Generating a New Chiral Ligand System for High-Valent Early Transition Metals — Synthesis and Structural Characterization of C_3-Symmetrical Tripodal Alkyl/Silyl Amido Complexes

Patrick Renner,[a] Christian H. Galka,[a] Lutz H. Gade,*[a] Sanja Radojevic,[b] and Mary McPartlin[b]

Dedicated to Professor Max Herberhold on the occasion of his 65th birthday

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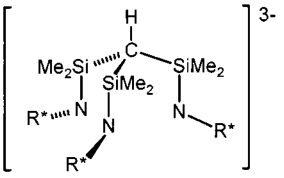
The novel C_3-chiral tripodal amine HC{SiMe$_2$NH[(*S*)-3,3-dimethyl-2-butyl]}$_3$ (**1**) and its trilithium triamido derivative [HC{SiMe$_2$N(Li)[(*S*)-3,3-dimethyl-2-butyl]}$_3$] (**2**) have been synthesized and characterized by X-ray diffraction. The lithium reagent was used for the synthesis of a C_3-chiral amidozirconium complex [HC{SiMe$_2$N[(*S*)-3,3-dimethyl-2-butyl]}$_3$ZrCl] (**3**); the preparation of the analogous titanium compound was precluded by the redox activity of the metal. Instead, the lithium amide-lithium chloride adduct [HC{SiMe$_2$N(Li)[(*S*)-3,3-dimethyl-2-butyl]}$_3$LiCl(Et$_2$O)$_3$] (**4**) was isolated from these reactions and structurally characterized by X-ray structure analysis. In this cage compound the chloride ion bridges the three amido lithium atoms and is itself coordinated to an {(Et$_2$O)$_3$Li}$^+$ fragment. Its isolation sheds new light upon the complex reaction sequences leading to halide substitution by a polydentate amido ligand.

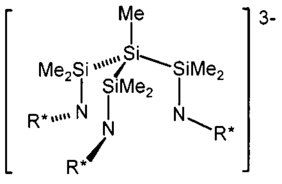
Introduction

Ligand design in early transition metal chemistry has, to a large extent, focussed on amides during the past decade.[1−4] It is the realization that the amido donor function R$_2$N$^-$ may be placed into a great variety of structural environments which has driven this development. It may be readily incorporated into complex polydentate ligand systems of podand or macrocyclic topology.[3] The synthesis of the ligands normally proceeds via the (secondary) amines, which can then be deprotonated and coordinated to transition metals.

We have developed a series of tripodal amido ligands which derive from such amine precursors.[5−7] Their synthesis is based either on the derivatization of a primary triamine containing the ligand backbone or the condensation of a suitably activated backbone unit with primary amines. The latter strategy has been applied in the preparation of triamido ligands derived from trisilylmethane (**A**) or trisilylsilane (**B**). An important point in this approach is the great variety of peripheral substituents at the N-functions which may be introduced in what is essentially a one-step synthesis. In this paper we report a novel tripodal ligand containing a trisilylmethane skeleton in which the peripheral substituents are chiral. The tridentate ligand therefore possesses C_3-chirality, and will be applied in the coordination chemistry of the early transition metals.



A



B

In spite of the burgeoning interest in C_3-chiral reagents and molecules,[8−11] by far the majority of the known systems are late transition metal compounds. The coordination of high-valent early transition metals requires highly charged ligands with strong σ- and π-donor functions such as alkoxides and amides in which chirality may either be introduced in the backbone structure or the peripheral substituents. While the former strategy has been pursued by Nugent, Knochel and Moberg,[12] we report an amido system in which the chiral centre is in the α-position of the peripheral substituent and thus close to a potential reactive site.[13]

Results and Discussion

Synthesis and Crystal Structures of HC{SiMe$_2$NH[(*S*)-3,3-dimethyl-2-butyl]}$_3$ (1) and Its Trilithium Triamido Derivative [HC{SiMe$_2$N(Li)[(*S*)-3,3-dimethyl-2-butyl]}$_3$] (2)

Reaction of the previously characterized trisilylmethane derivative HC(SiMe$_2$Br)$_3$ [6,14] with three molar equivalents

