ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

Cite this: *Chem. Commun.*, 2014, 50, 2311

Received 7th December 2013, Accepted 7th January 2014

DOI: 10.1039/c3cc49308c

www.rsc.org/chemcomm

Hydrosilylation catalysis by an earth alkaline metal silyl: synthesis, characterization, and reactivity of bis(triphenylsilyl)calcium†

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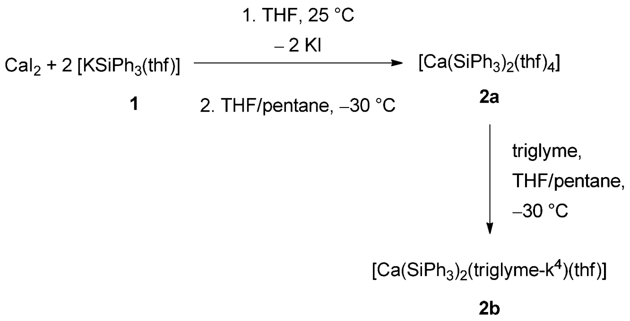
Bis(triphenylsilyl)calcium [Ca(SiPh$_3$)$_2$(thf)] obtained in high yield as a crystalline ether adduct catalyzes the hydrosilylation of activated C–C double bonds efficiently and regioselectively.

Catalytic hydrosilylation of alkenes is a commercially utilized process for the efficient synthesis of organosilicon compounds.[1] Potent catalysts such as Speier's[2] and Karsted[3] catalysts are based on late transition metals. Recently attention has shifted to more inexpensive alternatives based on main group metals including $AlCl_3$ and $B(C_6F_5)_3$.[4] The first series of well-defined catalysts based on s-block metals (K, Ca, and Sr), with presumably a metal hydride as the catalytic active species, was introduced by Harder *et al.*[5] A metal silyl was also implicated as active species in the hydrosilylation of C–C double bonds. Although used in synthetic chemistry,[6] metal silyls have never been applied as hydrosilylation catalysts before. Herein we report that structurally well-characterized bis(triphenylsilyl)calcium (**2a**) catalyzes the regioselective hydrosilylation of aromatic olefins.

Bis(triphenylsilyl)calcium, [Ca(SiPh$_3$)$_2$(thf)$_4$] (**2a**), was prepared in quantitative yield by salt metathesis of anhydrous CaI_2 and two equivalents of [KSiPh$_3$(thf)] (**1**) (Scheme 1).[7] The pale yellow product is soluble in THF and benzene, but insoluble in aliphatic hydrocarbons. It decomposes with a half life of $t_{1/2}$ = 7 d in THF and $t_{1/2}$ = 40 d in benzene. $HSiPh_3$ was identified by ^1H NMR spectroscopy as the major decomposition product in solution. Single crystals of **2a** were obtained from a saturated THF/pentane solution upon cooling to −30 °C and characterized by X-ray diffraction.



Scheme 1 Synthesis of calcium silyls **2a** and **2a**.

2a crystallizes in the monoclinic space group $P2_1/c$ with $Z = 2$. The octahedral calcium atom acts as the inversion center with two silyl ligands (Ca–Si: 3.1503(8) Å) in the axial and four THF ligands in the equatorial positions. The angles Si1–Ca1–Si1′ of 180.00°, Si1–Ca1–O1 of 89.64(5)° and Si1–Ca1–O2 of 86.56(5)° suggest an octahedral geometry (Fig. 1). Distorted trigonal bipyramidal coordination geometry was observed for [Ca{Si(SiMe$_3$)$_3$}$_2$(thf)$_3$].[8] Metal-to-ligand distances of **2a** are similar to those of the calcium-silyl [Ca{Si(SiMe$_3$)$_3$}$_2$(thf)$_3$].

