DOI: 10.1002/ejic.200701255

Reduction of Ketones with Hydrocarbon-Soluble Calcium Hydride: Stoichiometric Reactions and Catalytic Hydrosilylation

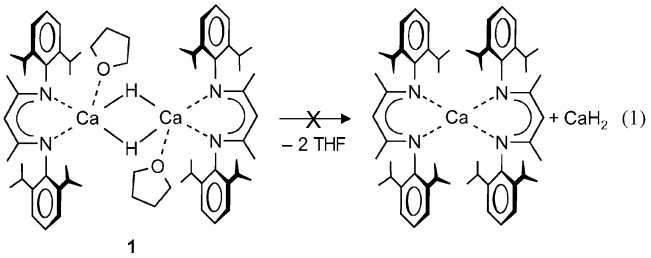
Jan Spielmann[a] and Sjoerd Harder*[a]

Keywords: Alkaline earth metals / Calcium / Hydride / Catalysis / Hydrosilylation

Reactions of the dimeric calcium hydride complex [(DIPP-nacnac)CaH·thf]$_2$ {**1**; DIPP-nacnac = CH[(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)]$_2$} with the *α*-hydrogen containing ketones acetophenone, acetone, dibenzylketone and 2-adamantone are smooth. In most cases not only addition but also substantial enolization is observed as a side reaction and in some cases also aldol condensation was found. Despite this unselectivity, the addition products could be isolated crystalline pure. Crystal structures of [(DIPP-nacnac)CaOCH(Me)Ph]$_2$ (**3**), [(DIPP-nacnac)CaOCH(CH$_2$Ph)$_2$]$_2$ (**6**) and [(DIPP-nacnac)-Ca(2-adamantoxide)]$_2$ (**7**) have been determined. The calcium hydride complex **1** is an effective catalyst in the hydrosilylation of ketones. Independent from the silane/ketone ratio, a strong preference for formation of *bis*-alkoxy silanes [PhSiH(OR)$_2$] is observed. In most cases no enoxy groups have been found in the product. This indicates that the mechanism does not involve addition of the calcium hydride to the ketone functionality. A concerted addition of silane to ketone through a six-coordinate hypervalent silicon intermediate is proposed.

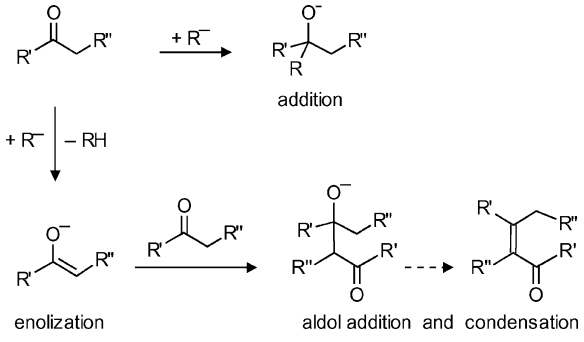
Introduction

We recently published a synthetic route and crystal structure for the first well-defined calcium hydride complex (**1**) [Equation (1)].[1] This dimeric complex, which readily dissolves in hydrocarbons like benzene, is stabilized towards ligand exchange and concomitant precipitation of insoluble CaH_2 by the bulky β-diketiminate ligand.



1

As we have shown in a first screening study on the reactivity of this reagent, **1** smoothly adds to unsaturated substrates like conjugated alkenes, ketones, imines, and (iso)-cyanides. In most cases well-defined calcium complexes could be isolated and have been characterized by crystal structure determinations.[2] Since the nucleophilic addition to ketones is one of the most versatile reactions in organic syntheses,[3] we now expand the scope of this new hydride reagent by a more detailed study on the reduction of various ketones. As nucleophilic conversion of ketones is often plagued by competing side reactions like enolization and aldol condensation (Scheme 1),[4] we are especially interested in: a) the selectivity of nucleophilic addition of **1** to a variety of ketones and b) successful isolation of well-defined products which would broaden the general scope of reagent **1** as a synthetic precursor in calcium chemistry.



Scheme 1.

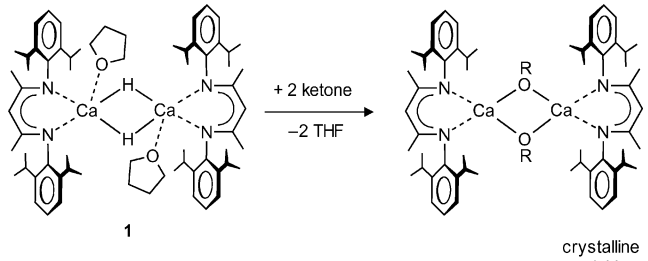
Since calcium hydride complexes have been proposed as intermediates in the recently investigated Ca-mediated hydrosilylation of alkenes,[5e] we are also particularly interested in the application of dimeric calcium hydride **1** in the catalytic hydrosilylation of ketones. This would add to the rapidly growing field of low-cost biocompatible calcium catalysts for an increasing number of catalytic conversions.[5]

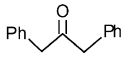
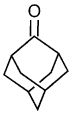
[a] Anorganische Chemie, Universität Duisburg-Essen, Universitätsstraße 5–7, 45117 Essen, Germany
E-mail: sjoerd.harder@uni-due.de
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

Results and Discussion

Stoichiometric Reactions

The reaction of **1** and benzophenone in benzene is smooth and the expected addition product could be isolated in the form of a heteroleptic calcium alkoxide complex in good yield (**2**, Scheme 2).[2] As benzophenone is not prone to any of the side reactions summarized in Scheme 1, we screened a variety of α-hydrogen containing ketones.



		crystalline yield
	**2**, R = $CH(Ph)_2$	73 %[2]
	**3**, R = CH(Me)(Ph)	25 %
	**4**, R = $CH(Me)_2$	–
	**5**, R = Cy	23 %
	**6**, R = $CH(CH_2Ph)_2$	9 %
	**7**, R = adamantyl	67 %

Scheme 2.

