Guanidinate Complexes of Heavier Alkaline-Earth Metals (Ca, Sr): Syntheses, Structures, Styrene Polymerization and Unexpected Reaction Behaviour

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The guanidinate complex [Ca{(Cy)N–C{N(SiMe$_3$)$_2$}–N(Cy)}$_2$] can be prepared in good yields and in crystalline purity by two different routes: 1) addition of [Ca{N(SiMe$_3$)$_2$}$_2$] to (Cy)-N=C=N(Cy) or 2) addition of KN(SiMe$_3$)$_2$ to (Cy)N=C=N(Cy) followed by a metathesis reaction of the obtained potassium guanidinate complex with CaI$_2$. Crystallization from Et$_2$O yielded [Ca{(Cy)N–C[N(SiMe$_3$)$_2$]–N(Cy)}$_2$·(Et$_2$O)] (**1**), which shows a C_2-symmetric structure in the crystal. A Sr analogue could be prepared likewise and also crystallizes as the mono-etherate [Sr{(Cy)N–C{N(SiMe$_3$)$_2$}–N(Cy)}$_2$·(Et$_2$O)] (**2**) with a very similar crystal structure. The Schlenk equilibrium between (**1**) and [Ca{α-(Me$_3$Si)-*o*-(Me$_2$N)-benzyl}$_2$·(THF)$_2$] (**3**) in benzene is not completely on the heteroleptic side; however, an excess of (**1**) yields predominantly the heteroleptic benzylcalcium complex [Ca{(Cy)N–C{N(SiMe$_3$)$_2$}–N(Cy)}{α-(Me$_3$Si)-*o*-(Me$_2$N)-benzyl}] (**4**). Styrene polymerization with this mixture results largely in atactic polystyrene of which the molecular weight distribution shows a tailing in the lower range. This could be due to decomposition of the guanidinate ligand under the given polymerization conditions. It is shown that heating a mixture of **1** and **3** gives the crystalline decomposition product [Ca{(Cy)N–C{N(SiMe$_3$)$_2$}–N(Cy)}{(Cy)-(TMS)N}] (**5**), which crystallizes as a dimer with bridging amide ligands.

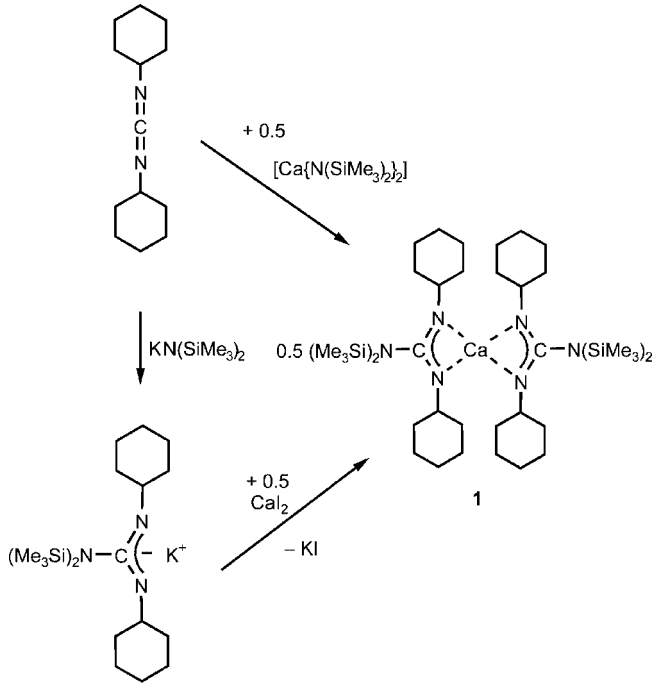
Introduction

The coordination chemistry of amidinates and the related guanidinates has been well-explored for main-group metals as well as for transition metals.[1–9] These powerful electron-donating ligands not only coordinate to a remarkably wide range of metal ions from all parts of the periodic table, but also show a rich variety of coordination modes.[1–3] Other advantages of this class of ligands are their easy accessibility and the possibility of substituent variation, which allows for tuning of their steric and electronic properties. The latter advantage makes these ligands well-suitable as spectator ligands in catalysis and this opportunity has been well-exploited in the design of polymerization catalysts.[10–22]

In the course of our studies on polymerization catalysts based on alkaline-earth metals,[23–27] we have now prepared guanidinate complexes of the heavier alkaline-earth metals Ca and Sr and explored their structures, reactivity and their behaviour in styrene polymerization.

