EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201800231

Link to VoR: http://dx.doi.org/10.1002/ejic.201800231

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Tetranuclear Strontium and Barium Siloxide/Amide Clusters in Metal-Ligand Cooperative Catalysis

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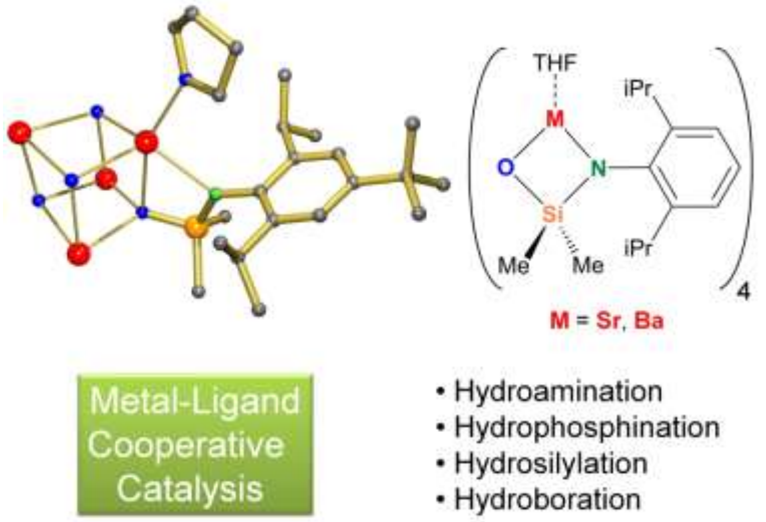
Abstract: One-pot reaction of 2,6-*i*Pr_2-aniline (DIPP-NH_2) with $(Me_2SiO)_3$ and $Sr[N(SiMe_3)_2]_2$ (SrN''_2) gave a tetranuclear cluster consisting of four dianions $[OSiMe_2N\text{-}DIPP]^{2-}$ and four Sr^{2+} ions solvated each by one THF ligand (**1**-Sr). The general applicability of this method was investigated by variation of amine and metal. Anilines with smaller substituents led to insoluble uncharacterized coordination polymers whereas bulkier anilines gave soluble product mixtures that could not be purified. Primary alkylamines neither led to isolable products. Introduction of a *t*Bu group in *para*-position of DIPP-NH_2, however, gave an isostructural cluster with increased solubility: **1**-Sr(*t*Bu). Similar clusters could be obtained with barium: **1**-Ba and **1**-Ba(*t*Bu). Both, the Sr and Ba clusters, were found to be active catalysts for a wide range of transformations: intramolecular alkene hydroamination, alkene hydrophoshination, pyridine hydroboration, pyridine hydrosilylation, and alkene hydrosilylation. The Ba catalysts were generally more active than the Sr catalysts. The *t*Bu-substituent in *para*-position also had an accelerating effect which is likely due to improved solubility.

Keywords: Alkaline Earth Metal – Strontium – Barium – Catalysis – Non-innocent ligand

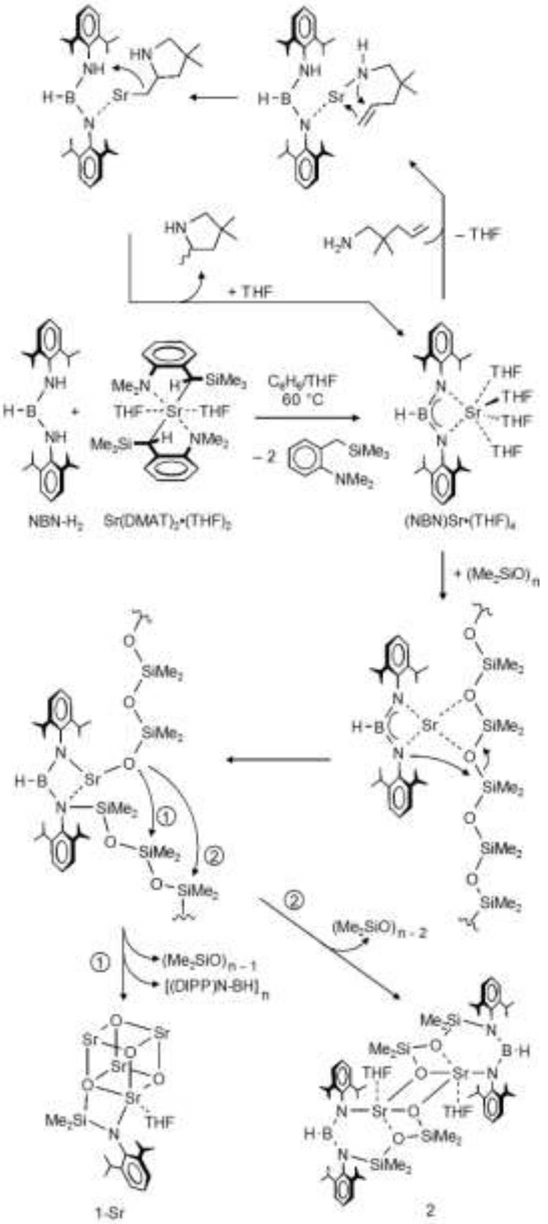
Figure for Table of Contents



Text for Table of Contents: Serendipitously obtained tetranuclear Sr and Ba clusters can now be prepared reproducibly. In various catalytic transformations, the siloxide/amide ligand combines the role of spectator and active ligand.

