base-free conditions are sought. The process developed here avoids the built-up of strong acids or the use of a base as typically encountered when employing more common starting materials such as R_2SiCl_2 or the corresponding triflates. Moreover, polymerisation of dihydrosilanes with water is highly atom economic and produces H_2 as a neutral, gaseous, and potentially useful side product.

Conclusion

Rhodium(III) dicarbene complexes activate Si–H bonds and catalyse the hydrolytic oxidation of hydrosilanes to form silanol and siloxane, with H_2 as the only side product. The product selectivity was adjusted by changing the reaction conditions and can be directed to either exclusive silanol formation or to selective siloxane production. Mechanistic investigations suggest that abnormally C4-bound carbenes induce a slightly higher catalytic activity than the C2-bound normal carbenes, and that these abnormal carbenes are involved in what may be best described as a ligand-assisted heterolytic Si–H/D bond cleavage process. The catalytic system has been successfully applied to the silylation of various alcohols, thus providing a mild alternative for the protection of alcohols by silyl groups. Selectivity tests towards different functional groups revealed a low reactivity to olefin hydrosilylation and no reactivity towards ketones, thus enabling silylether formation with functionalised alcohols. The innocence of the formed H_2 as side product and the insensitivity of the silane reagent towards moisture and air may provide great advantages in organic syntheses. In addition, siloxane formation has been expanded to polymerisations, thus disclosing a mild method for the production of polysiloxanes and silicones. The tolerance of complex **1** towards a variety of functional groups may become particularly relevant when preparing custom-tailored silicones, as the use of pre-functionalised dihydrosilane monomers may be more attractive than post-functionalisation of polymeric materials.

Experimental Section

General comments. The complexes **1–6** were prepared according to published procedures.^[11,15] All other reagents were commercially available and were used as received. $MeNO_2$ (puriss., absolute, over molecular sieves, $\geq 98.5\%$), $MeCN$ (HPLC grade, $\geq 99.9\%$) and THF (absolute, over molecular sieves, $\geq 99.5\%$) were purchased from Sigma-Aldrich and used without further purification. All NMR spectra were recorded at 25 °C on Varian spectrometers operating at 400 MHz (1H NMR) and 100 MHz ($^{13}C\{^1H\}$ NMR), respectively. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to residual solvent resonances. Assignments are based on homo- and heteronuclear shift correlation spectroscopy. GC-MS and HRMS were performed by the Analytical Laboratory at University College Dublin, Ireland

Procedures for the formation of siloxanes, silanols, and silylethers. In a typical reaction, $MePhSiH_2$ (136 mg, 1.0 mmol) and mesitylene (120 mg, 1.0 mmol) as internal standard were dissolved in $MeNO_2$ (2 mL) and added to a solution of complex **1** (7.3 mg, 1.0 mol%) dissolved in $MeNO_2$ (3 mL). The mixture was immediately immersed into a preheated oil bath (110 °C). Aliquots were taken at regular intervals, treated with Et_2O , filtered over Celite and subsequently analysed by GC-MS. The product identity was confirmed by the pertinent mass spectrometric and 1H and ^{13}C NMR spectroscopic data. For the formation of silylethers and silanols, ROH and H_2O , respectively, was added to the solution of the silane and mesitylene before addition to the complex. Aliquots were analysed by NMR spectroscopy after careful solvent evaporation.

Typical procedure for polymerisation experiments. Complex **1** (7.3 mg, 1 mol%) was dissolved in $MeNO_2$ (3 mL). $MePhSiH_2$ (122 mg, 1.0 mmol) or 1,4-bis(dimethylsilyl)benzene (194 mg, 1.0 mmol) was dissolved in $MeNO_2$ (3 mL) and added to the reaction mixture which was immediately placed in a preheated oil bath

(110 °C) and refluxed for 17 h. The resulting suspension was filtered, thus giving an off-white solid (<5 mg, form $MePhSiH_2$; 65 mg, 31%, from 1,4-bis(dimethylsilyl)benzene) which was analysed by IR spectroscopy. The filtrate was added to Et_2O , filtered, and all volatiles were removed *in vacuo*. The residual oil (131 mg, 96% from $MePhSiH_2$; 30 mg, 14% from 1,4-bis(dimethylsilyl)benzene) was analysed by MS and NMR spectroscopy.