The THF ligands in **2a** are labile and easily replaced with triglyme to give [Ca(SiPh$_3$)$_2$(triglyme-κ^4)(thf)] (**2b**) in 70% yield (Scheme 1). The solid state structure of the adduct **2b** shows, according to single crystal X-ray analysis, a pentagonal bipyramidal coordination geometry with the silyl ligands in the axial and triglyme and one THF ligand in the equatorial positions (ESI†). Ca–Si bond lengths are 3.175(3) and 3.242(3) Å. Other bond lengths and angles are comparable to those of known calcium triglyme complexes.[9] Compound **2b** decomposes with a half life of $t_{1/2}$ = 12 h in THF, methyltriphenylsilane was identified as a major decomposition product by ^1H NMR spectroscopy.

DFT calculations at the B3PW91 level were carried out to understand the nature of the Ca–Si bond in **2a**. The optimized structure compares well with the crystal structure, represented by a Ca–Si bond length of 3.215 Å (0.06 Å longer than in **2a**).

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† Electronic supplementary information (ESI) available: Experimental section, details of DFT calculations, NMR spectra, and X-ray crystallographic data. CCDC 963862 (**2a**) and 963863 (**2b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc49308c

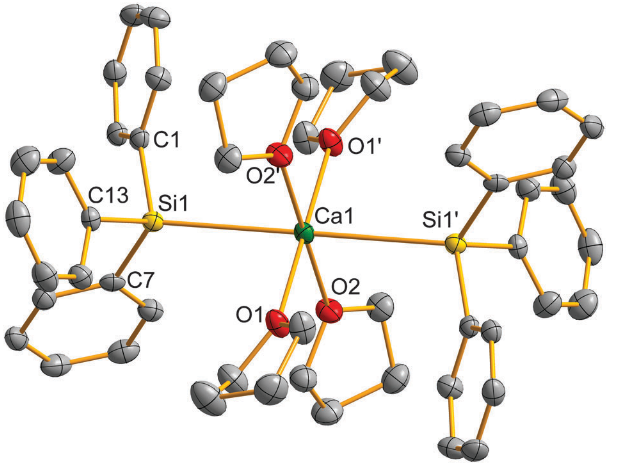


Fig. 1 Molecular structure of **2a**. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ca1–Si1 3.1503(8), Ca1–O1 2.438(2), Ca1–O2 2.3838(19), Si1–Ca1–Si1′ 180.00, Si1–Ca1–O1 89.64(5), Si1–Ca1–O2 86.56(5), Ca1–Si1–C1 108.73(8), Ca1–Si1–C7 122.11(8), Ca1–Si1–C13 115.38(8).

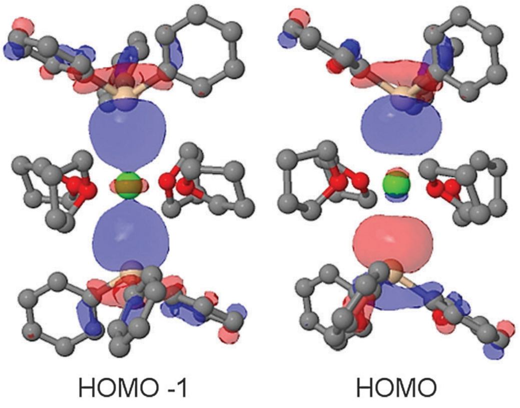
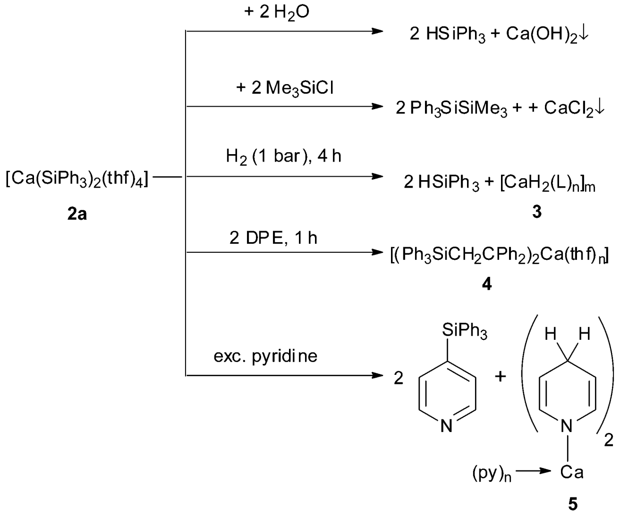


Fig. 2 Selected molecular orbitals of complex **2a**.