Reactions of these selected ketones with **1** were generally fast and gave full conversion. Analyses of the products after quenching with Me_3SiCl indicate a large variation in selectivity (Table 1). For acetophenone 85% addition and 15% enolization was observed. Reactions with cyclohexanone and the readily enolizable 1,3-diphenylacetone were even more unselective. For the substrate acetone no addition product but only enolization and aldolcondensation could be observed. 2-Adamantone, which is less enolizable due to the in-plane orientation of the α-CH bonds in respect to the ketone functionality, gave in reaction with **1** only addition (possible enolization products are below the GC-MS detection limit).

Despite the unselectivity in the reaction of **1** with various α-hydrogen containing ketones, crystalline pure addition products could be obtained in most cases (**3** and **5**–**7**, Scheme 2). The yields roughly reflect the chemoselectivities observed in the reduction reactions. Consequently, a good crystalline yield is obtained for **7** (the product obtained in reaction with 2-adamantone) whereas **4** could not be obtained via this route.

Table 1. Selectivity of the reaction of **1** in benzene with various ketones[a] and subsequent quenching with Me_3SiCl.

Ketone	% Addition	% Enolization	% Aldol cond.
PhC(O)Ph	100	–	–
PhC(O)Me	85	15	<1
MeC(O)Me	<1	76	24
cyclohexanone	58	35	7
$PhCH_2C(O)CH_2Ph$	68	32	<1
adamantone	100	<1	<1

[a] A solution of **1** in benzene was stirred with the ketone at 20 °C (16 h) and then quenched with Me_3SiCl. The product distributions have been analyzed by GC-MS.

The crystalline products **3** and **6**–**7** have been characterized by single-crystal X-ray diffraction (Figure 1). Structures of **2** and **5** have been published earlier (the latter was obtained in reaction of **1** with cyclohexene oxide). In all cases a thf-free dimeric structure is observed in which β-diketiminate ligands are bound terminally while the alkoxide ligands occupy the bridging positions. Likewise, in all cases the structures are crystallographically centrosymmetric. Apparently, their constitution as well as their nuclearity and general assembly are fully independent on the alkoxide ligand. All crystal structures exhibit surprisingly similar Ca–ligand bond lengths (Table 2). Deviations from symmetrical bridging of the alkoxide ligands is only found for **2** and is supposedly correlated to intramolecular Ph(π)···Ca interaction.[2] The crystal structure of **3** shows the centrosymmetric (*R*,*S*)-diastereomer (Figure 1). Like in **2**, the coordination sphere of Ca^{2+} is completed by interaction with the Ph ring of the alkoxide ligand. Whereas in **2** this contact has been described as a Ph(π)···Ca interaction [Ca···C 3.180(2) Å],[2] the geometry of the Ph···Ca contact in **3** is more conclusive for an agostic interaction: the Ca···C37′ distance is short [3.191(5) Å] but the Ca···H37′ distance (2.79 Å) is considerably shorter. Also the obtuse C37′–H37′···Ca angle of 107° is more in agreement with an agostic interaction. Complex **6** contains potentially donating Ph rings, however, no Ph···Ca interactions are evident in this structure. In **7** the steric bulk of the adamantoxide ligand induces a slight tilt of the β-diketiminate ligand and consequently some asymmetry in its chelating coordination mode (Table 2).

Table 2. A comparison of selected distances for the dimeric calcium alkoxide complexes **2**–**3** and **5**–**7** (Å).

Complex	Ca–O	Ca–N	Ca···Ca′
2[2]	2.261(1)	2.398(1)	3.5910(4)
	2.317(1)	2.405(1)	
3	2.227(1)	2.376(3)	3.488(1)
	2.254(3)	2.363(3)	
5[2][a]	2.226(2)	2.351(3)	3.4414(9)
	2.226(2)	2.363(3)	
6	2.233(1)	2.371(2)	3.4494(6)
	2.252(1)	2.354(2)	
7	2.247(1)	2.341(1)	3.4412(4)
	2.258(1)	2.447(1)	

[a] The crystal of complex **5** has two independent dimers in the asymmetric unit. The values for the non-disordered molecule are summarized here.