Results and Discussion

The homoleptic calcium bis(guanidinate) complex (**1**) was prepared by two alternative routes (Scheme 1): i) direct addition of [Ca{N(SiMe$_3$)$_2$}$_2$] to 1,3-dicyclohexylcarbodiimide or ii) addition of KN(SiMe$_3$)$_2$ to 1,3-dicyclohexylcarbodiimide and subsequent reaction of the potassium guanidinate with CaI$_2$. The analogous strontium bis(guanidinate)



Scheme 1.

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complex **2** was synthesized by reaction of the potassium guanidinate with SrI_2.

The calcium bis(guanidinate) complex **1** crystallizes as a mono-etherate. The crystal structure has two independent molecules in the asymmetric unit, which are geometrically similar within their standard deviations (Figure 1). Both molecules show crystallographic C_2-symmetry with the C_2-axis going through Ca and O.

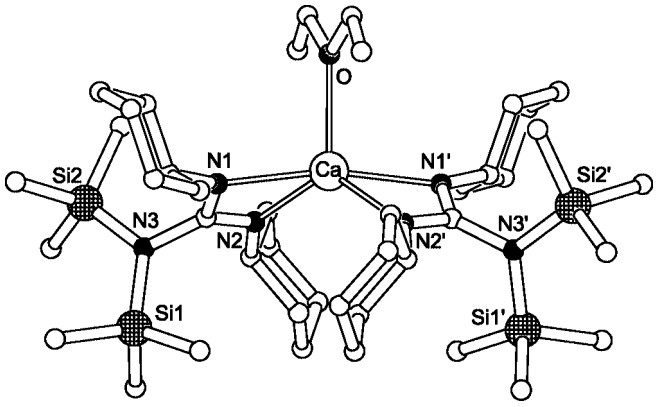


Figure 1. (a) Crystal structure of **1**. Hydrogen atoms have been omitted for clarity and only one of the two crystallographic independent, but very similar, molecules is shown. Selected bond lengths [Å] and angles [°] (values for the other independent molecule are given in square brackets): Ca–N1 2.387(2) [2.369(3)], Ca–N2 2.380(3) [2.388(3)], Ca–O 2.424(3) [2.421(3)]; N1–Ca–N2 56.12(8) [56.47(8)]. The strontium complex **2** is isostructural with **1**; selected bond lengths [Å] and angles [°]: Sr–N1 2.534(3) [2.526(3)], Sr–N2 2.514(3) [2.520(3)], Sr–O 2.559(3) [2.559(3)]; N1–Sr–N2 53.01(9) [53.13(9)].

