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Barium siloxides and catalysed formation of Si-O-Si' motifs

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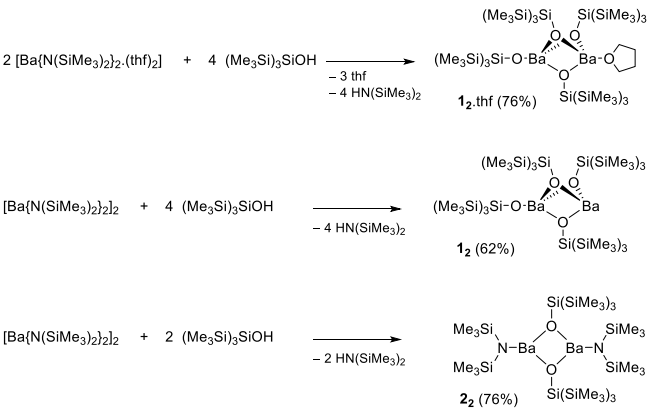
Abstract: The first unsupported barium siloxide, the homoleptic dimer $[Ba_2\{\mu_2\text{-}OSi(SiMe_3)_3\}_3\{OSi(SiMe_3)_3\}]$, is presented, and its structural features are discussed in the light of DFT computations. This complex, together with the related $[Ba\{\mu_2\text{-}OSi(SiMe_3)_3\}\{N(SiMe_3)_2\}]_2$ and their parent $[Ba\{N(SiMe_3)_2\}_2]_2$, mediate the formation of asymmetric siloxanes $R_3Si\text{-}O\text{-}SiR'_3$ through the first case of main group metal-mediated dehydrocoupling of silanols and hydrosilanes. Early kinetic analysis highlights an unusual catalytic manifold.

Molecular alkaline-earth (Ae = Ca, Sr, Ba) alkoxides and fluoroalkoxides have been employed as useful precursors for deposition of metal oxide or fluoride thin films.[1,2] More recently, they have also been used as effective ring-opening polymerisation catalysts.[3] Yet, the π-donating ability of alkoxides combined to the hard, oxophilic nature of Ae metals often leads to the formation of multinuclear or ill-defined alkoxides of limited solubility or volatility. The propensity to produce aggregates increases upon descending group 2, and is particularly pronounced for the very large (1.35 Å) Ba^{2+} cation. It generates complexes where bonding is essentially ionic, and where coordination numbers often reach 8 or more. While a number of heterobimetallic barium alkoxides species are also known,[4] homometallic Ba-alkoxides are scarce and form aggregates, e.g. $[Ba_5(Omesityl)_5(OMe)_5(dme)_4]\cdot dme$.[5] Some other derivatives of Ba-alkoxides of low nuclearity have also been reported, e.g. two-coordinate Ba-boryloxides that catalyse the dehydrocoupling of hydrosilanes and borinic acids.[6] Some Ba-siloxides also exist. Yet, they are either stabilised by solvent or macrocyclic donors, as in $[Ba_3(OSiPh_3)_6.thf].(thf)_{1/2}$,[7] $[Ba(OSiPh_3)_2(15\text{-crown-5}).thf]$[8] $[Ba_2(OSi\textit{t}Bu_3)_4.thf]$,[9] and $[Ba_3(OSiPh_2OSiPh_2O)_3(tetraglyme)_2]$,[10] or the siloxide is the anionic part of a multidentate ligand.[11-12] To our knowledge, no occurrence of solvent-free, unsupported Ba-siloxide is known to date.