Acknowledgements

We thank A. Coburn and K. Conboy for analytical assistance and the Swiss National Science Foundation, the Alfred Werner Foundation, and Sasol Ltd for financial support of this work.

- [1] a) S. J. Clarson, J. J. Fitzgerald, M. J. Owen, S. D. Smith, M. E. van Dyke (Eds.), *Synthesis and Properties of Silicones and Silicone-Modified Materials*, ACS Symposium Series 838, Wiley (Washington, D.C.) 2003; b) E. Pouget, J. Tonnar, P. Lucas, P. Lacroix-Desmazes, F. Ganachaud, B. Boutevin, *Chem. Rev.* **2010**, *110*, 1233-1277.
- [2] Silanols in cross coupling: a) S. E. Denmark, C. S. Regens, *Acc. Chem. Res.* **2008**, *41*, 1486-1499; b) M. N. Missaghi, J. M. Galloway, H. H. Kung, *Organometallics* **2010**, *29*, 3769-3779.
- [3] a) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Synthesis*, Wiley (New York, NY) 2000; b) V. Chandrasekhar, R. Boomishankar, S. Nagendran, *Chem. Rev.* **2004**, *104*, 5847-5910.
- [4] a) S. Chang, E. Sharrer, M. Brookhart, *J. Mol. Catal. A: Chem.* **1998**, *130*, 107-119; b) A. Biffis, M. Basato, M. Briccese, L. Ronconi, C. Tubaro, A. Zanella, C. Graiff, A. Tiripicchio, *Adv. Synth. Catal.* **2007**, *349*, 2485-2492; c) D. E. Barber, Z. Lu, T. Richardson, R. H. Crabtree, *Inorg. Chem.* **1992**, *31*, 4709-4711; d) L. D. Field, B. A. Messerle, M. Rehr, L. P. Soler, T. W. Hambley, *Organometallics* **2003**, *22*, 2387-2395.
- [5] a) E. A. Ison, R. A. Corbin, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2005**, *127*, 11938-11939; b) R. A. Corbin, E. A. Ison, M. M. Abu-Omar, *Dalton Trans.* **2009**, 2850-2855; c) Y. Lee, D. Seomoon, S. Kim, H. Han, S. Chang, P. H. Lee, *J. Org. Chem.* **2004**, *69*, 1741-1743.
- [6] a) T. Mitsudome, S. Arita, H. Mori, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem. Int. Ed.* **2008**, *47*, 7938-7940; b) B. P. S. Chauhan, A. Sarkar, M. Chauhan, A. Roka, *Appl. Organomet. Chem.* **2009**, *23*, 385-390.
- [7] E. Ludevics, M. Dzintara, *J. Organomet. Chem.* **1985**, *295*, 265-315.
- [8] For seminal mechanistic work, see: a) S. R. Klei, T. D. Tilley, R. G. Bergman, *Organometallics* **2002**, *21*, 3376-3387; b) L. Turculet, J. D. Feldman, T. D. Tilley, *Organometallics* **2004**, *23*, 2488-2502; c) P. Sangtrirutnugul, T. D. Tilley, *Organometallics* **2007**, *26*, 5557-5568.
- [9] C. S. Wei, C. A. Jiménez-Hoyos, M. F. Videia, J. F. Hartwig, M. B. Hall, *J. Am. Chem. Soc.* **2010**, *132*, 3078-3091.
- [10] a) F. L. Taw, R. G. Bergman, M. Brookhart, *Organometallics* **2004**, *23*, 886-890; b) J. Campos, A. C. Esqueda, J. López-Serrano, L. Sánchez, F. P. Cossio, A. de Cozar, E. Álvarez, C. Maya, E. Carmona, *J. Am. Chem. Soc.* **2010**, *132*, 16765-16767.
- [11] A. Krüger, A. Neels, M. Albrecht, *Chem. Commun.* **2010**, *46*, 315-317.
- [12] a) Confirmed by comparison of GC-MS and NMR analyses with the values published in reference [6a] and [12b]; b) K. Rühlmann, H. Grosse-Ruyken, D. Scheller, U. Scheim, *J. Organomet. Chem.* **1988**, *356*, 39-47.
- [13] a) The oxygen source required for siloxane generation from hydrosilanes using the rhodium dicarbene complexes most presumably is residual H_2O , which was identified by Karl-Fischer titrations. Addition of extraneous H_2O accelerates the rate of silane oxidation substantially, however this change also switches the product selectivity from siloxanes to silanols (*cf* Table 1). No support was obtained for the active participation of O_2 , suggested earlier [12b] to promote the rate of silane oxidation and catalyst regeneration. No significant variation of reaction rates was observed when carrying out the reaction either under an inert atmosphere of N_2 or under an atmosphere of pure O_2 (1 bar), and reactions were thus typically run under aerobic conditions. Further confirmation of O–H bond activation to generate siloxanes was obtained from reactions using ROH instead of H_2O as nucleophile, see below. (b) K. Mori, M. Tano, T. Mizugaki, K. Ebitani, K. Kaneda, *New J. Chem.* **2002**, *26*, 1536-1538.
- [14] A gradual increase of the siloxane/silanol ratio was observed over time. For example, when the product mixture obtained from wet $MeNO_2$ (entry 5) was kept at reflux for a further hour after reaching full conversion, the siloxane/silanol ratio raised from initially 10:90 to 15:85 (Fig. 2). This