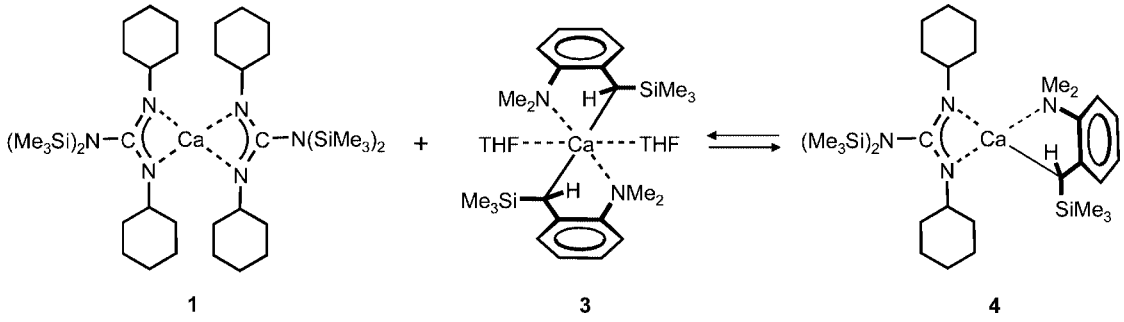
The N_3C units of the guanidinate ligands are planar (maximum deviations from their least-squares planes are 0.004 and 0.008 Å). The $N(SiMe_3)_2$ substituents oriented themselves perpendicular to the NCN plane with dihedral Si_2N/NCN angles of 96.1(1)° and 91.7(1)°, thus preventing N(*p*)–$CN_2(\pi)$ interactions. A similar conformation has been observed in the alkali-metal salts of the (Cy)N–C{N-$(SiMe_3)_2$}–N(Cy) anion.[9]

The guanidinate ligands act as bidentate ligands with an average bite angle of 56.3(8)° and are twisted with respect to each other, which gives rise to C_2-chirality of the molecule. The two independent molecules in the asymmetric cell are nearly mirror images. The coordination geometry of the Ca metal is not clear-cut due to the small bite angle of the guanidinate ligands.

The Ca^{2+} ion is located slightly out of the N_3C planes by 0.301 and 0.358 Å. The Ca–N bond lengths [average 2.381(3) Å] are shorter than those in the structure of the calcium amidinate complex [Ca{Me_3SiN–C(Ph)–$NSiMe_3$}$_2$·$(THF)_2$] for which an average Ca–N bond of 2.431(2) Å has been reported.[28] The longer amide–metal coordination in the latter can be explained by the presence of two neutral ether donor ligands instead of one. The steric bulk of the two guanidinate ligands in **1** allows only one ether molecule in the coordination sphere of Ca and is therefore comparable to the steric bulk of 1,3-$(SiMe_3)_2Cp^-$ or *i*$Pr(Me)_4Cp^-$. Both these Cp ligands form calcocenes also with only one Et_2O molecule in the coordination sphere of Ca.[29]

The strontium bis(guanidinate) complex **2** likewise crystallizes as a mono-etherate complex which is isostructural to **1** (Figure 1). The Sr–N and Sr–O bond lengths are, on average, 0.143 Å and 0.137 Å longer than those in the Ca analogue, which nicely represents the difference of 0.13 Å in the ionic radii of the two alkaline-earth metals. The Sr–N bond lengths in **2** [average 2.524(3) Å] are somewhat shorter than those in the strontium amidinate complex [Sr{Me_3SiN–C(Ph)–$NSiMe_3$}$_2$·$(THF)_2$] for which the average Sr–N bond measures 2.583(9) Å.[30] The longer metal–ligand bond length in the latter complex can again be explained by the presence of one extra donor molecule. The N–Sr–N′ bite-angle in **2** [53.1(1)°] is, however, very similar to that in the amidinate complex [Sr{Me_3SiN–C(Ph)–$NSiMe_3$}$_2$·$(THF)_2$] [53.3(3)°].

Our continuing interest in the use of benzylcalcium complexes for the living and syndiotactic polymerization of styrene spurred us to prepare heteroleptic benzylcalcium complexes containing the chelating guanidinate ligand. Such heteroleptic initiators were prepared by ligand exchange between homoleptic **1** and the dibenzylcalcium complex **3** (Scheme 2). Mixing benzene solutions of **1** and **3** does not result in complete ligand exchange, but a Schlenk equilibrium between homoleptic (**1** and **3**) and heteroleptic (**4**) species is observed. NMR studies in [D_6]benzene show that the equilibrium constant at 20 °C amounts to about 6. For this reason, further polymerization studies were performed with



1 **3** **4**

Scheme 2.

mixtures of **1** and **3** in which homoleptic **1** is in excess. This largely results in the formation of heteroleptic **4** mixed with homoleptic **1**. Since the latter is not an active initiator in styrene polymerization, the polymerization is mainly initiated by the heteroleptic benzylcalcium species **4**.