Metal-mediated dehydrocoupling catalysis, notably for the dehydrogenation of amine-boranes,[13-15] has been attracting sustained interest. Ae complexes provide effective catalysts for these reactions.[16] They also enable the formation of silazanes through N-H/H-Si heterodehydrocoupling,[17-20] and that of borasiloxanes from BO-H/H-Si coupling.[6] Yet, metal catalysts, and *a fortiori* Ae-based ones, have seldom been implemented in the controlled production of siloxanes, despite the commercial importance of oligo- and polysiloxanes.[21-22] Asymmetric $R_3Si\text{-}O\text{-}SiR'_3$ siloxanes can be prepared by conventional condensations involving a silanol (with a base) or a metal silanolate and a halosilane R_3SiX, but these protocols generate large amounts of waste by-products.[23] Instead, a handful of catalysed processes relying on late transition metals are known. Rhodium(I) compounds[24] and $[AuCl(PPh_3)]$[25] catalyse the coupling of tertiary silanols with hydrosilanes. $[Ru_3(CO)_{12}]$ allows the one-pot functionalisation of polyhedral oligomeric silsesquioxanes (POSS) upon coupling of hydrosilanes with POSS-silanols.[26] In addition, the coupling of silanols with alkoxysilanes promoted by $B(C_6F_5)_3$ also yields siloxanes[27-28] and can be used to synthesise oligosiloxanes.[29-30]

As part of our programme aimed at implementing Ae metals complexes in molecular catalysis as an alternative to expensive transition metals, we describe here the first examples of unsupported, soluble barium-siloxides. Structural features are examined in the light of DFT computations. The utilisation of these main group metal complexes to catalyse the selective formation of asymmetric siloxanes is discussed, along with preliminary kinetic insight.

The reaction of $[Ba\{N(SiMe_3)_2\}_2.(thf)_2]$ with two equivalents of the bulky silanol $(Me_3Si)_3SiOH$[31] afforded the dinuclear thf adduct $[Ba_2\{OSi(SiMe_3)_3\}_4.thf]$ (**1₂**.thf, Scheme 1). This compound, which only contains one molecule of coordinated thf for two Ba cations, was characterised by NMR spectroscopy. The ^1H NMR spectrum recorded in benzene-d_6 indicates that the thf molecule remains bound to a metal in this solvent (δ_{1H} = 3.40 and 1.30 ppm).



Scheme 1. Synthesis of barium-siloxides (reactions in petroleum ether, 20 °C).

Single crystals of **1₂**.thf were analysed by X-ray diffraction methods. Although the refined XRD structure of the compound is crippled by excessive anisotropy for some methyl groups (see the SI), the connectivity was established without ambiguity. The complex exists as a dimer bridging by three $O_{siloxide}$ atoms, with an

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additional terminal siloxide moiety on one barium, and a capping thf molecule on the other one. Both Ba atoms are four-coordinate. The structure recalls that established for $[Ba_2(OSi\textit{t}Bu_3)_4.thf]$.[9]

The targeted solvent-free homoleptic complex, $[Ba_2\{\mu_2\text{-}OSi(SiMe_3)_3\}_3\{OSi(SiMe_3)_3\}]$ (**1₂**), was obtained upon reaction of $[Ba\{N(SiMe_3)_2\}_2]_2$ with $(Me_3Si)_3SiOH$. It was reproducibly isolated as colourless crystals in a non-optimised 60-65% yield after recrystallisation. In benzene-d_6, compound **1₂** gives rise to single resonances at δ_{1H} = 0.35 ppm and δ_{13C} = 1.76 ($^1J_{Si\text{-}C}$ = 41 Hz) ppm in its ^{1}H and ^{13}C{^{1}H} NMR spectra. The ^{29}Si{^{1}H} NMR spectrum is characterised by two resonances at δ_{29Si} = –19.37 (major) and –27.02 (minor) ppm, assigned respectively to Si(*Si*Me$_3$)$_3$ and *Si*(SiMe$_3$)$_3$ atoms.[31] The molecular solid-state structure of **1₂** is depicted in Figure 1 (one of the four independent but very similar molecules in the asymmetric unit represented). The complex forms a C_3-symmetric dimer. The overall arrangement resembles that in **1₂**.thf, except for the absence of thf at Ba1. There are hence three bridging siloxides, and a single terminal one, with non-equivalent barium atoms: one (Ba1) is formally three-coordinate, while the other (Ba2) is four-coordinate. Atypically for barium, the geometry about Ba1 is trigonal pyramidal. The interatomic distances and angles around Ba1 are commensurate with those in $[Ba_2(OSi\textit{t}Bu_3)_4.thf]$.[9] Short intra- and intermolecular Ba1-H interatomic distances are present in **1₂** (Figure 2). This suggests the existence of Ba1···H-C agostic interactions and formation of monodimensional coordination polymers, although spectroscopic evidence could not be found to support this picture. These interactions bring steric protection and electronic density to the otherwise accessible Ba1 metal atom; by comparison, the pertaining coordination site is occupied by a thf molecule in **1₂**.thf.