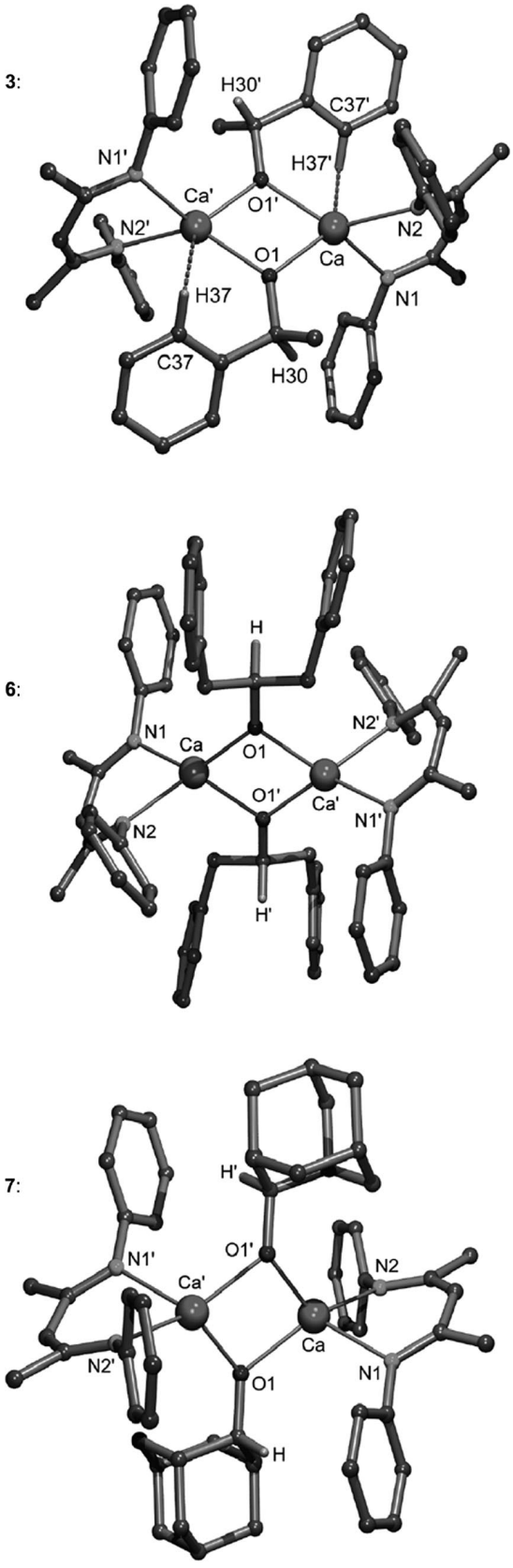


Figure 1. Crystal structures of the dimeric calcium alkoxide complexes **3**, **6** and **7**. In all cases the *i*Pr substituents and hydrogens (except for the hydrogen transferred in the addition reaction) have been omitted for clarity.

Catalytic Hydrosilylation of Ketones

Catalytic hydrosilylation of ketones, i.e. the formal addition of a silane R_3SiH to a ketone $R'_2C{=}O$ to give $R_3Si{-}OCHR'_2$, is a convenient one-step procedure for preparation of protected alcohols.[6] The numerous catalysts for this conversion are based on typical transition metals (Ni, Pd, Rh) but lately also catalysts based on Sn,[7] Cu,[8] Zn,[9] Li and Na[10] have been reported. In addition, it has been shown that a strong Lewis acid like $(C_6F_5)_3B$ also efficiently catalyzes this reaction.[11] As recently well-defined organocalcium complexes have shown efficient catalytic activity and remarkable selectivity in alkene hydrosilylation, hydrosilylation of ketones with calcium hydride **1** seems another promising application of calcium complexes in catalysis.

Hydrosilylation of cyclohexanone with phenylsilane (1:1 ratio) and catalytic amounts of **1** in benzene unexpectedly gave $PhSiH(OCy)_2$ as the main product. Investigations on the product distribution as a function of the silane/ketone ratio (Table 3) show that the dialkoxy silane is the favoured product under all circumstances. Even at high silane/ketone ratio of 2:1 the major product is $PhSiH(OCy)_2$. At low silane/ketone ratio also small amounts of the trialkoxy product can be obtained. Hydrosilylation of cyclohexanone gave mainly products originating from addition of the hydride to the ketone, however, besides the main product $PhHSi(OCy)_2$ also small amounts of $PhHSi(OCy)(OC_6H_9)$ could be detected in the GC-MS spectra, i.e. a dehydrogenative product has been formed by formal incorporation of the cyclohexenolate anion $C_6H_9O^-$. Interestingly, the trialkoxy product which was formed only in minor amounts consists mainly of $PhHSi(OCy)_2(OC_6H_9)$. The overall alkoxy/enoxy ratio of 98:2, however, is much higher than the addition/enolization ratio in reaction of **1** with cyclohexanone (Table 1). Thus, hydrosilylation of cyclohexanone appears to be considerably more selective than the stoichiometric addition of calcium hydride **1** to this ketone.

Table 3. Product distribution in the catalytic hydrosilylation of cyclohexanone with $PhSiH_3$ in benzene at 50 °C (1.25 mol-% **1**).

Entry	Silane/ ketone	PhH_2SiOR (%)	$PhHSi(OR)_2$ (%)	$PhSi(OR)_3$ (%)	Total alkoxy/ enoxy
1	2/1	29	69 (95:5)[a]	2 (11:89)[b]	98:2
2	1:1	20	78 (95:5)[a]	2 (11:89)[b]	98:2
3	1:2	0	91 (94:6)[a]	9 (4:96)[b]	96:4
4	1/3	0	89 (91:9)[a]	11 (1:99)[b]	98:2

[a] In parentheses: ratio $PhHSi(OCy)_2/PhHSi(OCy)(OC_6H_9)$. [b] In parentheses: ratio $PhSi(OCy)_3/PhHSi(OCy)_2(OC_6H_9)$.

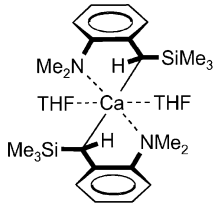
As the dialkoxy silane is the major hydrosilylation product, catalytic experiments for a larger variety of ketones were carried out with a silane/ketone ratio of 1:2 (Table 4). In all cases the dialkoxy products $PhHSi(OR)_2$ were formed in >90% yield. In addition, the well-defined dibenzylcalcium catalyst **8** was also tested and gave similar results. Whereas for cyclohexanone also a small percentage of products originating from an enolate intermediate could be de-

tected, other ketone substrates exclusively gave products with alkoxy substituents. These observations hint to a possible mechanism for this catalytic reaction.

Table 4. Hydrosilylation of ketones with $PhSiH_3$ and the calcium catalysts **1** or **8** (1.25 mol-%); reaction conditions: benzene, 50 °C. Results for catalyst **8** are given in square brackets.