Styrene polymerizations (see Exp. Sect. for details) with 2:1 or 4:1 mixtures of **1** and **3** both yield predominantly atactic polystyrene (also in the absence of solvent). Although the guanidinate ligand has no effect on the stereoselectivity of the polymerization, it has a distinct accelerating influence on the polymerization rate. Styrene polymerization with a 2:1 mixture of **1** and **3** (k = $5.7 \pm 0.3\ L\,mol^{-1}\,s^{-1}$) is more than twice as fast as styrene polymerization with **3** ($k = 2.48 \pm 0.11\ L\,mol^{-1}\,s^{-1}$). This increased polymerization rate could be the consequence of the excellent donor properties of the chelating bidentate guanidinate ligand: this would weaken the benzylcalcium bond and increase the nucleophilicity of the propagating chain-end. Although fast propagation is advantageous for a stereoselective polymerization (the competing inversion of the chiral chain-end results in racemization and therefore loss in stereocontrol)[24] we find essentially atactic polymer. Apparently the guanidinate ligand also increases the rate of inversion of the chiral chain-end.

The molecular-weight distributions of the obtained polymers all show relatively large dispersion indices (>1.5) and a very pronounced tailing in the low molecular weight range. This could be an indication of decomposition of the propagating species during the polymerization experiment. Since it is known from our earlier work that the benzylic group in heteroleptic benzylcalcium compounds can react with the spectator ligand,[27,31] we investigated a benzene solution of **1** and **3** at higher temperatures, i.e. the conditions of the polymerization experiment. Keeping the initiator solution overnight at 80 °C yielded, after subsequent concentration and cooling, a colourless crystalline product (**5**), which dissolves badly in benzene. Analysis of these crystals by X-ray diffraction revealed that one of the guanidinate ligands had decomposed into the amide (Cy)-$(Me_3Si)N^-$, which forms a heteroleptic complex with the original guanidinate ligand (Figure 2). In the solid state, this complex forms a centrosymmetric dimer in which the amide ligands bridge the Ca^{2+} ions and the guanidinate anions act as bidentate ligands located in terminal positions.

The geometry of the guanidinate ligand in **5** is very similar to that observed in **1** and **2**: the N_3C unit is planar (maximum deviation from the least-squares plane is 0.005 Å) and the $(Me_3Si)_2N$ substituent is oriented perpendicular to this plane [the dihedral Si_2N/NCN angle is 87.1(1)°]. The Ca^{2+} ion is located only 0.023 Å out of the N_3C plane. The bite angle of the chelating bidentate guanidinate ligand amounts to 57.6(1)° and is similar to that in **1**. As can be seen from the somewhat shorter Ca–N bond lengths [average 2.337(3) Å], the guanidinate ligand in **5** binds slightly more strongly to the metal than that in **1**. The Ca–N bond lengths to the bridging amides are longer [average 2.435(3) Å].

The formation of $(Cy)(Me_3Si)N^-$ can only be explained by assuming a 1,3-shift of the Me_3Si substituent as the first step (a precedent for a similar shift in an amidinate ligand[22] is known). A possible mechanism for the formation of the amide is proposed in Scheme 3. Ring-flip of the cyclohexane substituents brings the attached N into the axial position and creates more space for the $(Me_3Si)_2N$ substituent in the backbone of the ligand. This allows for rotation of the $(Me_3Si)_2N$ group and delocalization of the N lone-pair into the π-system. Such a resonance structure with enhanced ligand basicity is known for guanidinate ligands with smaller substituents in the backbone.[5,8] A 1,3-shift of the Me_3Si substituent gives a new guanidinate ligand, which could be in equilibrium with $(Cy)(Me_3Si)N^-$ and (Cy)-N=C=N–$SiMe_3$. Such an equilibrium would be strongly on the side of the guanidinate ligand. However, trapping of the

