Samarium-mediated redistribution of silanes and formation of trinuclear samarium–silicon clusters

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The samarium complex $Cp^*_2SmCH(SiMe_3)_2$ (Cp^* = C_5Me_5), unlike the related alkyls $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Y, Nd), mediates the redistribution of hydrosilanes while being converted to trisamarium clusters, including $Cp^*_6Sm_3(\mu\text{-}SiH_3)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}SiH_2SiH_2)$.

Lanthanide–silicon chemistry is an emerging area with considerable potential, as indicated by recent reports which describe lanthanide-catalysed silane dehydrocouplings[1] and hydrosilylations.[2] The development of this area has undoubtedly been slowed by the scarcity of lanthanide–silicon bonded compounds available for reactivity studies.[3] We have recently reported a σ-bond metathesis route to isolable lanthanide silyl derivatives $Cp^*_2LnSiH(SiMe_3)_2$ (Ln = Y, Nd, Sm), which occurs by an autocatalytic reaction of alkyl complexes $Cp^*_2LnCH(SiMe_3)_2$ with $H_2Si(SiMe_3)_2$.[4] In investigating the reactivity of lanthanide alkyls toward other silanes, we have also observed silane dehydrocoupling[4a–c] and silyl–alkyl coupling.[4a,b] Here, we report a new type of transformation resulting from interaction of a silane with a lanthanide alkyl complex, which leads to redistribution at silicon and formation of novel samarium–silicon clusters.

Reaction of $Cp^*_2SmCH(SiMe_3)_2$[5] **1** with $PhSiH_3$ (1 equiv.) in [$^2H_6$]benzene occurs rapidly after a variable induction time (5–20 min)† to produce a deep red solution. By ^1H NMR spectroscopy, this reaction gives a quantitative yield of $CH_2(SiMe_3)_2$, along with H_2 (26%), $PhSiH_2\text{–}SiH_2Ph$ (11%), Ph_2SiH_2 (46%), and Ph_3SiH (trace). Quantitative transfer of deuterium label from $PhSiD_3$ to the alkyl group [to produce $CHD(SiMe_3)_2$] implies that the first step in the reaction is formation of $Cp^*_2SmSiH_2Ph$, but this species has not been identified as an intermediate. Similar distributions of products are observed for reactions of $PhSiH_3$ with **1**, $[Cp^*_2SmH]_2$,[5,6] $Cp^*_2SmSiH(SiMe_3)_2$,[4] and Cp^*_2Sm.[7] Complex **1** reacts slowly with Ph_2SiH_2 (1 equiv., [$^2H_6$]benzene, 22 °C) *via* redistribution at silicon, to give Ph_3SiH (10% after 2 d at 25 °C) and unidentified silicon-containing compounds, but no $PhSiH_3$ or $Ph_2HSi\text{–}SiHPh_2$. In contrast, related alkyl complexes $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Y, Nd) react with $PhSiH_3$ (1 equiv., [$^2H_6$]benzene) to produce only dehydrocoupling products [$CH_2(SiMe_3)_2$, Cp^*_2LnH, PhH_2SiSiH_2Ph, and higher silane oligomers].[4c]

The appearance of redistribution products in the reaction of **1** with $PhSiH_3$ is accompanied by formation of one major Cp^*_2Sm-containing product (**2**; 64%) giving rise to a ^1H NMR resonance for the Cp* ligands at δ 1.01 ([$^2H_6$]benzene). This species is unstable and cleanly converts within 1 h to a second complex (**3**), which displays two Cp^*_2Sm resonances in the ^1H NMR spectrum, at δ 0.86 and 1.04 (1 : 1; coalescence temp. 75 °C). Based on the presence of a ν(SiH) stretching frequency at 1988 cm^{-1} ([$^2H_6$]benzene solution) and the absence of ^1H NMR resonances for Ph groups, **2** appears to be a simple hydrosilyl derivative of samarium.[4,8] The ^{13}C NMR resonances for the inequivalent Cp* ligands of **3** (δ 20.01, 20.61, 116.33, 116.92) characterize this complex as possessing only Sm^{III} centres.[9] Treatment of **3** with benzoic acid produced a mixture of both SiH_4 and Si_2H_6 (1 : 0.7); it is likely that at least some disilane results from dehydrocoupling between SiH_4 and $Sm\text{–}SiH_3$ species.[10]