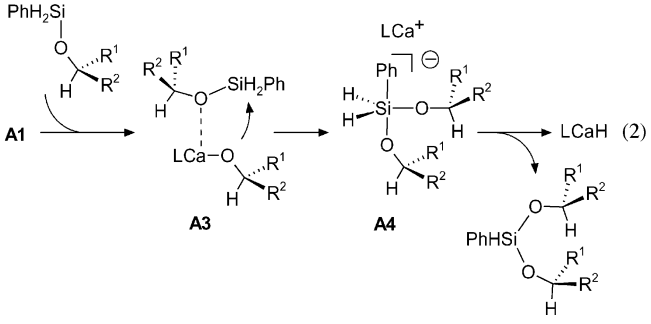
Entry	Ketone	Time / h	% $PhHSi(OR)_2$	Total alkoxy/enoxy
1	PhC(O)Ph	15 [15]	96 [96]	–
2	PhC(O)Me	34 [38]	95 [95]	100:0 [100/0]
3	cyclohexanone	3 [3]	91 [96]	96:4 [95/5]
4	$PhCH_2C(O)CH_2Ph$[a]	34 [54]	96 [95]	100:0 [100/0]
5	adamantone[b]	0.2 [1.5]	95 [98]	100:0 [100/0]

[a] 5 mol-% catalyst used. [b] Reactions at 20 °C.

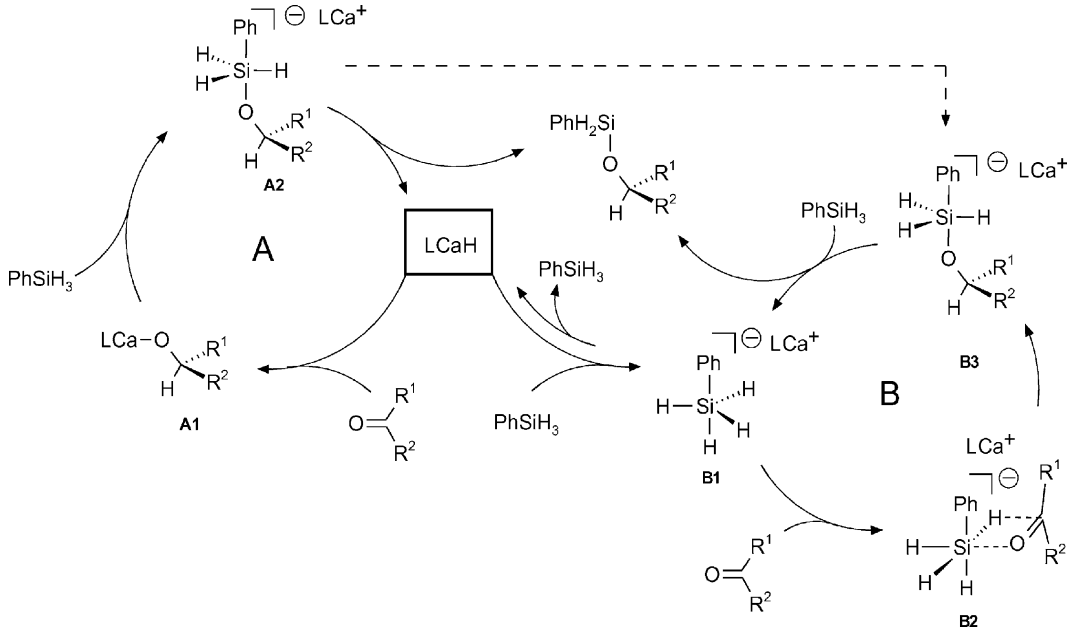


8

As for most hydrosilylation catalysts,[6–9] the mechanism could proceed through a cycle in which a hydride species is the actual catalyst (Scheme 3, cycle A). The first step in the mechanism is addition of the calcium hydride to the ketone. The addition reaction is irreversible[12] and results in formation of the calcium alkoxide complex **A1**. Addition of this alkoxide to $PhSiH_3$ gives the hypervalent intermediate **A2** which after elimination of the hydrosilylation product, the monoalkoxy silane, generates the original catalyst (LCaH). The observed preference for formation of a dialkoxy silane can be explained by precoordination of product PhH_2SiOR to the intermediate **A1** followed by intramolecular alkoxide/hydride exchange [Equation (2)], i.e. **A1** reacts faster with PhH_2SiOR than with $PhSiH_3$ on account of a complex-induced proximity effect (CIPE).[13] Further conversion of $PhHSi(OR)_2$ to $PhSi(OR)_3$ is likely hindered for steric reasons.



Although a similar mechanism has been proposed for the Ca-mediated hydrosilylation of alkenes, there are several reasons to believe that the Ca-mediated hydrosilylation of ketones does not proceed through cycle A. i) Stoichiometric addition of the various ketones to **1** gave in most cases sub-

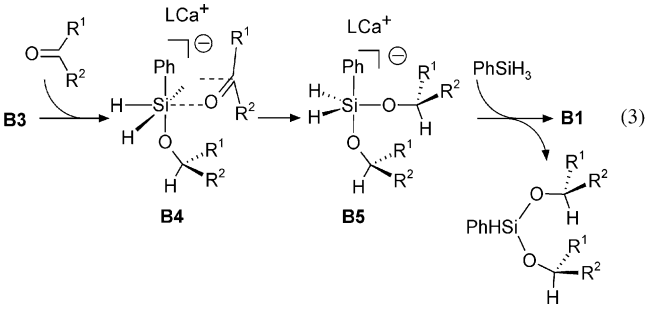


Scheme 3.

stantial enolate formation (Table 1), whereas the overall enoxy content in the hydrosilylation products is low. ii) Under stoichiometric conditions the calcium hydride catalyst (LCaH) could not be generated by addition of $PhSiH_3$ to a well-defined heteroleptic calcium alkoxide species (**A1**); i.e. the pathway **A1**→**A2**→LCaH could not be verified experimentally. The ^1H NMR spectrum of a solution of **7** and $PhSiH_3$ in C_6D_6 showed only signals for the separate species and no signs for calcium hydride **1** could be observed. Addition of a small amount of cyclohexanone, however, gave immediate reaction and the products PhHSi(O-adamantyl)(OCy) and $PhH_2Si(OCy)_2$ could be detected. This suggests that the calcium hydride species is not the intermediate but instead a proton is transferred directly from silane to ketone. It also indicates that heteroleptic calcium alkoxide species are active catalysts. The latter was verified by experiment.