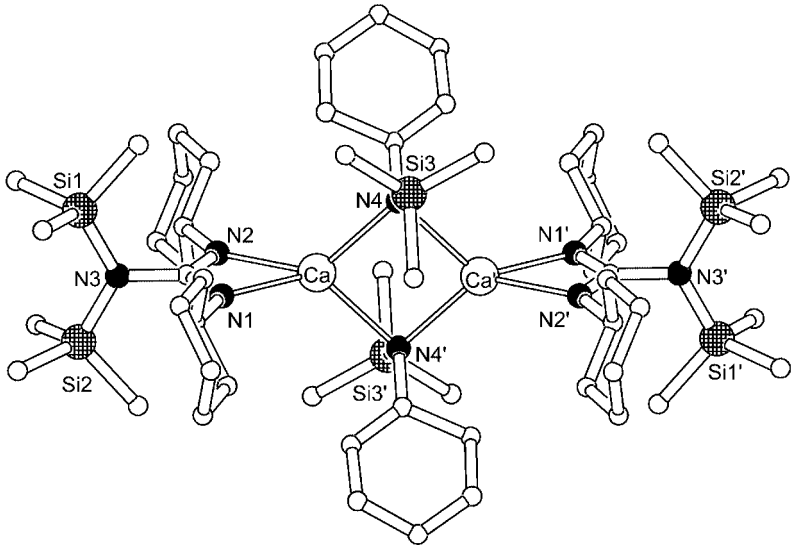
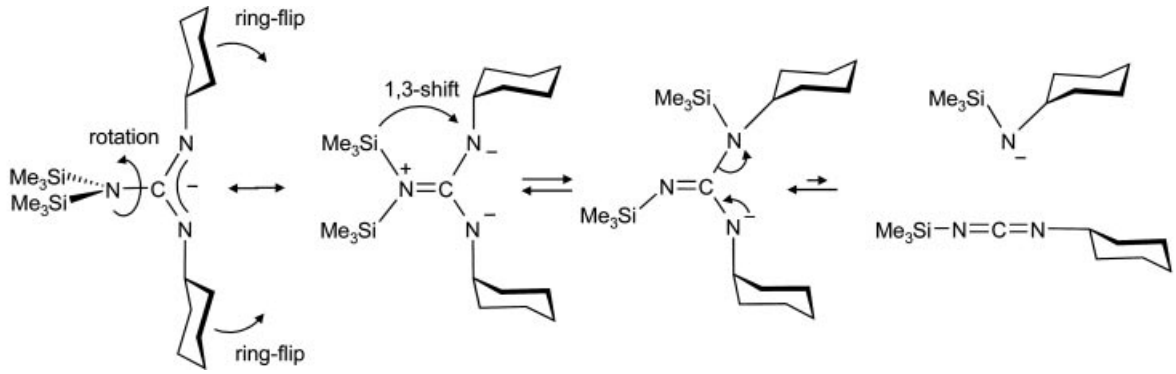


Figure 2. (a) Crystal structure of centrosymmetric **5**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ca–N1 2.316(4), Ca–N2 2.357(3), Ca–N4 2.422(3), Ca–N4′ 2.447(3); N1–Ca–N2 57.6(1), N4–Ca–N4′ 90.1(1).



Scheme 3.

carbodiimide by-product by addition of the α-(Me_3Si)-*o*-(Me_2N)-benzyl anion to the C=N bond would result in formation of (Cy)(Me_3Si)N^-.[38] A similar mechanism during the polymerization of styrene would result in partial degradation of the guanidinate ligand and partial quenching of the polystyryl chain-end due to reaction with the carbodiimide.

Conclusions

The homoleptic calcium bis(guanidinate) complex **1** can be prepared in high yields and crystalline purity by two routes, both based on addition of an organometallic compound to a carbodiimide. The analogous strontium complex **2** was obtained likewise. Both the Ca and the Sr complex crystallize as C_2-symmetric mono-etherates. This indicates that the steric bulk of the anionic (Cy)N–C{N-($SiMe_3$)$_2$}–N(Cy) ligand is similar to that of 1,3-($SiMe_3$)$_2$-Cp^- or *i*Pr(Me)$_4$$Cp^-$.