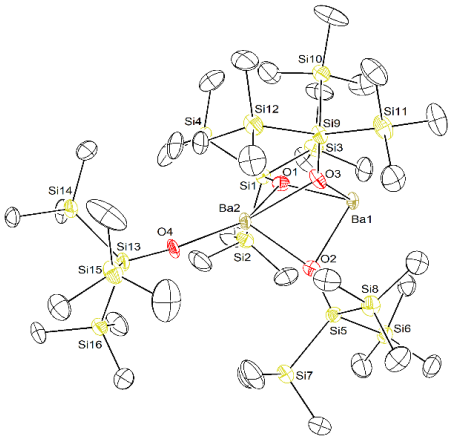


Figure 1. ORTEP view of the molecular solid-state structure of $[Ba_2\{\mu_2\text{-}OSi(SiMe_3)_3\}_3\{OSi(SiMe_3)_3\}]$ (**1₂**). Only one of the four similar molecules in the asymmetric unit is depicted. H atoms omitted for clarity. Ellipsoids at the 50% probability level. Representative interatomic distances (Å) and angles (°): Ba1-O3 = 2.477(8), Ba1-O1 = 2.509(8), Ba1-O2 = 2.514(7), Ba2-O4 = 2.414(7), Ba2-O2 = 2.612(8), Ba2-O1 = 2.673(7), Ba2-O3 = 2.719(7); O3-Ba1-O1 = 82.00(2), O3-Ba1-O2 = 79.00(2), O1-Ba1-O2 = 78.80(2), O4-Ba2-O2 = 125.80(3), O4-Ba2-O1 = 138.30(3), O2-Ba2-O1 = 74.20(2), O4-Ba2-O3 = 142.10(3), O2-Ba2-O3 = 73.10(2), O1-Ba2-O3 = 74.70(2), Si13-O4-Ba2= 173.50(5).

The geometry about Ba2 forms a distorted tetrahedron (τ_4 = 0.56).[32] The Ba2-O_{bridge} distances to bridging O-atoms (2.612(8)-2.719(7) Å) are substantially longer than the Ba1-O_{bridge} ones (2.477(8), 2.509(8) Å). The Ba2-O4 bond length to the terminal siloxide (which is nearly linear, Si13-O4-Ba2= 173.50(5) °) of 2.414(7) Å is much shorter.

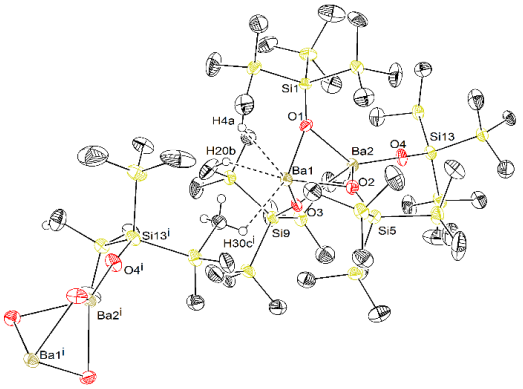


Figure 2. ORTEP representation of the molecular solid-state structure of $[Ba_2\{\mu_2\text{-}OSi(SiMe_3)_3\}_3\{OSi(SiMe_3)_3\}]$ (**1₂**), showing intra- and intermolecular Ba···H-C interactions as dashed lines. Non-interacting H atoms not shown. Interatomic distances (Å): Ba1-H4a = 2.7447(6), Ba1-H20b = 2.7859(9), Ba1-H30c^i = 2.8762(6). Symmetry operations: -x, y+1/2, -z.