Introduction

Over the last decade, group 2 metal catalysis rapidly developed from obscurity to a mature field.[1] Due to the high energy of the metal's *d*-orbitals, substrate activation differs from that in transition metal catalysis.[2] The major principles, however, are similar. In both fields the catalyst L-M-R generally consists of a spectator ligand L and a reactive group R. We recently reported on the first examples of group 2 metal catalysts in which a dianionic bidentate ligand acts cooperatively.[3] *E.g.* the bora-amidinate complex (NBN)Sr·$(THF)_4$ (NBN = HB$[N(DIPP)]_2$, DIPP = 2,6-diisopropylphenyl) is active in intramolecular alkene hydroamination (Scheme 1, top). We also found that reaction of NBN-H_2 with the dibenzylstrontium reagent Sr$(DMAT)_2$·$(THF)_2$ (DMAT = *ortho*-Me_2N-α-Me_3Si-benzyl) in a Schlenk tube with well-greased joints led to the serendipitous formation of the tetranuclear strontium siloxide/amide cluster **1**-Sr that could be isolated in the form of colorless crystals in 24% yield (Scheme 1, bottom).[4] Nucleophilic depolymerization of silicone grease and insertion of the Me_2SiO-unit plays a key role in the proposed mechanism.[5] Isolation of a second product with a $(Me_2SiO)_2$-unit in traces (**2**, 3% yield) supports this mechanism. There are several more unidentified compounds present. Cluster **1**-Sr is a major product formed by self-organization which due to its high symmetry crystallized from the reaction mixture.

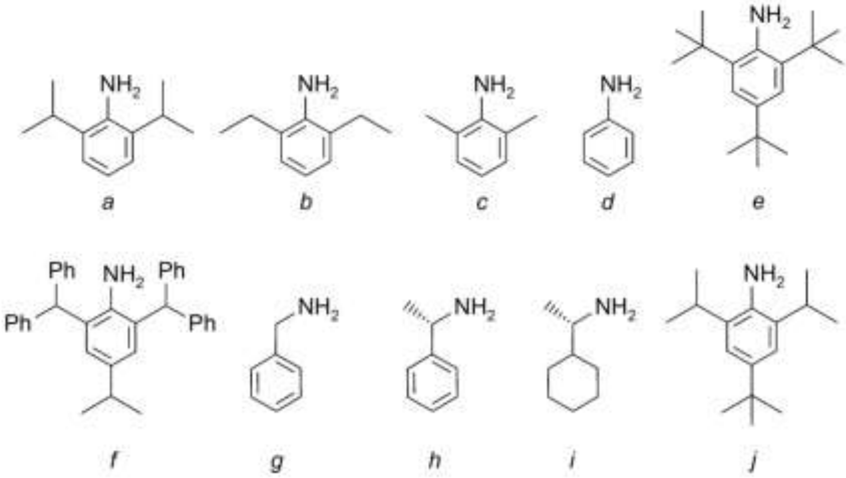


Scheme 1. Top: Synthesis of (NBN)Sr·$(THF)_4$ and use as catalyst for the intramolecular alkene hydroamination. Bottom: Proposed mechanism for the serendipitous formation of the tetranuclear strontium siloxide/amide cluster **1**-Sr (only one (DIPP)$NSiMe_2O^{2-}$ anion shown) and the minor side product **2**.

Further research showed that the strontium complex **1**-Sr can also be obtained by replacing NBN-H_2 for DIPP-NH_2, silicon grease for the siloxane $(Me_2SiO)_3$ and the dibenzylstrontium reagent Sr$(DMAT)_2$·$(THF)_2$ for the easier accessible complex Sr$[N(SiMe_3)_2]_2$, abbreviated as SrN''$_2$. Although the yields are low, the simplicity of the method tempts the question whether this synthetic method can be generalized. This could give easy access to a large variety of alkaline earth metal complexes with siloxide/amide ligands. Another quest for our current research is an evaluation of the potential of **1**-Sr and related complexes in catalysis. Similar to the NBN ligand in (NBN)Sr·$(THF)_4$, the siloxide/amide ligand in **1**-Sr could be active as a cooperative ligand in catalysis by succesively deprotonating the substrate and protonating the intermediate.
Herein we report investigations towards the generalization of the synthetic method by variation of the amine or metal. In addition, we present the use of these heavier group 2 metal complexes in a wide range of catalytic conversions.

Results and Discussion

In order to broaden the scope of the straightforward synthesis of tetranuclear strontium siloxide/amide clusters, a large variety of different anilines and some primary and secondary amines have been probed as building blocks for the one-pot self-assembly reaction (see Scheme 2). In view of the increasing interest in enantioselective group 2 metal catalysts,[6] also some chiral amines have been tested. A mixture of these anilines and amines with 0.6 equivalents of SrN''$_2$ and excess siloxane in benzene was heated to 60 °C. This method gave for the aniline DIPP-NH_2 (*a*) reproducible formation of crystalline product **1**-Sr that could be isolated by decantation. However, using the less sterically hindered anilines *b*-*d* gave powdery precipitates that were also in THF insoluble and could not be recrystallized. Characterization by X-ray diffraction or solution NMR methods was therefore not possible. Using anilines with smaller substituents apparently gave rise to formation of insoluble polymeric salt structures. In contrast, using anilines with larger substituents (*e*-*f*) did not lead to crystallization of the product (also not at lower temperatures and upon concentration of the reaction mixture or by changing the solvent). NMR investigations on raw product mixtures during synthesis indicate multiple species to be present. The formation and crystallization of **1**-Sr should therefore be regarded as a self-organization process that is easily disturbed by small changes in the sterics of the aniline precursor. Use of a primary alkyl amine like benzylamine (*g*) or the chiral secondary benzyl amines (*S*)-PhCH(Me)NH_2 (*h*) and (*S*)-CyCH(Me)NH_2 (*i*) did not lead to isolable products. Interestingly, using DIPP-NH_2 aniline with an additional *t*Bu-substituent in *para*-position (j) led to isolation of the corresponding tetranuclear cluster, which we abbreviate in here as **1**-Sr(*t*Bu), in crystalline yield of 27%. The product **1-**Sr(*t*Bu) is much better soluble in benzene than **1**-Sr. In order to maximize the yield of **1-**Sr(*t*Bu), the solvent benzene had to be replaced by *n*-hexane. Failure to isolate products from reactions with the amines *b*-*i* and the successful formation of **1-**Sr(*t*Bu) demonstrates that this convenient one-pot procedure cannot be generalized. However, changes in the periphery of aniline DIPP-NH_2 are allowed and do not disturb the self-organizing process.