The Schlenk equilibrium between homoleptic calcium bis(guanidinate) **1** and [Ca{α-(Me_3Si)-*o*-(Me_2N)-benzyl}$_2$·(THF)$_2$] is mainly, but not completely, on the heteroleptic side. An excess of **1**, however, results in nearly exclusive formation of the heteroleptic benzylcalcium complex. Polymerization of styrene with such mixtures yields atactic polystyrene. Since the molecular-weight distribution of these polymers shows a strong tailing in the low molecular weight range, it is expected that these polymerizations are not completely living. It has been shown that heating mixtures of **1** and **3** results in decomposition of the guanidinate ligand. A similar reaction could be responsible for quenching of the polymer chains during styrene polymerization.

Experimental Section

General Comments: All experiments were carried out under argon using predried solvents and Schlenk techniques. [Ca{N-($SiMe_3$)$_2$}$_2$][32] and [Ca{(2-Me_2N-α-Me_3Si-benzyl)}$_2$·(THF)$_2$][23] were prepared according to literature procedures. NMR spectra were recorded on Bruker AC250 and AMX600 machines. Polymerizations of styrene were performed in a thermostatted 100-mL, stainless-steel reactor at normal pressure. Polymerizations were carried out either in cyclohexane (0.1 M styrene solution, 0.1 mM catalyst, 50 °C) or in pure styrene (0.1 mM catalyst, 20 °C). In a typical polymerization experiment, the reactor was loaded with 90 mL of dry cyclohexane and 11.5 mL (ca. 100 mmol) of freshly distilled (from alox-perls) styrene. A solution of the initiator (0.05 mmol **3** and 0.1 or 0.2 mmol of **1**) in 1.0 mL of benzene/cyclohexane was added through a port. The usual appearance of a red colour indicated that the polymerization started immediately. After a polymerization time of 30 min, the mixture was quenched with oxygen-free methanol. Evaporation of all solvents yielded the polymer in quantitative yields. The polymers were analyzed by GPC and high temperature ^{1}H and ^{13}C NMR spectroscopy (solvent: [D_2]tetrachloroethane). The tacticity of the polymer was checked by analyzing the ^{13}C NMR signal for the C_{ipso} in the phenyl ring.[33]

Synthesis of [K{(Cy)NC{N($SiMe_3$)$_2$}N(Cy)}]: A solution of dicyclohexylcarbodiimide (1.00 g, 4.85 mmol) and KN($SiMe_3$)$_2$ (0.97 g, 4.85 mmol) in 30 mL of Et_2O was stirred overnight at room temperature. The solvents were removed under vacuum and the precipitate was washed twice with 10 mL portions of hexane. The residue was dried under vacuum (0.01 Torr, 50 °C, 30 min). The remaining white powder was identified by NMR analysis as [K{(Cy)-NC{N($SiMe_3$)$_2$}N(Cy)}] (1.92 g, 98%). ^{1}H NMR ([D_6]benzene/[D_8]THF (9:1), 600 MHz, 20 °C): δ = 0.31 (s, 18 H, Me_3Si), 1.30 (m, 4 H, Cy), 1.38 (m, 2 H, Cy), 1.51 (m, 4 H, Cy), 1.64 (m, 4 H, Cy), 1.79 (m, 2 H, Cy), 1.90 (m, 4 H, Cy), 3.26 (m, 2 H, Cy) ppm. ^{13}C NMR ([D_6]benzene/[D_8]THF (9:1), 62.86 MHz, 20 °C): δ = 2.9 (Me_3Si), 26.8 (Cy), 27.1 (Cy), 39.1 (Cy), 56.1 (Cy), 157.5 (NCN) ppm.