- instability of the product mixture points towards a secondary process involving silanol to siloxane transformation. Reference experiments confirmed that in refluxing nitromethane silanol undergoes condensation to form disiloxane (60% conversion after 2 h). The presence of **1** accelerates this process with 80% of silanol converted to siloxane after 2 h. Reactions aimed at producing silanols in high selectivity should therefore be stopped after reaching full conversion, as longer reaction times inherently derogate selectivity.
- [15] a) L. Yang, A. Krüger, A. Neels, M. Albrecht, *Organometallics* **2008**, *27*, 3161-3171; b) A. Krüger, L. J. L. Haller, H. Müller-Bunz, O. Serada, A. Neels, S. A. Macgregor, M. Albrecht, *Dalton Trans.* **2011**, *40*, in press (DOI:10.1039/C1DT11116G).
- [16] For examples of related Si–H bond addition across a M–L bond, see: P. J. Tiong, A. Nova, E. Clot, P. Mountford, *Chem. Commun.* **2011**, *47*, 3147-3149.
- [17] a) D. R. Anton, R. H. Crabtree, *Organometallics* **1983**, *2*, 855-859; b) G. M. Whitesides, M. Hackett, R. L. Brainard, J. P. P. M. Lavalleye, A. F. Sowinski, A. N. Izumi, S. S. Moore, D. W. Brown, E. M. Staudt, *Organometallics* **1985**, *4*, 1819-1830.
- [18] a) J. A. Widegren, R. G. Finke, *J. Mol. Catal. A* **2003**, *198*, 317-341; b) C. M. Hagen, J. A. Widegren, P. M. Maitlis, R. G. Finke, *J. Am. Chem. Soc.* **2005**, *127*, 4423-4432.
- [19] a) K. A. M. Ampt, S. B. Duckett, R. N. Perutz, *Dalton Trans.* **2004**, 3331-3337; b) M. V. Campian, J. L. Harris, N. Jasim, R. N. Perutz, T. B. Marder, A. C. Whitwood, *Organometallics* **2006**, *25*, 5093-5104; c) R. N. Perutz, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* **2007**, *46*, 2578-2592.
- [20] a) S. R. Klei, T. D. Tilley, R. G. Bergman, *J. Am. Chem. Soc.* **2000**, *122*, 1816-1817; b) N. Schneider, M. Finger, C. Haferkemper, S. Bellemin-Laponnaz, P. Hofmann, L. H. Gade, *Chem. Eur. J.* **2009**, *15*, 11515-11529.
- [21] a) A. R. Chinaese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 2461-2468; b) M. Heckenroth, A. Neels, M. G. Garnier, P. Aebi, A. W. Ehlers, M. Albrecht, *Chem. Eur. J.* **2009**, *15*, 9375-9386; c) D. G. Gusev, *Organometallics* **2009**, *28*, 6458-6461; d) E. Aldecoperez, A. J. Rosenthal, B. Donnadiou, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2009**, *326*, 556-559.
- [22] a) L. Bernet, R. Lalrempuia, W. Ghattas, H. Mueller-Bunz, L. Vigara, A. Llobet, M. Albrecht, *Chem. Commun.* **2011**, *47*, 8058-8060; b) A. Krüger, M. Albrecht, *Aust. J. Chem.* **2011**, *64*, 1113-1117.
- [23] For related metal-mediated formation of silylethers from hydrosilanes, see: a) E. Lukevics, M. Dzintara, *J. Organomet. Chem.* **1984**, *271*, 307-317; b) L. Horner, J. Mathias, *J. Organomet. Chem.* **1985**, *282*, 175-189; c) K. Yamamoto, M. Takemae, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2111-2113; d) M. P. Doyle, K. G. High, V. Bagheri, R. J. Pieters, P. J. Lewis, M. M. Pearson, *J. Org. Chem.* **1990**, *55*, 6082-6086.