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[a] Laboratoire de Chimie Organométallique et de Catalyse (UMR 7513), Institut Le Bel, Université Louis Pasteur,
4, rue Blaise Pascal, 67070 Strasbourg, France
Fax: (internat.) + 33-3/90241531
E-mail: gade@chimie.u-strasbg.fr
[b] School of Applied Chemistry, University of North London,
Holloway Road, London N7 8DB, UK

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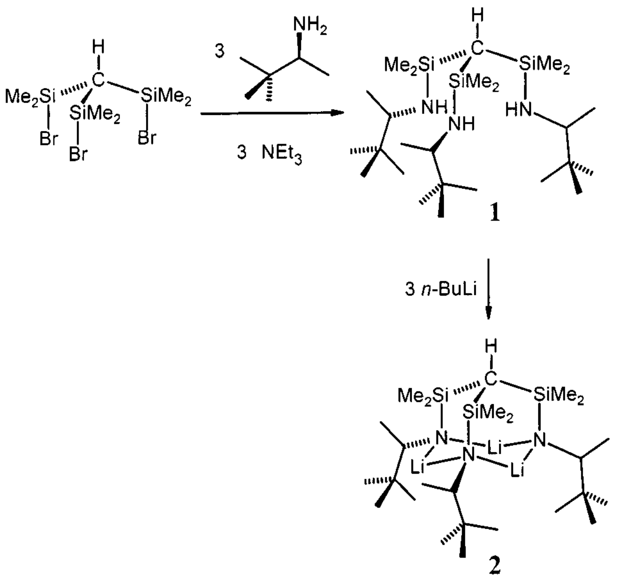
of (*S*)-3,3-dimethyl-2-butylamine in the presence of an excess of triethylamine as auxiliary base, after work up, cleanly gave the corresponding triamine HC{$SiMe_2NH$[(*S*)-3,3-dimethyl-2-butyl]}$_3$ (**1**) in good yield (Scheme 1). In a subsequent reaction step, the amine was converted into the corresponding trilithium triamide [HC{$SiMe_2N(Li)$[(*S*)-3,3-dimethyl-2-butyl]}$_3$] (**2**) by reaction with three equivalents of *n*BuLi.



Scheme 2. Synthesis of the triamine **1** and its lithiation giving **2**

The ^1H, ^{13}C and ^{29}Si NMR spectra of both compounds **1** and **2** are consistent with a threefold molecular symmetry on the time scale of the experiment. The ^1H NMR spectroscopic shifts of the apical CH protons in the trisilylmethane backbone are characteristically at high field. They are observed at $\delta = -0.81$ for the amine and at $\delta = -0.75$ in the spectrum of **2** recorded in C_6D_6. As a consequence of the chiral ligand periphery, the methyl groups of the $SiMe_2$ units are diastereotopic and are observed at $\delta = 0.27$ and 0.32 for **1** and slightly shifted to $\delta = 0.34$ and 0.38 for the lithiated derivative. In contrast to alkylamino derivatives of trisilylmethane which we studied previously,[6] the triamine **1** is stable in solution and no dissociation of a molecule of the chiral primary amine is observed even upon heating a sample to 70 °C.

It was possible to obtain single crystals of both compounds and thus establish their detailed molecular structure by an X-ray diffraction study. Both compounds **1** and **2** crystallize in the space group $P2_12_12_1$. The molecular structures of **1** and **2** are depicted in Figure 1 and 2, respectively, along with the principal bond lengths and angles. In both compounds the tripodal ligand adopts a "claw-like" arrangement which is part of an adamantane-related cage structure. In the amine **1** the base of this adamantane-related cage is formed by the three NH groups and, in contrast to the infrared data, the structure shows little evidence of intramolecular hydrogen bonding, with the N−H···N distances being in the range of 2.703−2.883 Å. This orientation of the ligand arms is in stark contrast to the "inverted" structural arrangement found for a range of aryl-substituted triamines of this type,[13a] but similar to the structure of the previously characterized chiral triamine HC{$SiMe_2NH$[(*S*)-1-phenylethyl]}$_3$.[13a] The positions of the NH hydrogen atoms in **1** were determined directly in difference Fourier maps, with the average N−H distance being 0.89 Å.