Crystals from reaction of **1** with Ph_2SiH_2 (1 equiv.) in [$^2H_6$]benzene over 2 d contain the trisamarium cluster **4** shown in Fig. 1.‡ This cluster possesses a planar Sm_3Si_3 core, and lies on a crystallographic twofold axis that passes through Sm(1) and Si(2). The Sm–Si distances in this molecule [Sm(1)–Si(1) 3.174(4), Sm(2)–Si(1) 3.093(4), Sm(2)–Si(2), 2.954(2) Å] are similar to the corresponding distance of 3.052(8) Å in $[Cp^*_2SmSiH(SiMe_3)_2]_2$,[4a] despite the unsubstituted nature of the Si centres. Hydrogen atoms on the silicons were not located, but based on the reasonable assumption that the cluster contains only Sm^{III} centres (see above) we can conclude that the ligands present are $\mu\text{-}SiH_3$ and $\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}SiH_2SiH_2$ (Scheme 1). The Si(1)–Si(1A) distance of 2.458(7) Å is consistent with a long Si–Si single bond. Typical Si–Si single bond lengths are 2.34–2.37 Å,[11] but steric elongation can lead to distances as high as 2.70 Å.[12] The bonding in this cluster may be characterized as electron deficient and involving a number of 'noncovalent' Sm···Si and/or Sm···H–Si interactions.

As described above, the reaction of **1** with $PhSiH_3$ is rather complex, and produces a number of soluble silane products. The red insoluble product from this reaction could be obtained as X-ray quality crystals only after repeated attempts, by allowing crystals to grow slowly from reaction mixtures produced by layering toluene solutions of the two reactants. Red crystals that grew over 12 h are disordered, and appear to result from cocrystallization of three trisamarium clusters, including **4**.‡ Although this disorder is rather severe, it is clear that the crystals contain the trimeric samarium silyl **5**. Furthermore, modelling of the disorder led to a final description of the structure as consisting of a solid solution of *three* trisamarium clusters **4**–**6** in a ratio of 1 : 5 : 4 (Scheme 2, Fig. 2).

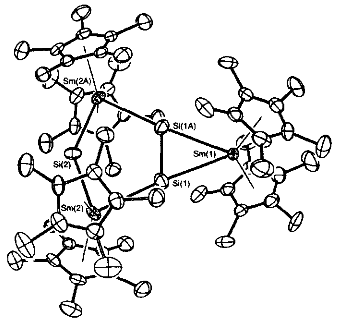
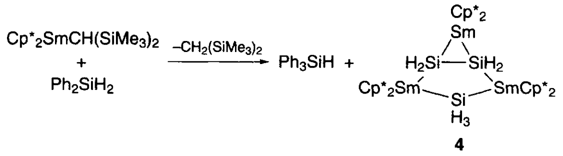


Fig. 1 ORTEP view of the molecular structure of **4** with thermal ellipsoids at the 35% probability level