Scheme 2. Variation of anilines and amines for cluster syntheses.

The crystal structure of **1**-Sr(*t*Bu) is depicted in Figure 1 and selected bond distances and angles are listed in Table 1. In contrast to the crystallographic S_4-symmetry observed for **1**-Sr (space group P-42$_1$*c*), complex **1**-Sr(*t*Bu) crystallizes in the triclinic space group *P*-1 with one tetranuclear cluster in the asymmetric unit. Despite the lack of crystallographic symmetry, the cluster displays approximate S_4-symmetry and expectedly distances and angles closely resemble those in the higher symmetric **1**-Sr (Table 1).

Fig. 1. Crystal structure of **1**-Sr(*t*Bu). (a) Hydrogen atoms and aryl substituents (except C_{ipso}) have been omitted for clarity. (b) Coordination of the siloxide/amide and THF ligands to the Sr_4O_4 cube.

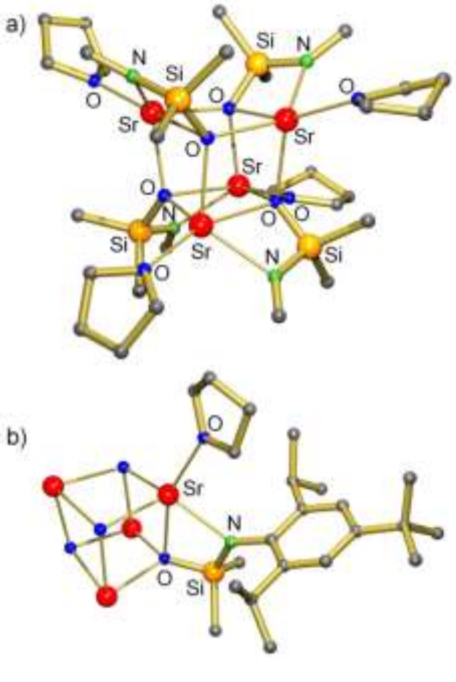


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Table 1. Selected bond distances (Å) and angles (°) for crystal structures of clusters: **1**-Sr,[4] **1**-Sr(*t*Bu), **1**-Ba and **1**-Ba(*t*Bu); range and average values between [ ].

	1-Sr	**1**-Sr(*t*Bu)	**1**-Ba	**1**-Ba(*t*Bu)
M-N	2.458(2)	2.464(2)-2.475(2) [2.461(2)]	2.602(2)	2.600(2)-2.616(2) [2.607(2)]
M-O within M-O-Si-N ring	2.674(1)	2.620(2)-2.680(2) [2.647(2)]	2.812(2)	2.805(2)-2.867(2) [2.834(2)]
M-O within M_4O_4 cube	2.428(1)-2.444(1) [2.436(1)]	2.409(2)-2.458(2) [2.435(2)]	2.570(2)-2.594(2) [2.582(2)]	2.557(2)-2.637(2) [2.585(2)]
M-O(THF)	2.544(2)	2.518(2)-2.549(2) [2.531(2)]	2.751(2)	2.735(2)-2.784(2) [2.755(2)]
Si-O	1.641(1)	1.640(2)-1.649(2) [1.646(2)]	1.640(2)	1.636(2)-1.640(2) [1.638(2)]
Si-N	1.674(2)	1.663(3)-1.690(2) [1.675(3)]	1.671(2)	1.658(2)-1.678(2) [1.669(2)]
Si-N-M	100.96(7)	98.9(1)-100.9(1) [99.7(1)]	102.1(1)	101.3(1)-102.5(1) [101.9(1)]
Si-O-M	93.68(6)	92.73(9)-94.73(9) [93.50(9)]	94.89(8)	93.45(7)-94.50(7) [94.02(8)]
O-M-N	61.09(5)	61.30(7) to 61.90(7) [94.72(7)]	57.91(6)	57.38(6) to 58.09(5) [57.80(6)]
Si-N-C^{ipso}	134.8(1)	127.6(2)-145.9(2) [135.9(2)]	141.7(2)	131.5(2)-152.2(2) [141.2(2)]
O-Si-N	104.14(8)	104.0(1) to 104.9(1) [104.5(1)]	105.0(1)	105.0(1)-106.6(1) [105.8(1)]

Although the *t*Bu substituent in *para*-position of the aniline moiety has no influence on the structure of the tetrameric cluster, complex **1**-Sr(*t*Bu) shows a markedly better solubility in THF than **1**-Sr and can even be dissolved to some extent in benzene. ^1H NMR investigations in THF reveal a remarkably simple spectrum with a single set of signals for the *i*Pr groups (one doublet, one septet), one singlet for the Me_2Si group and one aromatic singlet. This indicates a highly symmetric cluster with free rotation of the DIPP-group around the N-C_{ipso} axis. As previously discussed for **1**-Sr,[4] the tetranuclear cluster may form two different isomers (D_2 and S_4). Given the occurrence of only one signal set in the NMR spectra, it is likely that complex **1**-Sr(*t*Bu) resides also in solution only in its S_4-symmetric solid-state form but fast exchange between the D_2 and S_4 isomers cannot be excluded.

The scope of the cluster synthesis was further extended by variation of the metal. Heating DIPP-NH_2 with with 0.6 equivalents of BaN''$_2$ and excess siloxane in a mixture of benzene and THF for 2 days to 60 °C led to precipitation of colorless crystals that were isolated by decantation giving **1**-Ba in 13% yield. The crystal structure of **1**-Ba is shown in Figure 2 and selected bond distances and angles are listed in Table 1. Complex **1**-Ba crystallized similar as **1**-Sr as a tetranuclear cluster in the highly symmetric tetragonal space group $I4_1/a$ with one [($OSiMe_2N$(DIPP)]Ba·THF fragment in the asymmetric unit. Like **1**-Sr, which crystallized in the space group $P\text{-}42_1c$, cluster **1**-Ba is crystallographically S_4 symmetric. Considering a difference of 0.18 Å in the ionic radii for Sr^{2+} (1.18 Å) and Ba^{2+} (1.36 Å),[7] the Ba-O and Ba-N bond distances are shorter and the Ba-O(THF) distances longer than expected. Changing the metal from Sr to Ba has no major influence on the geometry of the ligand. The only exception is the somewhat larger Si-N-C_{ipso} angle in **1**-Ba. Complex **1**-Ba is poorly soluble in benzene but dissolves top some extent in THF-d_8. ^1H and ^{13}C NMR spectra in this solvent are essentially similar to those of **1**-Sr. Due to the high symmetry of the complex, remarkably few signals are observed (*vide supra*).