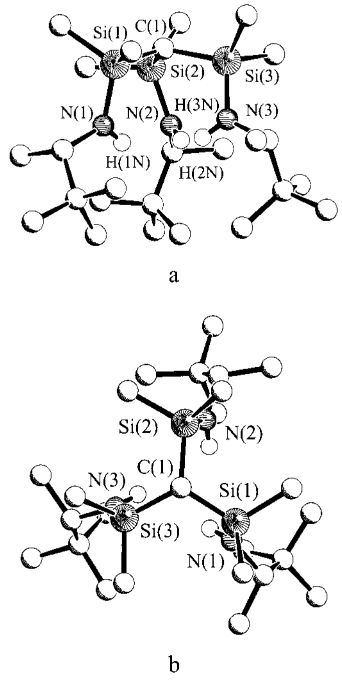


Figure 1. View of the molecular structure of **1** perpendicular (a) and along (b) the molecular axis of the tripod cage; the principal bond lengths (Å) and angles (°): C(1)−Si(1) 1.894(6), C(1)−Si(2) 1.874(6), C(1)−Si(3) 1.891(6), Si(1)−N(1) 1.720(5), Si(1)−C(2) 1.883(6), Si(1)−C(3) 1.884(6), N(1)−C(11) 1.472(7); Si(1)−C(1)−Si(3) 114.4(3), Si(1)−C(1)−Si(2) 114.7(3), Si(2)−C(1)−Si(3) 115.3(3), N(1)−Si(1)−C(1) 107.3(3), C(11)−N(1)−Si(1) 123.8(4), C(12)−C(11)−N(1) 110.0(5), C(13)−C(11)−N(1) 113.1(6)

The structural centrepiece of compound **2** is a heteroadamantane cage consisting of a puckered basal $(LiN)_3$ ring capped by the trisilylmethane unit. The Li−N−Li′−N′ torsion angles in the basal unit lie between 57.3(4) and 59.7(4)°, while the Li−N distances of between 1.890(6) and 1.983(6) Å are similar to those found in other cyclic lithium amides.[15] The lithium atoms are two coordinate [N−Li−N′ angles range between 124.2(3) and 127.8(3)°] although short Li····H−C contacts of between 2.04 and 2.17 Å with the isolated methyl groups of the $CH(CH_3)$*t*Bu units indicate "internal solvation" by the ligand periphery. Several cases of such interactions of low-coordinate lithium atoms and hydrocarbon units have previously been reported.[16]

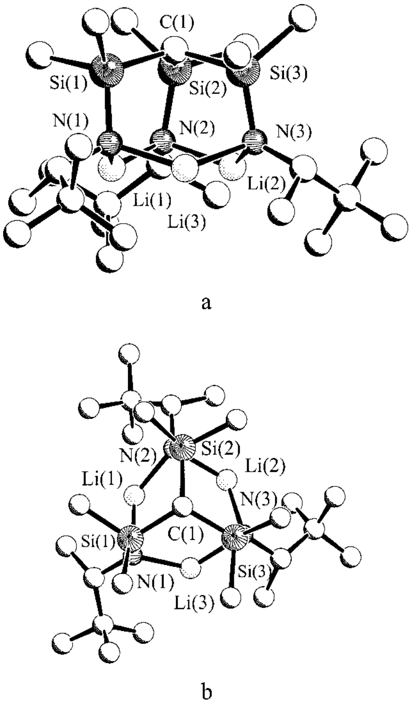
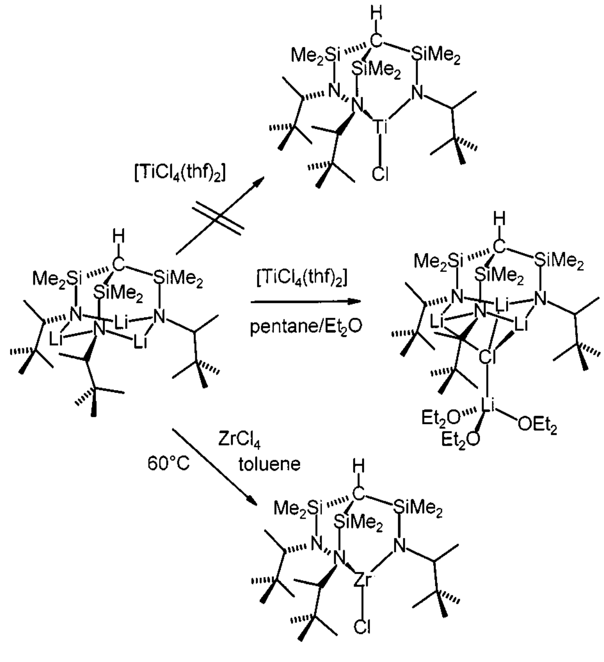