We propose cycle B (Scheme 3) as a catalytic cycle that agrees better with the observations. In the first step the catalyst (LCaH) does not react with the ketone but with $PhSiH_3$ to give a hypervalent species (**B1**). ^1H NMR investigation on a stoichiometric reaction of **1** with $PhSiH_3$ in [D_8]-THF shows that this is an equilibrium which at room temperature is fast on the NMR time scale: coalescence of the signals for the hydride and Si–H protons is observed. Cooling the solution gives decoalescence of signals in those for **1** and $PhSiH_3$. This equilibrium is confirmed by the observation of rapid H/D exchange between **1** and $PhSiD_3$ in C_6D_6. In a second step, transient **B1** forms a coordination complex with a ketone (**B2**) that after a concerted insertion gives a new hypervalent species (**B3**). Hydride transfer from **B3** to $PhSiH_3$ gives the product and the hypervalent intermediate **B1**.

Route B is similar to the mechanism proposed for the sodium alkoxide catalyzed hydrosilylation of ketones with Ph_2SiH_2.[10] Also in the latter reaction a high proportion of the dialkoxy silane $Ph_2Si(OR)_2$ is formed as the product. The observed preference for formation of a dialkoxy silane can be explained by coordination of the ketone to **B3** followed by insertion and elimination of the product [Equation (3)]. As the silicon center in **B3** is more Lewis acidic than that in **B1**, precoordination of the ketone to **B3** is preferred over coordination to **B1** thus explaining major formation of the dialkoxy silane. Further conversion of **B5** to a trialkoxy silane is likely hindered for steric reasons.

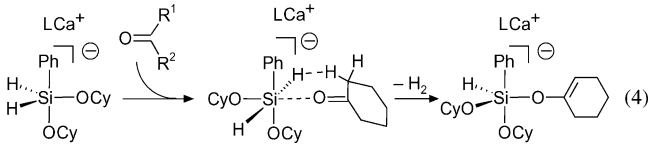


(3)

It should be noted that the intermediates **A2** in cycle A and **B3** in cycle B are equal. This explains why heteroleptic calcium alkoxide complexes (**A1**) also catalyze the hydrosilylation of ketones (**A1**→**A2** = **B3**→**B1**).

Hypervalent anions are the key intermediates in cycle B and the species LCa^+, which is likely solvated by ketones or silyl ether products, will hardly influence the catalytic reaction. This is in agreement with the observation that catalysts **1** and **8** give very similar results (Table 4).

It is noteworthy that the small amount of trisubstituted phenylsilane formed during hydrosilylation of cyclohexanone is largely $PhSi(OCy)_2(OC_6H_9)$. As the intermediate disubstituted phenylsilane mainly consists of $PhHSi(OCy)_2$, the last step involves almost exclusive introduction of the enoxy substituent. In principal two routes could explain formal incorporation of the cyclohexenolate anion. The latter anion could be formed by reaction of cyclohexanone with the calcium hydride (LCaH). As also substantial hydride addition would occur (Table 1), i.e. CyO^- formation, this reaction seems less likely. Alternatively, $PhSi(OCy)_2(OC_6H_9)$ could be formed in a concerted deprotonation reaction that involves a six-membered ring in the transition state [Equation (4)]. On account of steric crowding the six-membered ring transition state for α-deprotonation would be preferred over the four-membered ring transition state for addition (e.g. **B3**).



(4)

Conclusions

The stoichiometric reactions of the soluble heteroleptic calcium hydride complex **1** with ketones are generally smooth. Apart from addition of the hydride to the ketone, α-hydrogen containing ketones also show substantial enolization as a side reaction. Despite this unselectivity, crystalline pure addition products could be isolated in most cases. The rather low yields are partly due to the poor chemoselectivities. The calcium hydride complex **1** is also an effective catalyst for the hydrosilylation of ketones. Independent of the silane/ketone ratio, a dialkoxy silane [$PhHSi(OR)_2$] is found as the major product. As the overall alkoxy/enoxy ratio in the hydrosilylation products is very high (in most cases no enoxy substituents could be detected) it is likely that the mechanism for Ca-mediated hydrosilylation does not involve the addition of calcium hydride to the ketone. Instead an intermediate with a hypervalent six-coordinate silicon atom is proposed. In this catalytic cycle the hydride atom is transferred from silicon to ketone in a concerted step.

Experimental Section

General: All manipulations were performed under a dry and oxygen-free atmosphere (argon or nitrogen) by using freshly dried solvents and Schlenk line and glove box techniques. Following complexes have been prepared according to literature: **1**[1] and **8**.[14]

Synthesis of 3: A solution of **1** (250 mg; 0.24 mmol) and acetophenone (57 mg; 0.47 mmol) in benzene (1.8 mL) was stirred for ten minutes at room temperature. Overnight colourless octahedral crystals of **3** precipitated at room temperature in low yield: 68 mg (25%). The moisture sensitive crystals were suitable for X-ray analysis but are composed of both possible diastereomers in a ratio of about 2:1. Multiple recrystallisation in benzene afforded one of the diastereomers in sufficient purity for NMR characterization. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.35–6.98 (m, 11 H, H_{ar}), 4.77 (s, 1 H, DIPP-nacnac bridge), 4.75 [q, ^3J(H,H) = 6.8 Hz, 1 H, OC*H*CH$_3$Ph], 3.37 [sept, ^3J(H,H) = 6.8 Hz, 2 H, C*H*Me$_2$], 2.61 (br, 2 H, C*H*Me$_2$), 1.70 (s, 3 H, DIPP-nacnac Me), 1.48 (s, 3 H, DIPP-nacnac Me), 1.21 [d, ^3J(H,H) = 6.8 Hz, 3 H, OCH*CH$_3$*Ph], 1.21–0.91 (24 H, CH*Me*$_2$) ppm. ^{13}C NMR (500 MHz, C_6D_6, 60 °C): δ = 167.0, 151.8, 147.7, 142.1, 130.1, 128.5, 126.6, 125.1, 124.7, 124.1, 94.6 (aromatics, DIPP-nacnac bridge), 72.5 (O*C*HCH$_3$Ph), 31.3 (OCH*C*H$_3$Ph), 28.8 (Me$_2$*C*H), 28.3 (Me$_2$*C*H), 25.6 (DIPP-nacnac Me), 25.3 (DIPP-nacnac Me), 25.2 (*Me*$_2$CH), 25.1 (*Me*$_2$CH), 24.8 (*Me*$_2$CH), 28.8 (*Me*$_2$CH) ppm. $C_{37}H_{50}CaN_2O$ (578.90): calcd. C 76.77, H 8.71; found C 76.32, H 8.92.