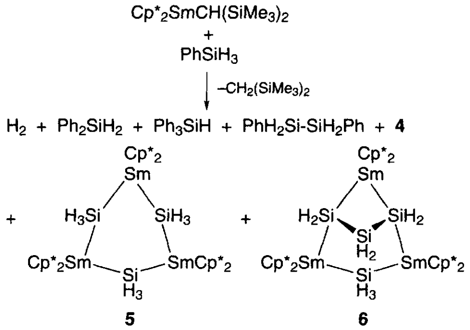


Scheme 1

Further support for this model was obtained by the structure analysis of a second crystal, obtained under similar conditions. This crystal exhibited the same disorder of compounds **4**–**6**, but with a different ratio of products (**4**:**5**:**6** = 4:5:11). Although the bond distances obtained from these structures are of limited reliability given the degree of disorder, it is apparent that the parameters derived for **4** in the disordered structure [*e.g.* Sm(1)–Si(4) 3.138(6) Å, Sm(2)–Sm(4) 3.15(4), Sm(2)–Si(2) 3.155(3), Si(4)–Si(4′) 2.37(9)] are in agreement with those obtained from the pure crystal. For **5**, the independent Sm–Si bond distances are 3.138(6), 3.134(6) and 3.155(3) Å. For **6**, additional disorder resulting from six possible orientations for the bridging $H_2SiSiH_2SiH_2$ group appears to introduce significant uncertainty into the Si–Si distances, which have values between 2.03(6) and 2.38(3) Å.

The redistribution of $PhSiH_3$ appears to rapidly produce an $Sm–SiH_3$ species which crystallizes in trimeric form as sparingly soluble **5**. Clusters **4** and **6** likely result from dehydrocoupling reactions of $Sm–SiH_3$ derivatives and/or SiH_4.[10] Different hydrogen contents for the reacting silanes ($PhSiH_3$ *vs.* Ph_2SiH_2) lead to different distributions of products in the two reactions, with the more hydrogen-limited substrate (Ph_2SiH_2) giving the least hydrogenated cluster **4**.

The redistribution of silanes is catalysed by acids or bases.[14] Thus, the reactions described here may be catalysed by samarium hydride or Lewis-acidic Sm centres, but this seems unlikely given the failure of related lanthanide complexes to mediate the same process. Alternatively, electron-transfer steps may be involved, and this is suggested by the available 3+/2+ redox chemistry for samarium[14] and the fact that Cp^*_2Sm redistributes $PhSiH_3$. Interestingly, the $PhSiH_3^-$ radical anion decomposes *via* the redistribution of phenyl groups at silicon.[15] Note, however, that the reactions of Cp^*_2Yb[16] and $[Cp^*_2YbMe]_2$[17] with $PhSiH_3$ do not lead to redistribution.[17] Other observations support the possible involvement of radical processes in reactions of **1** with silanes. For example, **1** reacts with $HSi(SiMe_3)_3$ to give $Cp^*_2SmSiH(SiMe_3)_2$ and Me_3Si-$SiMe_3$, and with $PhCH_2SiH_3$ to give **3**, $CH_2(SiMe_3)_2$ (85%) and $PhCH_3$ (100%), but no bibenzyl. The mechanism of this redistribution chemistry is currently under investigation.



Scheme 2

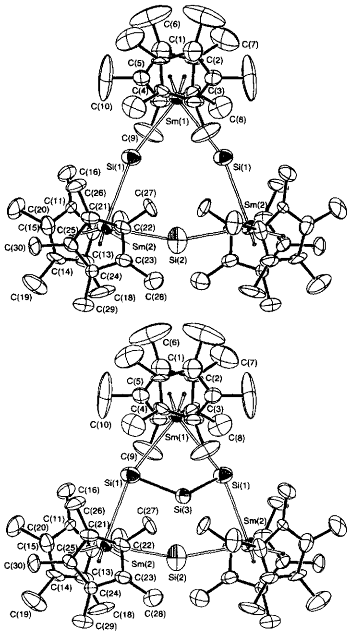


Fig. 2 ORTEP views of **5** (above) and **6** (below) in the disordered crystals containing **4**, **5**, and **6**, thermal ellipsoids represent the 50% probability surfaces

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Footnotes

† Other reactions of **1** with silanes have been characterized as possessing an induction time which precedes autocatalysis.[4c,d]

Crystal data, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/237.

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