Figure 2. View of the molecular structure of **2** perpendicular (a) and along (b) the molecular axis of the metal-tripod cage; the principal bond lengths (Å) and angles (°): C(1)−Si(1) 1.899(3), C(1)−Si(2) 1.895(3), C(1)−Si(3) 1.904(3), Si(1)−N(1) 1.721(2), N(1)−Li(1) 1.968(6), N(1)−Li(3) 1.890(6), N(1)−C(10) 1.472(4); Si(1)−C(1)−Si(3) 114.36(15), Si(1)−C(1)−Si(2) 114.67(15), Si(2)−C(1)−Si(3) 113.82(14), N(1)−Si(1)−C(1) 107.51(12), N(1)−Li(1)−N(2) 127.8(3), Li(1)−N(1)−Li(3) 93.6(3), Si(1)−N(1)−Li(1) 95.5(2), C(10)−N(1)−Li(1) 107.6(2), Si(1)−N(1)−Li(3) 112.1(2)



Scheme 2. Reaction of **2** with $[TiCl_4(THF)_2]$ and $ZrCl_4$

Synthesis of a C_3-Chiral Amidozirconium Complex and Isolation and Structural Characterization of the Lithium Amide−Lithium Chloride Adduct [HC{SiMe$_2$N(Li)][(*S*)-3,3-dimethyl-2-butyl]}$_3$LiCl(Et$_2$O)$_3$] (4)

Complexation of the chiral amido tripod was first attempted by reaction of **2** with $[TiCl_4(THF)_2]$ (Scheme 2). However, even after stirring for four days in diethyl ether at ambient temperature, no titanium complex could be identified in the reaction mixture or isolated from it. This is surprising since the related C_3-chiral titanium complexes [HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$TiCl] and [HC{SiMe$_2$N[(*S*)-1-indanyl]}$_3$TiCl] were readily obtained.[17] The lack of reactivity may be due to the sterically crowed peripheral substituents in **2**. Attempts to induce complexation by heating the reaction mixture failed due to the redox activity of the titanium compound under these conditions. Immediate darkening of the solutions and the observation of paramagnetic species in the NMR spectra indicated reduction to Ti^{III}. However, none of these paramagnetic components could be isolated and further characterized.

Analogous to the reaction with $[TiCl_4(THF)_2]$ in diethyl ether, stirring of **2** with $ZrCl_4$ at room temperature did not give the corresponding zirconium complex. However, the synthesis of [HC{SiMe$_2$N[(*S*)-3,3-dimethyl-2-butyl]}$_3$ZrCl] (**3**) was achieved by heating the starting materials in toluene at 60 °C for 1 hour (Scheme 2). The colourless compound was obtained as a microcrystalline solid after work up and its formulation established by elemental analysis. The NMR spectra recorded in solution are consistent with the threefold molecular symmetry of complex **3**. The apical C−H proton of the tripod is observed at $\delta = -0.48$ and the diastereotopic SiMe$_2$ methyl groups resonate at $\delta = 0.28$ and 0.39. A single resonance at $\delta = 1.1$ in the ^{29}Si NMR spectrum confirms the equivalence of all three "claws" in the tripod.

Whereas the titanium complex proved not to be isolable from the reaction mixtures of **2** with $[TiCl_4(THF)_2]$, a colourless highly crystalline solid precipitated from the solutions. While the quantities of this component varied, it was reproducibly obtained from these reactions. While the ^{1}H, ^{13}C and ^{29}Si NMR spectra were almost identical to those of **2**, the proton NMR spectrum displayed the signals of coordinated diethyl ether and two resonances at $\delta = 0.8$ and -2.9 were observed in the ^{7}Li NMR spectrum, indicating a second Li environment. Its identity was established by a single crystal X-ray structure analysis. The molecular structure is depicted in Figure 3 along with the principal bond lengths and angles.