- [24] a) G. A. Molander, S. Swallow, *J. Org. Chem.* **1994**, *59*, 7148-7151; b) J. M. Lassaletta, R. R. Schmidt, *Synlett.* **1995**, 925-927.
- [25] Silylethers are also accessible through hydrosilylation of ketones and aldehydes: a) B. Marciniec (Ed.), *Comprehensive Handbook on Hydrosilylation*, Elsevier (Oxford, UK) 1992; b) H. Nishiyama, in *Transition Metals for Organic Synthesis* (Eds. M. Beller, C. Bolm), Wiley-VCH (Weinheim, Germany) 2004, Vol 2, pp. 182-191; c) S. Diez-Gonzalez and S. P. Nolan, *Org. Prep. Proc. Int.*, **2007**, *39*, 523-559.
- [26] T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis* 3rd ed., Wiley-Interscience (Hoboken, NJ), 1999.
- [27] a) S. Diez-Gonzalez, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612; b) B. Cetinkaya, in *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools* (Ed. S. Gonzalez), RSC Catalysis Series (Cambridge, UK) 2011, pp. 366-398; c) for a recent contribution with rhodium(I) complexes with bidentate dicarbene ligands, which demonstrate orthogonal selectivity, see: S. K. U. Rieder, P. Gigler, M. P. Högerl, E. Herdtweck, B. Bechlars, W. A. Herrmann, F. E. Kühn, *Organometallics* **2010**, *29*, 5681-5692.
- [28] M. P. Doyle, K. G. High, V. Bagheri, R. J. Pieters, P. J. Lewis, M. M. Pearson, *J. Org. Chem.* **1990**, *55*, 6082-6086.
- [29] a) X.-L. Luo, R. H. Crabtree, *J. Am. Chem. Soc.* **1989**, *111*, 2527-2535; b) B. T. Gregg, A. R. Cutler, *Organometallics* **1994**, *13*, 1039-1043; c) U. Oehmichen, H. Singer, *J. Organomet. Chem.* **1983**, *243*, 199-204.
- [30] For a heterogeneous system, see: P. Raffa, C. Evangelisti, G. Vitulli, P. Salvadori, *Tetrahedron Lett.* **2008**, *49*, 3221-3224.
- [31] For a complementary system that does not affect triple bonds, see: C. Lorenz, U. Schubert, *Chem. Ber.* **1995**, *128*, 1267-1269.
- [31] D. Lin-Vien, N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules* Academic Press (San Diego, CA) 1991.
- [33] J. B. Grande, F. Gonzaga, M. A. Brook, *Dalton Trans.* **2010**, *39*, 9369-9378.

Received: ((will be filled in by the editorial staff))

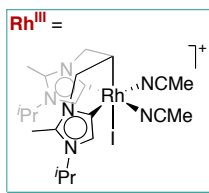
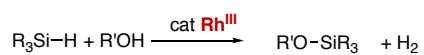
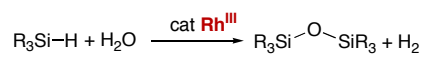
Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

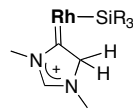
Si-H bond activation

A. Krüger, M. Albrecht*

Rhodium carbene complexes as versatile catalyst precursors for Si-H bond activation



Si-H activation possibly via



Rhodium-catalyzed Si-H bond activation provides a methodology for the silyl group to be transferred to oxygen centers, thus providing access to siloxanes and silanols (using H₂O), alkoxy silanes (using ROH), and to polysiloxanes such as silicones when using difunctional silanes. The process is pH neutral, avoids sensitive silylating agents, and produces H₂ as useful and exclusive side product.