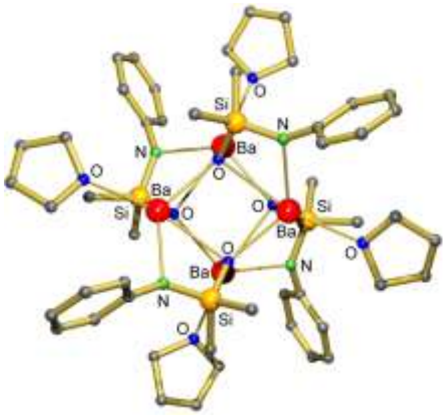

Figure 2. Crystal structure of **1**-Ba viewed along the four-fold screw axis. Hydrogen atoms and *i*Pr groups have been omitted for clarity.

Similar to **1**-Sr(*t*Bu), complex **1**-Ba(*t*Bu) could be isolated in 17 % yield. Although its crystal structure (Supplementary Information) is similar to that of **1**-Ba (see Table 1 for a comparison), the solubility of this *t*Bu-substituted complex is substantially higher. The ^{1}H and ^{13}C NMR spectra of **1**-Ba(*t*Bu) essentially match those of **1**-Sr(*t*Bu).

The ease of synthesis of the tetrameric clusters **1**-Sr, **1**-Sr(*t*Bu), **1**-Ba and **1**-Ba(*t*Bu) compensates for their generally low yields (13-35%). The metal siloxide/amide clusters reported herein may, similar to (NBN)Sr·$(THF)_4$, show catalytic activity by a metal-ligand cooperative mechanism. Therefore, these clusters were tested in a variety of catalytic transformations. The conversion times have been determined for essentially full conversion (> 99%) and products were analyzed by NMR and GC-MS (Supporting Information).

The intramolecular alkene hydroamination mediated by group 2 metal complexes has been first reported by Hill *et al.*[8] and is arguably one of the most investigated transformations.[9] It was found that the clusters **1**-Sr, **1**-Sr(*t*Bu), **1**-Ba and **1**-Ba(*t*Bu) all catalyze the ring closure of the aminoalkene $H_2NCH_2CPh_2CH_2CH=CH_2$, a substrate that generally reacts smoothly (Table 2, Entries 1-4). Although all catalysts tested reach essentially quantitative conversion, the reaction times are rather long (12-32 h). Their catalytic activity, however, is similar to that of SrN''$_2$·$(THF)_2$ (benzene, 2 mol% cat, 25 °C, 24 h, 98%).[9k] The Ba complexes are somewhat more active than the Sr complexes. The *t*Bu-substituent in the *para*-position of the aryl group has an accelerating effect on catalysis (Entries 3-4). This is probably related to their increased solubility (complexes **1**-Sr and **1**-Ba are hardly soluble in benzene). The poor catalytic activity of the Sr and Ba clusters may be related to the weak Brønsted basicity of the siloxide/amide dianion: the negative charge on N is stabilized by delocalization in the aryl substituent. In this respect, it is noteworthy that under the same reaction conditions the known Sr complex[10] $[(Me_3Si)(DIPP)N]_2Sr\cdot(THF)_2$ (**3**) was found to be fully inactive for cyclization of $H_2NCH_2CPh_2CH_2CH=CH_2$ (Entry 5).

Group 2 metal mediated alkene hydrophosphination was first reported by Hill *et al.*[11] and was later extended to alkyne substrates by Westerhausen *et al.*.[12] It should be considered an attractive atom-efficient transformation for the syntheses of phosphines. Carpentier *et al.* found increasing conversion rates for the heavier alkaline-earth metals: Ca < Sr < Ba.[9i] Investigations are generally limited to conversion of an activated C=C bond like that in styrene or derivatives thereof. Hydrophosphination of isolated (unactivated) alkenes or twofold substituted alkenes is significantly more challenging. For this reason, hydrophosphination of myrcene gives only functionalization of the terminal (mono-substituted and conjugated) C=C bond, leaving internal or unactivated double bonds unaffected.[9i] The siloxide/amide clusters are also active in alkene hydrophosphination (Entries 6-12). Notably, the catalyst **1**-Ba is able to convert disubstituted alkenes like α-Me-styrene (Entry 12) which is known to be slow.[9i] Disubstituted alkenes like 1,1-diphenylethylene hitherto were not tackled by group 2 metal catalysis but can be fully converted by **1**-Sr and **1**-Ba, albeit slow (Entries 10-11). Conversion rates increase along the row α-Me-styrene < 1,1-diphenylethylene < styrene. The Ba catalyst **1**-Ba is generally faster than the Sr catalysts **1**-Sr and **1**-Sr(*t*Bu). The activity of the latter Sr complexes is substantially lower than that of heteroleptic catalysts of the type LSrR in which L is a spectator ligand and R is N'' or $CH(SiMe_3)_2$. These generally show fast styrene/$HPPh_2$ addition (2 mol% cat, 60 °C, 3-15 min, 55-92%).[9i] In contrast to the homoleptic catalyst $[(Me_3Si)(DIPP)N]_2Sr\cdot(THF)_2$ (**3**, Entry 9) the conversions with the siloxide/amide catalysts are all quantitative. The poor activity of the latter homoleptic catalyst is due to the formation of insoluble $Sr(PPh_2)_2$. A similar explanation has been reported for the very poor catalytic activity of CaN''$_2$·$(THF)_2$ for styrene/$HPPh_2$ conversion (10 mol%, 75 °C, 36 h, 99%; precipation of $Ca(PPh_2)_2$ was observed).[11] The spectator ligand therefore has a solubilizing function. Along the lines of intramolecular alkene hydroamination, we propose for the catalysts **1**-Sr and **1**-Ba a mechanism in which the siloxide/amide dianion acts as a cooperative ligand. Deprotonation of $HPPh_2$ by the N-Ar arm is followed by phosphide/alkene addition after which the intermediate is protonated again. This mechanism is corroborated by the fact that aniline (pK_a 30.7)[13] is less acidic than $HPPh_2$ (pK_a 21.7).[14]