The colourless product isolated from the reaction of **2** with $[TiCl_4(THF)_2]$ was found to be the LiCl adduct [HC{SiMe$_2$N(Li)[(*S*)-3,3-dimethyl-2-butyl]}$_3$LiCl(Et$_2$O)$_3$] (**4**), the chloride deriving from the Ti complex. Compound **4** crystallizes in the polar trigonal space group *R*3 with two independent molecules in the asymmetric unit, each molecule aligned along a threefold crystallographic axis. The two molecules have virtually identical structures which are illustrated in Figure 3 by the first molecule. Chemically equivalent metric parameters are equal within experimental error

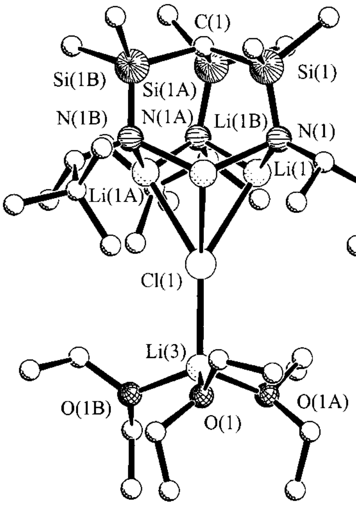


Figure 3. View of the molecular structure of **4** perpendicular to the molecular axis of the metal-tripod cage; the principal bond lengths (Å) and angles (°) (mean values): C(1)−Si(1) 1.887, Si(1)−N(1) 1.708, N(1)−Li(1) 1.990, N(1)−Li(1B) 1.993, Cl(1)−Li(1) 2.586, Cl(1)−Li(3) 2.396, Li(3)−O(1) 1.985; Si(1)−C(1)−Si(1A) 114.1, N(1)−Si(1)−C(1) 109.0, N(1)−Li(1)−N(1A) 122.2, Li(1)−N(1)−Li(1B) 82.0, O(1)−Li(3)−Cl(1) 107.9, Li(3)−Cl(1)−Li(1) 144.3, Cl(1)−Li(1)−N(1) 100.9, Li(1)−Cl(1)−Li(1A) 60.8

for the two molecules, and the mean values of selected bonds lengths and angles are given in the Caption to Figure 3. The chloride ion bridges the three amido lithium atoms and is itself coordinated to a $\{(Et_2O)_3Li\}^+$ fragment. The coordination environment of the anion is trigonally elongated along the molecular axis, probably in part because of the steric repulsion between the 3,3-dimethyl-2-butyl substituents and the Li-coordinated diethyl ether molecules. There are several examples in the literature of compounds in which a chloride ion connects four lithium centres in a fashion similar to that shown in Figure 3. Evans and co-workers reported the crystal structures of the yttrium complexes $[(Me_3SiCH_2)_x(Me_3CO)_{1-x}Y(\mu\text{-}OCMe_3)_4\{Li(THF)\}_4(\mu_4\text{-}Cl)]$ ($x = 0, 1$) in which the lithium atoms and the μ_4-chloride form pyramidal subunits,[18] while Floriani et al. reported $[MnCl(dag)_4Li_4(\mu_4\text{-}Cl)]$ (dag = mono anion of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) with the same Li_4Cl unit.[19] A Li_4Cl unit, which is highly distorted with respect to the idealized trigonal symmetry, was found by Deacon and White in the structure of $[\{Li(L^1)Li(\mu_4\text{-}Cl)Li(L^1)(THF)_2]$ (HL^1 = *N*,*N*-dimethyl-*N'*-trimethylsilylethane-1,2-diamine).[20]

The isolation of the LiCl adduct of **2** sheds some light upon the possible mechanism of the ligand substitution reactions involving lithium amides. Rather than direct nucleophilic attack by the amide upon a metal centre, the lithium ions play the role of a Lewis-acidic chloride acceptor. This notion of the active alkali metal ion is supported by the well established variations in reactivity upon going from lithium amides to their heavier congeners.

Conclusion

In this paper we have reported the synthesis of a novel C_3-chiral amido ligand, the structural chemistry of its amine precursor and lithiated derivative. While the preparation of a chiral triamidotitanium complex was not achieved due to competing single electron transfer, its zirconium homologue $[HC\{SiMe_2N[(S)\text{-}3,3\text{-dimethyl-2-butyl}]\}_3ZrCl]$ (**3**) was obtained in a straightforward way. This compound probably marks an extreme of steric congestion in the ligand periphery attainable in this class of compounds and current and future studies aim to exploit this structural feature. The isolation of the LiCl adduct of the chiral tripodal lithium amide has shed some light upon the possible primary steps in the mechanism of halide substitution in the synthesis of polydentate amido complexes.