Synthesis of [Ca{(Cy)NC{N($SiMe_3$)$_2$}N(Cy)}$_2$·(Et_2O)] (1): This complex was prepared by two different methods. **Method A:** A suspension of [K{(Cy)NC{N($SiMe_3$)$_2$}N(Cy)}] (1.46 g, 3.60 mmol) and CaI_2 (0.53 g, 1.80 mmol) in 30 mL of Et_2O was stirred for three days at room temperature. The solvent was removed under vacuum and the product was extracted with two 20-mL portions of hexane. The hexane layers were concentrated to 15 mL and 2 mL of Et_2O was added. Slow cooling of the remaining solution to –30 °C yielded large colourless crystals of **1** (yield: 0.98 g, 65%). **Method B:** A solution of dicyclohexylcarbodiimide (1.98 g, 9.60 mmol) and [Ca{N($SiMe_3$)$_2$}$_2$] (1.73 g, 4.80 mmol) in 30 mL of Et_2O was stirred overnight at room temperature. After removing the solvent under vacuum a white residue remained, which was recrystallized from 20 mL of hexane and 2 mL of Et_2O at –30 °C (yield: 3.10 g, 76%). Decomposition temperature: approx. 185 °C. $C_{42}H_{90}CaN_6OSi_4$ (847.65): calcd. C 59.51, H 10.70; found C 59.23, H 10.61. ^{1}H NMR ([D_6]benzene, 600 MHz, 20 °C): δ = 0.37 (s, 36 H, Me_3Si), 1.20 (t, J = 7.1 Hz, 6 H, Et_2O), 1.27 (m, 4 H, Cy), 1.36 (m, 8 H, Cy), 1.45 (m, 8 H, Cy), 1.70 (m, 4 H, Cy), 1.86 (m, 8 H, Cy), 1.92

Table 1. Crystal data for compounds **1**, **2** and **5**.

	1	**2**	**5**
Formula	$C_{42}H_{90}CaN_6OSi_4$	$C_{42}H_{90}N_6OSi_4Sr$	$C_{56}H_{120}Ca_2N_8Si_6$
Mol. mass	847.65	895.18	1154.31
Size [mm^3]	0.5×0.5×0.5	0.5×0.5×0.4	0.5×0.5×0.4
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P*2/c	*P*2/c	*C*2/*c*
a [Å]	26.118(8)	26.104(2)	25.763(4)
b [Å]	9.806(2)	9.9874(8)	11.950(3)
c [Å]	22.799(4)	22.549(4)	24.218(4)
α [°]	90	90	90
β [°]	114.260(10)	113.632(8)	91.501(12)
γ [°]	90	90	90
V [Å^3]	5324(2)	5386(1)	7453(3)
Z	4	4	4
ρ [g cm^{-3}]	1.058	1.104	1.134
μ (Mo-$K_α$) [mm^{-1}]	0.242	1.124	0.285
T [°C]	–90	–90	–90
θ (max.)	25.4	24.2	25.4
Unique reflections	9448	8482	6867
R_{int}	0.030	0.031	0.033
Obsd. reflections [$I > 2σ(I)$]	6213	6540	3208
Parameters	560	489	375
R_1	0.047	0.043	0.063
wR_2	0.164	0.111	0.154
GOF	1.04	1.02	0.93
Max./min. residual electron density [e Å^{-3}]	–0.39/0.46	–0.60/0.83	–0.38/0.46

(m, 8 H, Cy), 3.34 (m, 4 H, Cy), 3.35 (q, J = 7.0 Hz, 4 H, Et_2O) ppm. ^{13}C NMR ([D$_6$]benzene, 62.86 MHz, 20 °C): $δ$ = 2.8 (Me_3Si), 14.6 (Et_2O), 26.6 (Cy), 26.8 (Cy), 39.1 (Cy), 55.0 (Cy), 66.3 (Et_2O), 159.2 (NCN) ppm.