Ca-mediated alkene hydroboration was first reported by Harder *et al.*[15] and extended to Mg-catalyzed hydroboration of aldehydes, ketones and imines by the Hill group.[16] Mg-mediated hydroboration of pyridines is a special case of C=N bond hydroboration in which the regioselectivity (1,2- or 1,4-reduction) is challenging.[17,18] Attempts to use Ca catalysts in the latter reaction were frustrated by catalytic decomposition of the borane (pinacolborane, HBpin).[18] Herein we report the catalytic hydroboration of pyridine and related substrates with tetranuclear siloxide/amide Sr and Ba clusters (Entries 13-21). Catalytic pyridine hydroboration is quantitative and somewhat faster for **1**-Ba compared to **1**-Sr (Entries 13-14). Rates are of the same order compared to a recently reported Mg catalyst (10 mol% cat, 70 °C, 17 h, 92%).[17] The preference for 1,4-addition over 1,2-addition, which is for **1**-Sr 95/5, is substantially better than that for the Mg catalyst (1,4/1,2 = 63/37). As was previously reported for the Mg catalyst,[11] conversion of the activated substrates quinoline and isoquinoline is much faster and fully selective. In isoquinoline hydroboration, the homoleptic catalyst $[(Me_3Si)(DIPP)N]_2Sr\cdot(THF)_2$ (**3**) can compete with **1**-Sr and **1**-Ba (Entries 18-21). The catalyst **1**-Ba enabled conversion of chlorinated pyridine (Entry 15), a substrate that so far has only been converted using a Fe catalyst.[19]

Ca-mediated alkene hydrosilylation was pioneered by Harder and coworkers.[20] The Okuda group introduced calcium silanide catalysts.[21] Although mechanistically different, group 2 metal hydrosilylation catalysis has been extended to ketones[22] and pyridines.[23] Herein we report catalytic hydrosilylation of pyridines and alkenes with the siloxide/amide clusters of Sr and Ba (Entries 22-30). Hydrosilylation of styrene with $PhSiH_3$ is somewhat faster with the Ba catalyst **1**-Ba (Entries 27-28) but still slower compared to that with a dibenzylstrontium catalyst (2.5 mol% cat, 20 °C, < 0.1 h,

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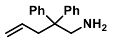
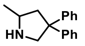
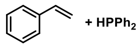
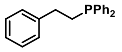
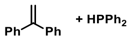
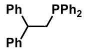
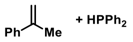
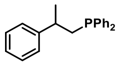
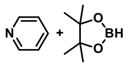
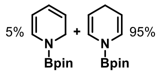
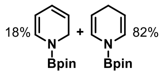
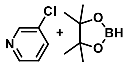
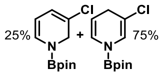
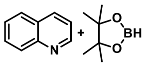
>99%).[20] Hydrosilylation of the more hindered 1,1-diphenylethylene is more challenging and slower (Entries 29-30). Similar to conversion with a dibenzylstrontium catalyst,[20] the branched product $Ph_2CH(SiH_2Ph)CH_3$ is formed selectively. It is at this stage not clear whether catalysis proceeds through a metal hydride intermediate (as proposed earlier).[20] Attempts to isolate intermediates by reaction of **1**-Sr with $PhSiH_3$ failed. Two possible routes could be envisioned: (i) The dianionic siloxide/amide ligand $^{-}OSiMe_2(DIPP)N^{-}$ may react with $PhSiH_3$ to give $^{-}OSiMe_2(DIPP)NSiH_2Ph$ and H^{-}, or (ii) Forced proximity of the latter two anions gives a silicate containing a pentacoordinate Si: $^{-}OSiMe_2(DIPP)NSiH_3Ph^{-}$. Both, hydride or silicate, may reduce the C=C double bond by hydride transfer. Hydrosilylation of quinoline and isoquinoline is selective and the latter substrate could also be converted by the homoleptic catalyst $[(Me_3Si)(DIPP)N]_2Sr{\cdot}(THF)_2$ (**3**); Entries 22-26.

Table 2. Various catalytic conversions with Sr and Ba catalysts (0.6 mol% based on tetramer or 2.4 mol% based on metal) in C_6D_6 at 70 °C. Reactions were followed by ^1H NMR and times have been given for >99% conversion (unless noted otherwise).

Entry	Cat.	Subtrates	Products	Time (h)
1	**1**-Sr			32[a]
2	**1**-Sr(*t*Bu)	,,	,,	16[a]
3	**1**-Ba	,,	,,	28[a]
4	**1**-Ba(*t*Bu)	,,	,,	12[a]
5	**3**	,,	,,	-[a]
6	**1**-Sr			7.25
7	**1**-Sr(*t*Bu)	,,	,,	7
8	**1**-Ba	,,	,,	1.25
9	**3**	,,	,,	24[b]
10	**1**-Sr			60
11	**1**-Ba	,,	,,	36
12	**1**-Ba			9 days
13	**1**-Sr			48[c]
14	**1**-Ba	,,		23[c]
15	**1**-Ba			5 days[c]
16	**1**-Sr			4
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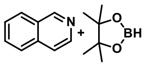
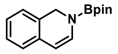
18	**1**-Sr			1
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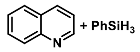
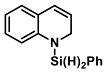
21	**3**	,,	,,	0.5
22	**1**-Sr			5
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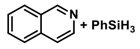
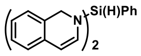
24	**1**-Sr			2
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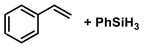
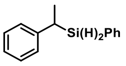
27	**1**-Sr			7.25
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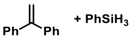
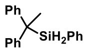
29	**1**-Sr			31
30	**1**-Ba	,,	,,	20