Scheme 2 Reaction of **2a** with water and Me_3SiCl at 25 °C in C_6D_6. Activation of dihydrogen, regioselective addition to DPE, and silylation of pyridine with **2a** at 60 °C in C_6D_6.

The bonding nature was analyzed by molecular orbital (MO) analysis. Two MOs corresponding to the Ca–Si interaction, HOMO − 1 and the HOMO, were found. HOMO − 1 corresponds to a bonding interaction between Ca and Si, involving the $d_z{}^2$ orbital of Ca. The HOMO corresponds to an antibonding interaction between Ca and Si, involving the p_z orbital of Ca (Fig. 2). This suggests no fully covalent interaction between Ca and Si. Therefore natural bond orbital (NBO) analysis was carried out to determine the amount of donor–acceptor interaction. A Wiberg index of 0.363 for the Ca–Si bond, which would be 1 for a covalent single bond, indicates a substantial donor–acceptor interaction. Analyzing the second order donor–acceptor interaction, a 70 kcal mol^{-1} interaction is found between a filled sp^3 lone pair on Si and an empty hybrid sd orbital of Ca. It is noteworthy that the carbon homologue of **2a**, $[Ca(CPh_3)_2(thf)_6]$, was characterized as a solvent-separated ion-pair.[10] The involvement of d orbitals of Ca[11] and the interaction between Ca and Si represents a unique bonding situation.

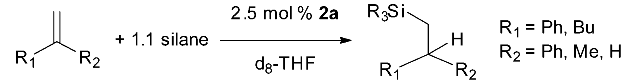
Reactivity studies of **2a** were monitored by NMR spectroscopy (Scheme 2). In analogy to the bulky supersilyl anions SiR_3 (R = ^{t}Bu, $SiMe_3$), a solution of **2a** in C_6D_6 reacts with water by protonation.[13] In a nucleophilic substitution reaction of **2a** with chlorotrimethylsilane, 1,1,1-trimethyl-2,2,2-triphenyldisilane was identified as the only product of the reaction.[12,13]

Bis(triphenylsilyl)calcium **2a** is able to cleave dihydrogen at elevated temperatures within 4 h. After full consumption of **2a** the ^1H NMR spectra showed triphenylsilane as the sole product of the reaction with dihydrogen. As $HSiPh_3$ was formed in quantitative yield, a calcium hydride $[CaH_2(L)_n]_m$ (**3**, L = neutral Lewis base) appeared to have formed. A very broad proton resonance (3.9–5.4 ppm) was assigned to the hydride signal of **3**, but this compound could not be crystallized from the reaction mixture. To verify the existence of a hydride species in solution, 9-fluorenone was added to the degassed reaction mixture. The solution turned yellow-green with concomitant evolution of H_2. Although no proton resonances could be assigned due to overlap with the signals of triphenylsilane, a fluorenone ketyl complex $[Ca(OC_{13}H_8)_2(thf)_n]$ is proposed to be the product of the reaction. This reaction path is in contrast to the reactivity of the fully characterized calcium hydride [{CaH(DIPP-nacnac)(thf)}$_2$] (DIPP-nacnac = (2,6-*i*Pr_2Ph)NC(Me)C(H)C(Me)N(2,6-*i*Pr_2Ph)), which reacts with benzophenone by hydride transfer.[14] Fluorenone ketyl complexes of calcium have been reported before.[15]

1,1-Diphenylethylene (DPE) reacted with **2a** at 60 °C. The formation of the insertion product **4** was verified by ^1H NMR spectroscopy. Attempts to crystallize the insertion product failed. The regioselective addition of alkaline metal silyls to DPE is known.[16] High regio- and stereoselectivities in the addition of silyl compounds to activated C–C double bonds can be achieved by using silylcuprates.[17] Main group silyls such as lithium silyls are useful silylating reagents in organic synthesis.[6d]

DPE was selectively hydrosilylated by $HSiPh_3$ using **2a** as the catalyst within 62 h (Table 1, entry 1).[18] Increase of the temperature to 100 °C gave full conversion to the hydrosilylated product within 2 h (Table 1, entry 3).