$[Ba\{\mu_2\text{-}OSi(SiMe_3)_3\}\{N(SiMe_3)_2\}]_2$ (**2₂**), a mixed siloxo/amido complex,[33] was isolated in 76% yield as colourless single crystals by reacting $[Ba\{N(SiMe_3)_2\}_2]_2$ with one equivalent of $(Me_3Si)_3SiOH$. The NMR data for **2₂** recorded in benzene-d_6 are unremarkable, other than the fact that each bridging siloxide gives rise to its own set of resonances in ^{1}H, ^{13}C{^{1}H} and ^{29}Si NMR spectroscopy (see SI). The complex crystallised as a dimer bridged by siloxo ligands (Figure 3, C_1-symmetry). Each of the non-equivalent barium atoms is three-coordinate, in a geometry between trigonal pyramidal and trigonal planar. The Ba1-$O_{siloxide}$ and Ba2-$O_{siloxide}$ interatomic distances, in the range 2.549(5)-2.612(5) Å, average those found in **1₂**. There is no indication for the presence of Ba···H-C agostic contacts in the solid-state structure of **2₂**. The Ba1-N1 and Ba2-N2 distances (2.600(7) and 2.607(6) Å) are slightly longer than in $[Ba\{N(SiMe_3)_2\}_2]_2$ (2.576(3) Å),[34] the only other three-coordinate barium complex with a terminal $N(SiMe_3)_2^-$ amide in the CCDC database. This presumably reflects the steric constraint imposed by the bulky siloxide $(Me_3Si)_3SiO^-$.

The DFT-optimised[35] geometries for **1₂**.thf, **1₂** and **2₂** are fully consistent with their X-ray structures (Tables S35 and S36). Interestingly, that of **1₂** displays weaker Ba1···H interactions than suggested by XRD analysis, with only one Ba1···H contact (2.90 Å) lower than 3.1 Å, suggesting moderate unsaturation for Ba1. This is supported by the near-identical natural atomic orbital (NAO) charges of Ba1 and Ba2 (resp. +1.88 and +1.87) and by the non-negligible HOMO-LUMO gap of 4.28 eV (**1₂**.thf: 4.49 eV; **2₂**: 5.21 eV). The LUMO of **1₂** can be viewed as an sp^3 hybrid on Ba1 (Figure S33). This accepting orbital is involved in the bonding with thf in **1₂**.thf (bonding energy = 19.1 kcal·mol^{-1}). The electrostatic potential of **1₂** (Figure S34) indicates also strong electrophilicity at Ba1. Surprisingly, the hypothetical symmetrical isomer of **1₂**, $[Ba\{\mu_2\text{-}OSi(SiMe_3)_3\}\{OSi(SiMe_3)_3\}]_2$ (**1₂'**, Figure S35), is 13.7 kcal·mol^{-1} less stable than **1₂**.