[a] Reaction temperature 60 °C. [b] 20 % conversion due to precipitation of $Sr(PPh_2)_2$. [c] Solvent is THF-d_8

Conclusions

The serendipitous synthesis of **1**-Sr is reproducible but slight changes of the aniline used in its synthesis (2,6-*i*Pr_2-aniline) gave complications. Using less sterically encumbered anilines gave products that were completely insoluble and difficult to purify or characterize. Anilines with bulkier substituents led to highly soluble product mixtures. Addition of a *t*Bu group in the *para*-position of the aniline, however, led to the crystalline product **1**-Sr(*t*Bu) that could be fully characterized. This shows that substitution in the periphery of the ligand does not disturb self assembly. The *t*Bu substituent in *para*-position increases the solubility of the cluster significantly. Exchanging the Sr metal for the larger Ba led to isolation of the complexes **1**-Ba and **1**-Ba(*t*Bu) which are isostructural to the analogue Sr complexes. Although yields are low, the synthetic procedure using cheap starting materials is simple and gives generally crystalline products.

The tetranuclear siloxide/amide clusters were shown to be catalytically active in a wide range of substrate functionalizations among which the intramolecular alkene hydroamination, alkene hydrophosphination, pyridine hydroboration, pyridine hydrosilylation, and alkene hydrosilylation. Although in some cases the reaction times were long, in the majority of experiments clean and full conversion was reached. The Ba catalysts react generally faster than the Sr catalysts. Catalysts with *t*Bu substituents in *para*-position of the aniline unit performed better than those without. The latter is likely related to their better solubility which is often an issue. All catalytic conversions are highly selective, except for the hydroboration of pyridine. The 1,4/1,2 product ratios (**1**-Sr: 95/5; **1**-Ba: 82/18) are, however, better than that for a Mg catalyst (63/37). It is noteworthy that the similar but mononuclear catalyst $[(Me_3Si)(DIPP)N]_2Sr\cdot(THF)_2$ (**3**) performed much poorer in most conversions. This suggests that this class of cluster catalysts in which the ligand cooperates in the catalytic cycle could be advantageous for a wide range of transformations. We continue to investigate group 2 metal catalysis with ligands that combine the functions of spectator and reactive group.

Experimental Section

General Considerations

All experiments were performed under a nitrogen atmosphere by using standard Schlenk line and glove box techniques. The solvents were dried on alumina columns and were degassed by bubbling nitrogen through the solvent reservoir. Following compounds were prepared according to their reported literature procedures: $Sr[N(SiMe_3)_2]_2\cdot(THF)_2$,[24] $Ba[N(SiMe_3)_2]_2$,[25] and $[(Me_3Si)(DIPP)N]_2Sr\cdot(THF)_2$.[10] Following compounds were obtained commercially: hexamethylcyclotrisiloxane (Sigma Aldrich), aluminum chloride (ABCR), *tert*-butyl chloride (ABCR) and 2,6-di*iso*propylaniline (ABCR). All chemicals were use as received, except *tert*-butyl chloride and 2,6-di*iso*propylaniline, which were distilled prior to use. NMR spectra were recorded on BRUKER Avance III HD (400 MHz) and Avance III HD (600 MHz) spectrometer. Crystals were measured on an Agilent Supernova with an Atlas S2 CCD detector and Nova (Cu) and Mova (Mo) X-ray microsources. GC-MS analysis has been performed with a Thermo Scientific™ Trace™ 1310 gas chromatography system (carrier gas Helium) with detection by a Thermo Scientific™ ISQ™ LT Single Quadrupole mass spectrometer (EI-MS, 70 eV). Elemental analyses on the complexes were performed with a Hekatech Eurovector EA3000 analyzer. CH-Elemental analyses of complexes with Ca (or heavier alkaline earth metals like Sr and Ba) are generally strongly affected by the very high air-sensitivity of the complexes, partial loss of coordinated or crystal lattice solvent molecules, and particularly by formation of very stable metal carbide or metal carbonate products that also with additional oxidizers like V_2O_5 do not fully react to CO_2. This results in lower C-content values than expected and is well-documented for the heavier alkaline-earth metal complexes of Ca, Sr and Ba.[26] CH-Elemental analyses are also complicated by a difficult work-up procedure. During synthesis of the complexes from Sr and Ba amide bases, aniline and excess siloxane, large amounts of oligo- and polysiloxanes are formed. Separation of the crystalline products from these siloxanes is often tedious and in many cases contamination with silicones cannot be avoided. All cluster syntheses can be up-scaled to circa 300 mg without a change in yield.