Synthesis of 5: A solution of **1** (170 mg; 0.16 mmol) and cyclohexanone (37 mg; 0.37 mmol) in benzene (3.0 mL) was stirred for three hours at 60 °C. After concentrating the solution to one-third of its original volume, the solution was cooled to 8 °C. Overnight colourless crystals of **5** precipitated: 40 mg (23%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.15–7.09 (m, 6 H, H_{ar}), 4.70 (s, 1 H, DIPP-nacnac bridge), 3.30 (m, 1 H, α-H Cy), 3.22 [sept, ^3J(H,H) = 6.8 Hz, 4 H, Me$_2$C*H*], 1.67–1.58 (br m, 5 H, Cy), 1.61 (s, 6 H, DIPP-nacnac Me), 1.52–1.38 (m, 2 H, Cy), 1.18 [d, ^3J(H,H) = 6.8 Hz, 12 H, *Me*$_2$CH], 1.07 [d, ^3J(H,H) = 6.9 Hz, 12 H, *Me*$_2$CH], 1.01–0.87 (m, 3 H, Cy) ppm. ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ = 166.7, 147.7, 142.2, 124.9, 124.5, 93.9 (aromatics, DIPP-nacnac bridge), 72.5 (α-C Cy), 40.1 (Cy), 29.2 (Me$_2$*C*H), 26.6 (Cy), 26.4 (Cy), 25.5 (DIPP-nacnac Me), 25.3 (*Me*$_2$CH), 25.2 (*Me*$_2$CH) ppm. $C_{35}H_{52}CaN_2O$ (556.90): calcd. C 75.49, H 9.41; found C 74.98, H 9.23.

Synthesis of 6: A solution of **1** (310 mg; 0.29 mmol) and 1,3-diphenylacetone (130 mg; 0.62 mmol) in toluene (3.5 mL) was kept overnight at room temperature. The alkoxide **6** precipitated from the mother liquor in form of colourless crystals and could be obtained in low yields: 35 mg (9%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.26–7.08 (m, 6 H, H_{ar} DIPP-nacnac), 6.96–6.80 [m, 10 H, OCH(CH$_2$*Ph*)$_2$], 4.60 (s, 1 H, DIPP-nacnac bridge), 4.56 [m, 1 H, OC*H*(CH$_2$Ph)$_2$], 3.24 [sept, ^3J(H,H) = 6.8 Hz, 4 H, Me$_2$C*H*], 2.96 [d, ^3J(H,H) = 12.6 Hz, 1 H, OCH(C*H*$_2$Ph)$_2$], 2.94 [d, ^3J(H,H) = 13.5 Hz, 1 H, OCH(C*H*$_2$Ph)$_2$], 2.56 [d, ^3J(H,H) = 9.4 Hz, 1 H, OCH(C*H*$_2$Ph)$_2$], 2.52 [d, ^3J(H,H) = 9.4 Hz, 1 H, OCH(C*H*$_2$Ph)$_2$], 1.67 (s, 6 H, DIPP-nacnac Me), 1.18 [d, ^3J(H,H) = 7.1 Hz, 12 H, *Me*$_2$CH], 1.15 [d, ^3J(H,H) = 6.1 Hz, 12 H, *Me*$_2$CH] ppm. ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ = 166.6, 147.6, 141.8, 139.2, 129.6, 128.0, 125.7, 124.5, 124.3, 93.8 (aromatics, DIPP-nacnac bridge), 75.4 [O*C*H(CH$_2$Ph)$_2$], 49.6 [OCH(*C*H$_2$Ph)$_2$], 28.5 (Me$_2$*C*H), 25.3 (DIPP-nacnac Me), 25.0 (*Me*$_2$CH), 24.8 (*Me*$_2$CH) ppm. $C_{44}H_{56}CaN_2O$ (669.03): calcd. C 78.99, H 8.44; found C 79.23, H 8.21.

Synthesis of 7: A solution of **1** (150 mg; 0.14 mmol) and 2-adamantone (42 mg; 0.28 mmol) in benzene (2.5 mL) was stirred for ten minutes at room temperature and then cooled to 8 °C. Overnight colourless blocks of **7** precipitated: 114 mg (67%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.21–7.10 (m, 6 H, H_{ar}), 4.64 (s, 1 H, DIPP-nacnac bridge), 3.81 (m, 1 H, α-H adamantyl), 3.24 [sept, ^3J(H,H) = 6.8 Hz, 4 H, Me$_2$C*H*], 1.87–1.82 (m, 2 H, adamantyl), 1.72–1.54 (m, 6 H, adamantyl), 1.61 (s, 6 H, DIPP-nacnac Me), 1.28–1.14 (m, 6 H, adamantyl), 1.18 [d, ^3J(H,H) = 6.8 Hz, 12 H, *Me*$_2$CH], 1.17 [d, ^3J(H,H) = 6.8 Hz, 12 H, *Me*$_2$CH] ppm. ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ = 166.7, 148.0, 141.8, 124.4, 124.0, 91.7 (aromatics, DIPP-nacnac bridge), 76.0 (α-C adamantyl), 38.3 (C-bridge adamantyl), 37.9 (C-bridge adamantyl), 37.5 (C-bridge adamantyl), 32.0 (CH_2 adamamtyl), 28.5 (CH_2 adamantyl), 28.3 (Me$_2$*C*H), 27.7 (CH_2 adamantyl), 25.7 (DIPP-nacnac Me), 25.4 (*Me*$_2$CH), 24.8 (*Me*$_2$CH) ppm. $C_{39}H_{56}CaN_2O$ (608.97): calcd. C 76.92, H 9.27; found C 76.43, H 9.16.