Table 1 Catalytic hydrosilylation of activated olefins using catalyst **2a**



Entry[a]	Substrate	Silane	T (°C)	t (h)	Yield[b] (%)
1	R_1=R_2=Ph	$HSiPh_3$	60	62	96[c]
2	R_1=R_2=Ph	$HSiPh_3$	80	27	97[c]
3	R_1=R_2=Ph	$HSiPh_3$	100	2	>99
4	R_1=R_2=Ph	H_2SiPh_2	60	3	85
5	R_1=R_2=Ph	H_3SiPh	60	2	80
6	R_1=Ph, R_2=Me	$HSiPh_3$	60	2	96[c]
7	R_1=Ph, R_2=H	$HSiPh_3$	25	—	Polymerization
8	R_1=Bu, R_2=H	$HSiPh_3$	80	—	—

[a] Reaction conditions: catalyst (2.5 μmol), olefin (0.1 mmol), silane (0.11 mmol). [b] Determined by ^{1}H NMR spectroscopy. [c] Catalyst deactivation after time indicated.

Using H_2SiPh_2 or H_3SiPh shortened reaction times drastically, but decreased the yield of the desired products to 85% and 80%, respectively (Table 1, entries 4 and 5). The substrate scope of catalytic hydrosilylation was further investigated by using α-methylstyrene and styrene as substrates. The hydrosilylation of α-methylstyrene with $HSiPh_3$ yielded 96% of the product (Table 1, entry 6), whereas styrene polymerized at 25 °C within 2 min (Table 1, entry 7). The catalytic activity and selectivity of **2a** as the hydrosilylation catalyst is comparable to other calcium complexes.[19] As implied by Harder *et al.* earlier,[19a] the catalytic cycle involves insertion of DPE into the calcium silicon bond to give an alkyl as exemplified by the formation of **4**, which then undergoes reaction with $HSiPh_3$ to give the silyl and the hydrosilylated product. Noteworthy is the fact that formally silane acts as a Brønsted acid rather than a latent silylium ion with reversed polarity of the silicon–hydrogen bond. Therefore neither oxidative addition following the Chalk–Harrod mechanism nor a hydride mechanism as known for lanthanides takes place here.[20]

Finally, **2a** reacted with an excess of pyridine within 5 min selectively to give 4-triphenylsilylpyridine and bis(1,4-dihydro-1-pyridyl)calcium (**5**), which were characterized by ^{1}H NMR spectroscopy (Scheme 2). A fast silylation at the *ortho* position of pyridine followed by rearrangement generates the 1,4-insertion product. Re-aromatization upon calcium hydride formation, instead of the C–H bond activation reported for pyridine derivatives,[21] gave 4-triphenylsilyl pyridine. This compound was reported by Gilman *et al.* previously as the product of the reaction of triphenylsilyl lithium with an excess of pyridine.[22] The calcium hydride formed reacted with pyridine to give **5**. Such a reactivity pattern is known for magnesium and zinc hydrides[23] and seems to apply for calcium hydride **3** as well.

In conclusion, earth alkaline metal silyl **2a** was synthesized by salt metathesis and characterized by spectroscopic, crystal diffraction and computational methods. It catalyzes the hydrosilylation of activated olefins, supporting the active role of calcium silyls in this catalysis. Furthermore, **2a** activates dihydrogen under mild conditions and undergoes with pyridine a dehydrogenative silylation. This reactivity pattern reflects the rather unique polarization of the calcium–silicon bond.

We thank the Cluster of Excellence RWTH Aachen "Tailor-Made Fuels from Biomass" for financial support and the Alexander von Humboldt Foundation for a fellowship to L.M.

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