Synthetic procedures

Synthesis of 4-(tert-butyl)-2,6-diisopropylaniline. $AlCl_3$ (4.00 g, 30.0 mmol) was dissolved in 1,2-dichloroethane (25 mL) and cooled to 0°C. Subsequently, 2,6-diisopropylaniline (4.00 g, 22.6 mmol) was added and the reaction mixture was cooled to -10°C. Freshly distilled *t*BuCl (dried over CaH_2) (7.88 g, 85.2 mmol) was added dropwise over a period of 45 min, during which the solution turned dark brown. After having stirred the solution for one hour at -10 °C, dichloromethane (50 mL) was added and the reaction mixture was poured on a mixture of ice (40 g) and aqueous ammonia solution (28%, 12 mL). The white precipitate was filtered off. The organic phase was separated, washed with water (2x40 mL) and brine (2x40 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure giving a viscous yellow oil which was recrystallized from pentane (5 mL) at -20°C. The crystals were further purified by sublimation (45°C, $3.0\cdot10^{-5}$ mbar) to give the pure product. Yield: 3.20 g, 13.7 mmol, 63%. ^1H NMR (600 MHz, $[D_6]$benzene, 25°C): $\delta = 1.21$ (d, $^3J_{(H,H)} = 6.9$ Hz, 12H, $C(CH_3)_2$), 1.38 (s, 9H, $C(CH_3)_3$), 2.72 (sept, $^3J_{(H,H)} = 6.8$ Hz, 2H, $CH(CH_3)_2$), 3.14 (s, 2H, NH_2), 7.21 (s, 2H, CH_{arom}) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $[D_6]$benzene, 25°C): $\delta = 22.6$ ($C(CH_3)_2$), 28.4 ($CH(CH_3)_2$), 31.9 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 119.6 (C_{arom}), 131.8 (C_{iPr}), 138.2 (CN), 140.6 (C_{arom}) ppm. GC/MS (EI-MS 70 eV): m/z (%): 233.22 (100) $[M]^+$, 218.17 (448) $[C_{15}H_{24}N]^+$, 202.15 (16) $[C_{14}H_{20}N]^+$, 176.16 (36) $[C_{12}H_{18}N]^+$, 134.12 (42) $[C_9H_{12}N]^+$.

Synthesis of 1-Sr. The complex was prepared according to the earlier procedure[4] but with slight variations giving an improved yield. A Schlenk tube was charged with $\mathrm{Sr[N(SiMe_3)_2]_2{\cdot}(THF)_2}$ (52.0 mg, 94.1 µmol), hexamethylcyclotrisiloxane (164 mg, 737 µmol) and 2,6-di*iso*propylaniline (25.0 mg, 141 µmol). Addition of benzene (1.12 mL) yielded a suspension that was subsequently heated to 60 °C for 3 days. The product was obtained in the form of colorless crystals, which were isolated by decantation, washed with benzene (2 x 1.5 mL) and dried under reduced pressure. Yield: 13.5 mg, 8.23 µmol, 35%. ^{1}H and ^{13}C NMR match the earlier reported product.[4]

Synthesis of 1-Sr(*t*Bu). A Schlenk tube was charged with $\mathrm{Sr[N(SiMe_3)_2]_2{\cdot}(THF)_2}$ (104 mg, 188 µmol), hexamethylcyclotrisiloxane (328 mg, 1.47 mmol) and 4-(*tert*-butyl)-2,6-di*iso*propylaniline (99.0 mg, 424 µmol). Addition of hexane (1.12 mL) yielded a suspension that was subsequently heated to 60 °C for 3 days. The product was obtained in the form of colorless crystals, which were isolated by decantation, washed with hexane (2 x 1.5 mL) and dried under reduced pressure. Yield: 23.6 mg, 12.7 µmol, 27%. ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): δ = 0.11 (s, 6H, $\mathrm{SiMe_2}$), 1.22 (d, $^3J_{\mathrm{H,H}}$ = 6.8 Hz, 12H, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.26 (s, 9H, $\mathrm{C(C}\mathit{H}_3)_3$), 1.76–1.79 (m, 4H, THF), 2.98 (sept, $^3J_{\mathrm{H,H}}$ = 6.8 Hz, 2H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 3.60–3.63 (m, 4H, THF), 6.97 (s, 2H, $\mathrm{C}\mathit{H}_{\mathrm{arom}}$) ppm; ^{13}C{^{1}H} NMR (151 MHz, [D$_8$]THF, 25°C): δ = 1.6 ($\mathrm{SiMe_2}$), 23.2 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 26.6 (THF), 28.9 ($\mathit{C}\mathrm{H(CH_3)_2}$), 32.2 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 34.8 ($\mathit{C}\mathrm{(CH_3)_3}$), 68.4 (THF), 119.9 ($\mathit{C}_{\mathrm{arom}}$), 132.2 ($\mathit{C}_{\mathrm{arom}}$), 139.8 ($\mathit{C}_{\mathrm{arom}}$), 140.1 ($\mathit{C}_{\mathrm{arom}}$) ppm. $\mathrm{C_{88}H_{156}NO_2SiSr}$ (1861.04): Calcd. C 56.79 H 8.45 N 3.01; found C 55.97 H 8.47 N 2.96. Although the C value is outside the range viewed as establishing analytical purity, it is provided to illustrate the best values obtained to date.

Synthesis of 1-Ba. A Schlenk tube was charged with $\mathrm{Ba[N(SiMe_3)_2]_2}$ (78.1 mg, 176 µmol) and hexamethylcyclotrisiloxane (39.2 mg, 176 µmol) and 2,6-di*iso*propylaniline (54.7 mg, 307 µmol). The educts were dissolved in 1.12 mL of benzene and 30 µL of THF, yielding a clear solution. Subsequently, 2,6-di*iso*propylaniline (54.7 mg, 307 µmol) was added and the reaction was heated to 60 °C for 4 days. The product was obtained in the form of colorless crystals, which were isolated by decantation, washed with benzene (2 x 1.5 mL) and dried under reduced pressure. Yield: 10.5 mg, 5.72 µmol, 13%. ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): δ = 0.05 (s, 6H, $\mathrm{SiMe_2}$), 1.15 (d, $^3J_{\mathrm{H,H}}$ = 6.7 Hz, 12H, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.72 (m, 4H, THF), 2.91 (sept, $^3J_{\mathrm{H,H}}$ = 6.1 Hz, 2H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 3.57 (m, 4H, THF), 6.52 (t, $^3J_{\mathrm{H,H}}$ = 7.7 Hz, 1H, $\mathrm{C}\mathit{H}_{\mathrm{arom}}$), 6.83 (d, $^3J_{\mathrm{H,H}}$ = 7.3 Hz, 2H, $\mathrm{C}\mathit{H}_{\mathrm{arom}}$) ppm; ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]THF, 25°C): δ = 1.2 ($\mathrm{SiMe_2}$), 22.8 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 28.2 ($\mathit{C}\mathrm{H(CH_3)_2}$), 117.9 ($\mathit{C}_{\mathrm{arom}}$), 122.8 ($\mathit{C}_{\mathrm{arom}}$), 132.2 ($\mathit{C}_{\mathrm{arom}}$), 142.0 ($\mathit{C}_{\mathrm{arom}}$) ppm. The crystalline product **1**-Ba cannot be easily separated from the polysiloxane side-product. Although the product could be clearly identified by NMR analysis (^{1}H and ^{13}C NMR data for **1**-Ba and **1**-Sr are similar), we have not been able to obtain an accurate CH-elemental analysis for **1**-Ba. This is probably due to contamination with oligosiloxanes. A side-product could be isolated from the washing liquid. The ^{1}H NMR data are conclusive for formation of $\mathrm{(DIPPNH)BaN(SiMe_3)_2{\cdot}(THF)_n}$ (see Supporting Information Figure S8).