Reaction of 1 with Ketones and Subsequent Quenching with Me_3SiCl: A mixture of **1** (30 mg, 0.057 mmol) and the ketone substrate (0.057 mmol) in benzene (0.45 mL) was kept overnight at room temperature (samples with cyclohexanone were heated at 60 °C for three hours). The Me_3SiCl used in the quench reaction, was freed from HCl impurities by addition of an equimolar amount of dry triethylamine to a solution of Me_3SiCl in dry THF and separating possibly formed ammonium chloride by centrifugation. The quenching solution (10% in THF, 0.30 mL, 0.20 mmol Me_3SiCl) was added to the reaction mixture of **1** and the ketone. After stirring overnight at room temperature a small amount of water was added and the organic layer was separated and analyzed by GC-MS.

Typical Procedure for the Catalytic Hydrosilylation of Ketones: The catalysts **1**[1] and **8**[14] were used in crystalline purity. In a typical hydrosilylation experiment a dried NMR tube was charged with the silane (0.30 mmol) and the ketone substrate (0.60 mmol) in C_6D_6 (0.45 mL). After addition of the catalyst, normally 1.25 mol-% **1** (calculated on the dimer) or **8**, the reaction mixture was heated to 50 °C (or in some cases allowed to stand at room temperature). At regular time intervals the conversion was determined by ^{1}H NMR spectroscopy. After at least 95% conversion the reaction mixture was quenched with small amounts of water to remove all calcium salts and the organic layer was analysed via GC-MS.

Crystal Structure Determination: All data were collected on a Siemens SMART CCD diffractometer at –70 °C. The structures have been solved by direct methods (SHELXS-97)[15] and were refined with SHELXL-97.[16] The geometry calculations and graphics have been performed with PLATON.[17] CCDC-660496 (for **3**), -660497 (for **7**) and -660498 (for **6**) contain the supplementary crystallographic data for this paper (excluding structure factors). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 3: $C_{37}H_{50}CaN_2O\cdot(C_6H_6)_{0.5}$, M_r = 617.92, monoclinic, space group $P2_1/n$, a = 12.1570(6) Å, b = 12.8541(6) Å, c = 23.3203(13) Å, β = 94.268(4), V = 3634.1(3) Å^3, Z = 4, $\rho_{calcd.}$ = 1.129 Mg·m^{-3}, F(000) = 1340, μ(Mo-K_α) = 0.204 mm^{-1}. Of the 13419 measured reflections, 3749 were independent (R_{int} = 0.068, θ_{max} = 20.8°) and 2721 observed [$I > 2\sigma(I)$]. The final refinement converged to $R1$ = 0.0538 for $I > 2\sigma(I)$, $wR2$ = 0.1619 and GOF = 1.06 for all data. The final difference Fourier synthesis gave a min./max. residual electron density of –0.30/+0.55 e Å^{-3}. All hydrogen atoms have been placed on calculated positions and were refined in a riding mode.

Crystal Data for 6: $C_{44}H_{56}CaN_2O\cdot(C_6H_6)_{2.5}$, M_r = 864.26, triclinic, space group $P\bar{1}$, a = 13.5135(6) Å, b = 13.6938(6) Å, c = 15.8605(8) Å, α = 82.900(3), β = 69.930(3), γ = 69.320(3), V =

2579.1(2) Å^3, Z = 2, $\rho_{calcd.}$ = 1.113 Mg·m^{-3}, F(000) = 934, μ(Mo-$K\alpha$) = 0.162 mm^{-1}. Of the 32045 measured reflections, 13110 were independent (R_{int} = 0.050, θ_{max} = 28.9°) and 8689 observed [$I > 2\sigma(I)$]. The final refinement converged to $R1$ = 0.0538 for $I > 2\sigma(I)$, $wR2$ = 0.1480 and GOF = 1.05 for all data. The final difference Fourier synthesis gave a min./max. residual electron density of –0.30/+0.31 e Å^{-3}. Most hydrogen atoms have been placed on calculated positions and were refined in a riding mode. The hydrogen transferred by the reduction reaction (C_α) has been located in the Fourier-difference map and was refined isotropically.

Crystal Data for 7: $C_{39}H_{56}CaN_2O\cdot(C_6H_6)$, M_r = 687.05, triclinic, space group $P\bar{1}$, a = 12.6423(6) Å, b = 13.2216(6) Å, c = 13.9195(6) Å, α = 112.101(2), β = 98.680(2), γ = 104.757(2), V = 2003.98(17) Å^3, Z = 2, $\rho_{calcd.}$ = 1.139 Mg m^{-3}, F(000) = 748, μ(Mo-K_α) = 0.191 mm^{-1}. Of the 93670 measured reflections, 10533 were independent (R_{int} = 0.044, θ_{max} = 29.0°) and 8819 observed [$I > 2\sigma(I)$]. The final refinement converged to $R1$ = 0.0403 for $I > 2\sigma(I)$, $wR2$ = 0.1126 and GOF = 1.02 for all data. The final difference Fourier synthesis gave a min./max. residual electron density of –0.25/+0.33 e Å^{-3}. Some hydrogen atoms have been located in the Fourier-difference map and were refined isotropically, others have been placed on calculated positions and were refined in a riding mode.