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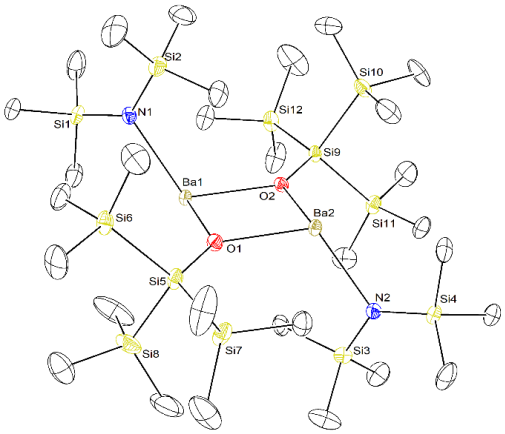
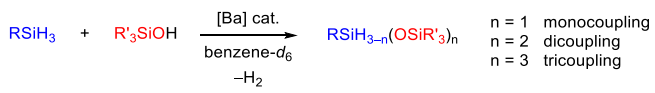


Figure 3. ORTEP representation of the molecular solid-state structure of [Ba{μ$_2$-OSi(SiMe$_3$)$_3$}{N(SiMe$_3$)$_2$}]$_2$ (**2$_2$**). Only the main component of the disordered SiMe$_3$ group (Si7) is depicted. H atoms omitted for clarity. Ellipsoids at the 50% probability level. Representative interatomic distances (Å) and angles (°): Ba1-O2 = 2.557(5), Ba1-N1 = 2.600(7), Ba1-O1 = 2.610(5), Ba2-O1 = 2.549(5), Ba2-N2 = 2.607(6), Ba2-O2 = 2.612(5); O2-Ba1-N1 = 116.76(19), O2-Ba1-O1 = 80.42(15), N1-Ba1-O1 = 114.93(19), O1-Ba2-N2 = 117.18(19), O1-Ba2-O2 = 80.52(16), N2-Ba2-O2 = 114.85(18).

The OSi(SiMe$_3$)$_3$ ligand indeed prefers to bind in bridging rather than in terminal fashion, despite the constrained pyramidal coordination at Ba1 in **1$_2$**. The bonding energy of this ligand to the rest of the molecule is 38.3 kcal·mol^{-1} stronger in **1$_2$** than in **1$_2$**'. Only part of this energy gain is lost in the unfavourable pyramidalisation of Ba1, so that **1$_2$** is the most stable isomer.

Complexes **1$_2$**, **2$_2$** and the parent [Ba{N(SiMe$_3$)$_2$}$_2$]$_2$ were used to catalyse the dehydrocoupling of hydrosilanes R$_3$SiH with silanols R'$_3$SiOH and deliver asymmetric siloxanes R$_3$Si-O-SiR'$_3$ (Scheme 2).[36] All reactions were run in benzene-d_6 at 30 °C unless otherwise specified. The products were all characterised by NMR and HRMS (see SI). In a benchmark reaction, all (pre)catalysts mediated with similar efficacy and full selectivity the formation of Ph$_2$HSiOSi(SiMe$_3$), starting from Ph$_2$SiH$_2$ and (Me$_3$Si)$_3$SiOH (1:1). All subsequent reactions were carried out with the most synthetically convenient precatalyst, [Ba{N(SiMe$_3$)$_2$}$_2$]$_2$. The coupling of (*p*-X-C$_6$H$_4$)SiH$_3$ (X = MeO, Me, H, F) with (Me$_3$Si)$_3$SiOH is quantitative and chemoselective in 4 h ([SiOH]$_0$/[SiH]$_0$/[Ba]$_0$ = 50:50:1 with [Ba]$_0$ = 1.8 mM), affording solely the monocoupled products (*p*-X-C$_6$H$_4$)H$_2$SiOSi(SiMe$_3$)$_3$. Traces of (*p*-X-C$_6$H$_4$)H$_{3-n}$Si{OSi(SiMe$_3$)$_3$}$_n$ (n = 2 or 3), i.e. the di- and tricoupled species arising from putative consecutive reactions, could not be detected by NMR. Besides, with PhSiH$_3$, the mono-coupled PhH$_2$SiOSi(SiMe$_3$)$_3$ was still the only product when the reactions were performed with a 2:1 or 3:1 excess of silanol vs. hydrosilane, after 12-24 h at 30-60 °C. The coupling of PhSiH$_3$ with ^{t}Bu$_3$SiOH ([SiOH]$_0$/[SiH]$_0$/[Ba]$_0$ = 50:50:1) returned quantitatively the monocoupled PhSiH$_2$OSi^{t}Bu$_3$ after 4 h.