Synthesis of [Sr{(Cy)NC{N(SiMe$_3$)$_2$}N(Cy)}$_2$·(Et$_2$O)] (2): A mixture of [K{(Cy)NC{N(SiMe$_3$)$_2$}N(Cy)}] (1.41 g, 3.48 mmol) and SrI_2 (0.59 g, 1.74 mmol) in 50 mL of Et_2O was stirred for five days at room temperature. The resulting suspension was centrifuged and the mother liquor was isolated. The solid residue was extracted with 20 mL of Et_2O and the solvent of the combined ether fractions was removed under vacuum. The solid product was dissolved in 10 mL of hexane and 10 mL of Et_2O and the solution was concentrated at 30 °C to a volume of about 8 mL. Slow cooling to room temperature yielded large colourless crystalline cubes of **2** (yield: 0.98 g, 68%). Decomposition temperature: approx 168 °C. $C_{42}H_{90}N_6OSi_4Sr$ (895.19): calcd. C 56.35, H 10.13; found C 55.98, H 9.98. ^{1}H NMR ([D$_6$]benzene/[D$_8$]THF (9:1), 600 MHz, 20 °C): $δ$ = 0.33 (s, 36 H, Me_3Si), 1.06 (t, J = 7.0 Hz, 6 H, Et_2O), 1.25 (m, 12 H, Cy), 1.40 (m, 8 H, Cy), 1.68 (m, 4 H, Cy), 1.81 (m, 8 H, Cy), 1.84 (m, 8 H, Cy), 3.27 (q, J = 7.0 Hz, 4 H, Et_2O), 3.33 (m, 4 H, Cy) ppm. ^{13}C NMR ([D$_6$]benzene/[D$_8$]THF (9:1), 62.86 MHz, 20 °C): $δ$ = 3.0 (Me_3Si), 14.6 (Et_2O), 26.8 (Cy), 27.0 (Cy), 39.3 (Cy), 55.5 (Cy), 66.3 (Et_2O), 162.4 (NCN) ppm.

Reaction of 1 with 3: A solution of **1** (0.30 g, 0.36 mmol) and [Ca{α-(Me_3Si)-*o*-(Me_2N)-benzyl}$_2$·(THF)$_2$] (**3**; 0.22 g, 0.37 mmol) in 10 mL of benzene was heated overnight at 80 °C. Concentration of the solution to 50% of its original volume yielded, after cooling to 5 °C, a batch of nicely formed colourless crystals of **5** (54 mg, 0.047 mmol, 26% yield). Decomposition temperature: approx. 160 °C. $C_{56}H_{120}Ca_2N_8Si_6$ (1154.3): calcd. C 58.27, H 10.48; found C 58.04, H 10.21. The crystals are only sparingly soluble in benzene or THF and NMR spectra in both solvents give broad signals also at higher temperatures. ^{1}H NMR ([D$_6$]benzene, 250 MHz, 50 °C): $δ$ = 0.25 (s, 18 H, Me_3Si), 0.33 (s, 36 H, Me_3Si), 1.03–2.15 (broad m's, 60 H, Cy), 3.31 (broad m's, 6 H, Cy) ppm. ^{13}C NMR spectroscopic data could not be recorded due to the low solubility of the complex and broad signals as a consequence of dynamic processes.

Crystal Structures: Crystal diffraction data were measured on an Enraf–Nonius CAD4 diffractometer (crystal data are given in Table 1). All crystal structures were solved with DIRDIF[34] and refined with SHELXL-97.[35] Absorption correction was applied for **2** using the psi-scans method incorporated in PLATON,[36] which was also used for geometry calculations and graphics for all structures described here. For all structures, hydrogen atoms were placed at calculated positions and were refined isotropically. The bridging amide in **5** shows disorder in the cyclohexane substituent but no appropriate disorder model could be found and the disordered molecule is described by large anisotropy in the ring atoms. Crystals of **5** also contain one equivalent of disordered benzene which was treated with the SQUEEZE procedure[37] incorporated in PLATON.

CCDC-272452–272454 (for **1**, **2** and **5**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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