Supporting Information (see also the footnote on the first page of this article): Experimental details on the stoichiometric quench reactions and the catalytic hydrosilylation reactions (including GC-MS and or NMR analyses of the products). Also a catalytic experiment on a preparative scale is described.

Acknowledgments

Prof. Dr. R. Boese and D. Bläser (University of Duisburg-Essen) are thanked for collection of X-ray diffraction data.

[1] S. Harder, J. Brettar, *Angew. Chem.* **2006**, *118*, 3554; *Angew. Chem. Int. Ed.* **2006**, *45*, 3474.
[2] J. Spielmann, S. Harder, *Chem. Eur. J.* **2007**, *13*, 8928.
[3] a) B. J. Wakefield, *Organomagnesium Methods in Organic Chemistry* Academic Press, San Diego, **1995**; b) H. G. Richey Jr, *Grignard Reagents: New Developments*, Wiley, Chichester, **2000**; c) Y.-H. Lai, *Synthesis* **1981**, 585; d) J. J. Eisch, *Organometallics* **2002**, *21*, 5439; e) P. Knochel, W. Dohle, N. Gommermann, F. F. Kneisel, F. Kopp, T. Korn, I. Sapountzis, V. A. Vu, *Angew. Chem. Int. Ed.* **2003**, *42*, 4302; f) A. Inoue, H. Shinokubo, K. Oshima, *J. Synth. Org. Chem. Jpn.* **2003**, *61*, 25; g) J. Christoffers, A. Baro, *Adv. Synth. Catal.* **2005**, *347*, 1473; h) B. M. Trost, C. Jiang, *Synthesis* **2006**, *3*, 369; i) O. Riant, J. Hannedouche, *Org. Biomol. Chem.* **2007**, *5*, 873.
[4] a) T. Imamoto, Y. Sugiura, N. Takiyama, *Tetrahedron Lett.* **1984**, *38*, 4233; b) T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima, Y. Kamiya, *J. Am. Chem. Soc.* **1989**, *111*, 4392; c) M. Hatano, T. Matsumura, K. Ishihara, *Org. Lett.* **2005**, *7*, 573; d) A. Krasovskiy, F. Kopp, P. Knochel, *Angew. Chem.* **2006**, *118*, 511; *Angew. Chem. Int. Ed.* **2006**, *45*, 497.
[5] a) S. Harder, F. Feil, K. Knoll, *Angew. Chem.* **2001**, *113*, 4391; *Angew. Chem. Int. Ed.* **2001**, *40*, 4261; b) M. H. Chisholm, J. Gallucci, K. Phomphrai, *Chem. Commun.* **2003**, 48; c) Z. Zhong, S. Schneiderbauer, P. J. Dijkstra, M. Westerhausen, J. Feijen, *J. Polym. Bull.* **2003**, *51*, 175; d) M. R. Crimmin, I. J. Casely, M. S. Hill, *J. Am. Chem. Soc.* **2005**, *127*, 2042; e) F. Buch, J. Brettar, S. Harder, *Angew. Chem.* **2006**, *118*, 2807; *Angew. Chem. Int. Ed.* **2006**, *45*, 2741; f) M. R. Crimmin, A. G. Barrett, M. S. Hill, P. A. Procopiou, *Org. Lett.* **2007**, *9*, 331; g) S. Datta, P. W. Roesky, S. Blechert, *Organometallics* **2007**, *26*, 4392; h) F. Buch, S. Harder, *Organometallics* **2007**, *26*, 5132.
[6] a) I. Ojima, *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**; b) B. Marciniec, *Comprehensive Handbook on Hydrosilation*, Pergamon, New York, **1992**; c) H. Brunner, Henri, *Transition Metals for Organic Synthesis* (Eds.: M. Beller, C. Bolm), Wiley-VCH, **1998**; d) J. Jun, S. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 5640; e) A. C. Fernandes, R. Fernandes, C. C. Romao, B. Royo, *Chem. Commun.* **2005**, 213; f) O. Riant, N. Mostefai, J. Courmarcel, *Synthesis* **2004**, *18*, 2943.
[7] N. J. Lawrence, S. M. Bushell, *Tetrahedron Lett.* **2000**, *41*, 4507.
[8] a) H. Brunner, W. Miehling, *J. Organomet. Chem.* **1984**, *275*, C17; b) B. H. Lipshutz, W. Chrisman, K. Noson, *J. Organomet. Chem.* **2001**, *624*, 367; c) S. Rendler, M. Oestreich, *Angew. Chem.* **2007**, *119*, 504; *Angew. Chem. Int. Ed.* **2007**, *46*, 498.
[9] H. Mimoun, *J. Org. Chem.* **1999**, *64*, 2582.
[10] L. Gan, M. A. Brook, *Organometallics* **2007**, *26*, 945.
[11] a) D. J. Parks, W. E. Piers, *J. Am. Chem. Soc.* **1996**, *118*, 9440; b) D. J. Parks, J. M. Blackwell, W. E. Piers, *J. Org. Chem.* **2000**, *65*, 3090.
[12] The reversibility of the reaction has been tested by addition of benzophenone to a solution of **7** in C_6D_6. Even under reflux conditions no signs of formation of **2** could be observed.
[13] B. Chauder, L. Green, V. Snieckus, *Pure Appl. Chem.* **1999**, *71*, 1521.
[14] S. Harder, F. Feil, A. Weeber, *Organometallics* **2001**, *20*, 1044.
[15] G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, **1997**, University of Göttingen, Germany.
[16] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, **1997**, University of Göttingen, Germany.
[17] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool* **2000**, Utrecht University, Utrecht, The Netherlands.

Received: November 22, 2007
Published Online: February 1, 2008