Scheme 2. Ba-mediated dehydrocoupling of hydrosilanes and silanols.

On the other hand, the reaction with Ph$_3$SiOH was more sluggish and less selective: hydrosilane conversion only reached 67% after 24 h yielding an equimolar mixture of PhH$_2$SiOSiPh$_3$ and the dicoupled PhHSi(OSiPh$_3$)$_2$.[37]

Ph$_2$SiH$_2$ is also a suitable substrate, affording within 4 h full and selective conversion to Ph$_2$HSiOSi(SiMe$_3$)$_3$ upon coupling with (Me$_3$Si)$_3$SiOH ([SiOH]$_0$/[SiH]$_0$/[Ba]$_0$ = 50:50:1). ^{n}BuSiH$_3$ reacted also near quantitatively, but more slowly than Ph$_2$SiH$_2$ (see also below). Et$_2$SiH$_2$ and Et$_3$SiH did not react under the same conditions, indicating that alkylsilanes are less reactive than arylsilanes. Moreover, it proved impossible to engage Ph$_3$SiH (or Et$_3$SiH) in effective couplings with (Me$_3$Si)$_3$SiOH, either at 30 or 60 °C. The reactivity of the hydrosilanes hence appears to decrease with increasing substitution: ArSiH$_3$ > Ar$_2$SiH$_2$ > ^{n}BuSiH$_3$ > Ar$_3$SiH, Et$_2$SiH$_2$, Et$_3$SiH. Finally, the generation of PhHSi(OSiR'$_3$)$_2$ or PhSi(OSiR'$_3$)$_3$ by consecutive couplings starting from PhSiH$_3$ was not selective: with excess R'$_3$SiOH vs PhSiH$_3$, the main product remained PhH$_2$SiOSiR'$_3$.[38]

Preliminary kinetic investigations were carried out by NMR monitoring of reactions performed in benzene-d_6 (see SI). The coupling of Ph$_2$SiH$_2$ and (Me$_3$Si)$_3$SiOH that produces Ph$_2$HSi{O(SiMe$_3$)$_3$} catalysed by [Ba{N(SiMe$_3$)$_2$}$_2$]$_2$ at 30 °C was chosen as a benchmark reaction, with [Ba]$_0$ = 1.8 mM unless otherwise specified. As mentioned, PhSiH$_3$ proved to be a substrate more reactive, less suited to kinetic monitoring, than Ph$_2$SiH$_2$ (k_{app} = 6.42(10)·10^{-4} and 7.02(9)·10^{-5} s^{-1}, respectively, at 30 °C; [(Me$_3$Si)$_3$SiOH]$_0$/[silane]$_0$/[Ba]$_0$ = 100:100:1).

The benchmark reaction revealed a partial first kinetic order in [Ph$_2$SiH$_2$] and zeroth order in [(Me$_3$Si)$_3$SiOH]. However, the catalyst is inhibited by (Me$_3$Si)$_3$SiOH: reaction rates decrease substantially upon increasing [(Me$_3$Si)$_3$SiOH]$_0$ (Figure 4). For this reason, we failed to determine the partial kinetic order in [Ba]. Although rare, substrate inhibition for Ae catalysts has been documented.[39] Consistently with the observed inhibition process, we found that **1$_2$**, thought to be the active species in the catalytic manifold, easily binds (Me$_3$Si)$_3$SiOH to return **1$_2$**.(Me$_3$Si)$_3$SiOH. The identity of this adduct was confirmed by XRD analysis, but high disorder over SiMe$_3$ sites prevented satisfactory refinement. Arrhenius analysis ([(Me$_3$Si)$_3$SiOH]$_0$/[Ph$_2$SiH$_2$]$_0$/[Ba]$_0$ = 100:100:1, 20 °C < T < 60 °C) provided E_a = 15.0(6) kcal mol^{-1}, a value consistent with the observed kinetically facile catalytic process.[40]