Synthesis of 1-Ba(*t*Bu). A Schlenk tube was charged with $\mathrm{Ba[N(SiMe_3)_2]_2}$ (78.1 mg, 176 µmol), hexamethylcyclotrisiloxane (39.2 mg, 176 µmol) and 4-(*tert*-butyl)-2,6-di*iso*propylaniline (73.0 mg, 308 µmol). Addition of hexane (1.12 mL) and THF (50 µL) yielded a suspension that was subsequently heated to 60 °C for 2 days. The product was obtained as white microcrystalline powder, which was isolated by centrifugation, washed with benzene (2 x 1.5 mL) and dried under reduced pressure. Yield: 15.4 mg, 7.48 µmol, 17%. ^{1}H NMR (600 MHz, [D$_8$]THF, 25°C): δ = 0.11 (s, 6H, $\mathrm{SiMe_2}$), 1.17 (d, $^3J_{\mathrm{H,H}}$ = 6.9 Hz, 12H, $\mathrm{C(C}\mathit{H}_3)_2$), 1.26 (s, 9H, $\mathrm{CH(C}\mathit{H})_3$), 1.76-1.79 (m, 4H, THF), 3.61-3.63 (m, 4H, THF), 3.85 (sept, $^3J_{\mathrm{H,H}}$ = 6.7 Hz, 2H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 6.94 (s, 2H, $\mathrm{C}\mathit{H}_{\mathrm{arom}}$) ppm; ^{13}C {^{1}H} NMR (151 MHz, [D$_8$]THF, 25°C): δ = 1.6 ($\mathrm{SiMe_2}$), 23.5 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 26.3 (THF), 28.0 ($\mathit{C}\mathrm{H(CH_3)_2}$), 32.5 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 34.8 ($\mathit{C}\mathrm{H(CH_3)_2}$), 68.8 (THF), 120.2 ($\mathit{C}_{\mathrm{arom}}$), 136.8 ($\mathit{C}_{\mathrm{arom}}$), 139.9 ($\mathit{C}_{\mathrm{arom}}$), 147.8 ($\mathit{C}_{\mathrm{arom}}$) ppm. $\mathrm{C_{88}H_{156}NO_2SiBa}$ (2059.84): Calcd. C 51.31 H 7.63 N 2.72; found C 49.24 H 7.35 N 2.66. Although the C value is outside the range viewed as establishing analytical purity, it is provided to illustrate the best values obtained to date.

Catalysis

All products were analyzed by ^{1}H and ^{13}C NMR as well as by GC-MS and compared to earlier reported analyses (see Supporting Information).

Intramolecular alkene hydroamination. The catalyst (1.2 µmol, 0.6 mol% based on tetramer or 2.4 mol% based on monomer) was added to a solution of the 2,2-diphenylpent-4-en-1-amine (47.5 mg, 0.200 mmol) in 500 µL benzene-d$_6$. The reaction mixture was heated to 60°C.

Alkene hydrophosphination. The catalyst (1.2 µmol, 0.6 mol% based on tetramer or 2.4 mol% based on monomer) was added to a solution of the corresponding alkene (0.200 mmol) and $\mathrm{HPPh_2}$ (41.0 mg, 38.3 µL, 0.220 mmol) in 500 µL of benzene-*d*$_6$ and the reaction mixture was heated to 70°C.

Hydroboration of pyridines. The catalyst (2.4 µmol, 0.6 mol% based on tetramer or 2.4 mol% based on monomer) was added to a solution of the corresponding pyridine or quinoline (0.400 mmol) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56.3 mg, 63.8 µL, 0.440 mmol) in 500 µL of benzene-*d*$_6$ (in the case of 3-chloropyridine THF-*d*$_8$ was used as solvent). The reaction mixture was heated to 70°C.

Hydrosilylation of pyridines. The catalyst (2.4 µmol, 0.6 mol% based on tetramer or 2.4 mol% based on monomer) was added to a solution of the corresponding pyridine or quinoline (0.400 mmol) and $PhSiH_3$ (47.6 mg, 54.2 µL, 0.440 mmol) (in the case of *iso*quinoline the amount of $PhSiH_3$ is reduced to 0.220 mmol) in 500 µL of benzene-d_6.The reaction mixture was heated to 70°C.

Hydrosilylation of alkenes. The catalyst (2.4 µmol, 0.6 mol% based on tetramer or 2.4 mol% based on monomer) was added to a solution of the corresponding alkene (0.400 mmol) and $PhSiH_3$ (47.6 mg, 54.2 µL, 0.440 mmol) in 500 µL of benzene-d_6. The reaction mixture was heated to 70°C.

Crystal Structure Determination

Crystal data and details for refinement can be found in the Supporting Information. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1819032 **1**-Sr(*t*Bu), 1819033 **1**-Ba, 1819034 **1**-Ba(*t*Bu)**.** Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Supporting Information. Crystal data, details for structure determination, selected ^{1}H NMR spectra and analyses of products from catalytic reactions.

Acknowledgements

We kindly acknowledge Christina Wronna for numerous elemental analyses and the DFG for financial support (HA 3218/8-1).

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