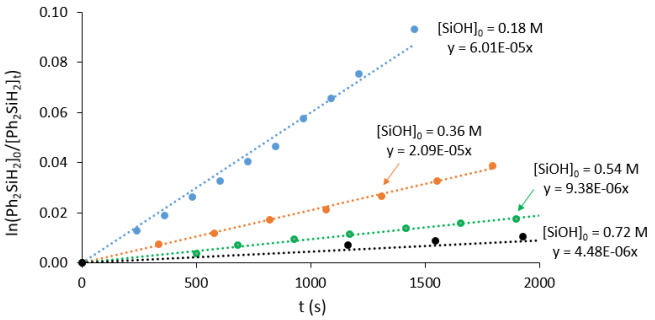


Figure 4. Semi-logarithmic plot of Ph$_2$SiH$_2$ conversion in the dehydrocoupling of Ph$_2$SiH$_2$ and (Me$_3$Si)$_3$SiOH catalysed by [Ba{N(SiMe$_3$)$_2$}$_2$]$_2$, with up to a 3-fold excess of silanol vs hydrosilane ([SiOH]$_0$/[SiH]$_0$/[Ba]$_0$ = X:100:1, benzene-d_6, 30 °C, [Ba]$_0$ = 1.8 mM, X = 100-400). Decreasing reaction rates (10^6·k_{app} = 60.1, 20.9, 9.38 and 4.48 s^{-1} for X = 100, 200, 300 and 400) with increasing [(Me$_3$Si)$_3$SiOH]$_0$ indicate catalyst inhibition by the silanol.

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Under identical conditions ($[(Me_3Si)_3SiOH]_0/[Ph_2SiH_2]_0/[Ba]_0$ = 100:100:1, 30 °C), the thf-adduct $[Ba\{N(SiMe_3)_2\}_2.(thf)_2]$ and $[Ba\{N(SiMe_3)_2\}_2]_2$ displayed equal efficacy, k_{app} = 6.08(2)·10^{-5} and 7.02(9)·10^{-5} s^{-1}. The presence of coordinated thf in the precatalyst is therefore not detrimental to the reaction rate.[41] The complexes $[Sr\{N(SiMe_3)_2\}_2]$ and $[Ca\{N(SiMe_3)_2\}_2]$ built around the smaller Ae elements were inactive under these conditions. With the more reactive substrate $PhSiH_3$, they showed a lower activity (resp. k_{app} = 2.10(4)·10^{-4} and 2.31(4)·10^{-5} s^{-1}) than $[Ba\{N(SiMe_3)_2\}_2]_2$ (6.41(10)·10^{-4} s^{-1}), hence giving the trend Ca<<Sr<Ba. The rates of couplings between (p-X-C_6H_4)SiH_3 (X = MeO, Me, H, F) and $(Me_3Si)_3SiOH$ catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ augmented with electron-withdrawing groups, and decreased with electron-donating ones: OMe<Me<H<F; ^{n}BuSiH$_3$ was slower than the least reactive of these *para*-functionalised arylhydrosilanes.[42] This reactivity trend suggests the presence of a negative charge localised on the $Si_{hydrosilane}$ atom in the rate-limiting step and stabilised by electron-withdrawing substituents. The kinetic data gathered so far agree with a mechanism involving nucleophilic attack of the Ba-bound $O_{siloxide}$ atom onto the incoming hydrosilane, thus generating a pentavalent hydrosilicate. Such scenario is akin to that established for the Ba-catalysed formation of silazanes[18] and borasiloxanes,[6] but further investigations are required to support this working hypothesis.

In summary, we have prepared unsupported Ba-siloxides, including the unusual $[Ba_2\{\mu_2\text{-}OSi(SiMe_3)_3\}_3\{OSi(SiMe_3)_3\}]$. This complex and its amido parent $[Ba\{N(SiMe_3)_2\}_2]_2$ catalyse the fast and chemoselective dehydrocoupling of silanols and hydrosilanes to create asymmetric siloxanes with minimal release of by-products (H_2). This catalysis is most effective with Ba, while Sr and even more so Ca are less efficient. We are now working on expanding the substrate scope for this process, and on delineating its operative mechanism. However, mechanistic investigations are hampered by catalyst inhibition by the silanol substrate.

Keywords: barium • siloxide • asymmetric siloxanes • dehydrocoupling catalysis • low-coordinate complex

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[35] PBE0/Def2-TZVP-D3 level. See computational details in the SI.
[36] Couplings do not occur without barium (pre)catalyst.
[37] With Ph_3SiOH, dehydrocouplings are plagued by the formation of $Ph_3SiOSiPh_3$ generated upon Ba-promoted dehydration of the silanol.
[38] For instance, the reaction with $[(Me_3Si)_3SiOH]_0/[PhSiH_3]_0/[Ba]_0$ = 40:20:1 for 24 h at 25 °C only returned a 2:1 mixture of $PhSiH_2OSi(SiMe_3)_3$ and $PhSiHO\{Si(SiMe_3)_3\}_2$ after near-quantitative conversion of $PhSiH_3$.
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[40] Full Eyring analysis could not be performed, as we could not assess the intrinsic rate constant k owing to the uncertainty on the partial kinetic order in [Ba]. $\Delta H^{\ddagger}$ = 14.4(6) kcal·mol^{-1}, was determined unambiguously. Uncertainty concerned $\Delta S^{\ddagger}$; values of –16.8(5) and –4.3(5) cal·mol^{-1}·K^{-1} were estimated assuming partial kinetic orders of 1 or 2 in [Ba]. These values are consistent with an associative mechanism, as might be expected for such Ae-mediated dehydrocouplings, see refs [17-20].
[41] As seen in the preliminary experiments, complexes **1₂** and **2₂** (k_{app} = 6.44(7)·10^{-5} and 5.72(7)·10^{-5} s^{-1}) displayed reaction rates identical to those of these two Ba-amide precatalysts.
[42] $[(Me_3Si)_3SiOH]_0/[(p\text{-}X\text{-}C_6H_4)SiH_3]_0/[Ba]_0$ = 100:100:1, 30 °C, $[Ba]_0$ = 1.8 mM. For X = OMe/Me/H/F, $10^5 \cdot k_{app}$ = 8.83(2)/26.3(1)/64.1(1)/133.8(1) s^{-1}. For ^{n}BuSiH$_3$, k_{app} = 2.94(5)·10^{-5} s^{-1}.

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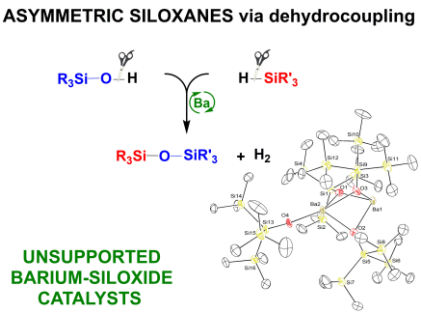
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The first unsupported barium siloxides have been structurally authenticated. They act as effective molecular catalysts for the dehydrocoupling of hydrosilanes with silanols to generate asymmetric siloxanes $R_3Si\text{-}O\text{-}SiR'_3$.



Erwann Le Coz, Samia Kahlal, Jean-Yves Saillard, Thierry Roisnel, Vincent Dorcet, Jean-François Carpentier and Yann Sarazin**

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Barium siloxides and catalysed formation of Si-O-Si' motifs

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