Experimental Section

All manipulations were performed under an inert gas atmosphere of dried argon in standard (Schlenk) glassware which was flame dried with a bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried over 4Å molecular sieves.

The ^1H, ^{13}C, ^{29}Si and ^7Li NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable temperature unit (at 77.77 MHz) or on a Bruker AMX 400 spectrometer (at 400.13, 100.61 and 79.50 MHz, respectively) with tetramethylsilane or LiI/H_2O (1 M) as reference. The IR spectra were recorded on a Bruker IFS 25 FT-IR spectrometer.

Elemental analyses were carried out in the microanalytical laboratory of the chemistry department at Würzburg. The ligand pre cursor $HC(SiMe_2Br)_3$ was prepared as reported in the literature.[6,14]

Preparation of $HC\{SiMe_2NH[(S)\text{-}3,3\text{-dimethyl-2-butyl}]\}_3$ (1): To a stirred solution of (*S*)-3,3-dimethyl-2-butylamine (3.80 mL, 28.1 mmol) and NEt_3 (4.20 mL, 30.3 mmol) in diethyl ether (30 mL) was added $HC(SiMe_2Br)_3$ (4.00 g, 9.36 mmol) in diethyl ether (20 mL) at 0 °C. After stirring for 14 h at room temperature the ammonium salt formed during the reaction was removed by centrifugation and was washed three times with diethyl ether (ca. 20 mL). The solvent and the unreacted NEt_3 were removed under reduced pressure and the resulting yellow oil was redissolved in diethyl ether (ca. 10 mL) and stored at 4 °C. Compound **1** was obtained as a colourless, highly crystalline solid (yield: 3.87 g, 85%). − M.p.: 110 °C. − ^1H NMR (400.13 MHz, C_6D_6, 295 K): $\delta = -0.81$ [s, 1 H, $HC(Si...)_3$], 0.27, 0.32 [2 × s, 2 × 9 H, $Si(CH_3)_2$], 0.93 [s, 27 H, $C(CH_3)_3$], 0.99 [d, $^3J_{HCNH}$ = 12.7 Hz, 3 H, N*H*), 1.09 (d, $^3J_{HH}$ = 6.9 Hz, 9 H, $HCCH_3$), 2.48 (dq, $^3J_{HCNH}$ = 12.7 Hz, $^3J_{HH}$ = 6.9 Hz, 3 H, $HCCH_3$). − $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 295 K): δ = 3.9, 4.4 [$Si(CH_3)_2$], 5.5 [$HC(Si...)_3$], 20.6 ($HCCH_3$), 27.0 [$C(CH_3)_3$], 35.4 [$C(CH_3)_3$], 56.6 ($HCCH_3$). − $^{29}Si\{^1H\}$ NMR (79.50 MHz, C_6D_6, 295 K): δ = 0.9. − IR (benzene): $\tilde{\nu}$ = 3355 (s), 2964 (vs), 2903 (s), 2869 (s), 1477 (w), 1412 (m), 1400 (m), 1369 (m), 1362 (w), 1252 (vs), 1122 (vs), 1011 (s), 956 (s), 870 (s), 826 (s), 812 (vs), 668 (m) cm^{-1}. − $C_{25}H_{61}N_3Si_3$ (488.04): calcd. C 61.53, H 12.60, N 8.61; found C 60.65, H 11.88, N 8.40.

Preparation of [HC{SiMe$_2$N(Li)[(*S*)-3,3-dimethyl-2-butyl]}$_3$] (2): To a stirred solution of **1** (3.39 g, 6.95 mmol) in *n*-pentane (30 mL) at −78 °C was added a 2.5 M solution of *n*BuLi in *n*-hexane (8.34 mL, 20.86 mmol). After stirring for 14 h at room temperature the yellow solution was concentrated to ca. 7 mL. Storage of the solution at 4 °C yielded colourless crystals of **2** (yield: 3.32 g, 94%). − M.p.: 172 °C. − ^{1}H NMR (400.13 MHz, C_6D_6, 295 K): δ = −0.75 [s, 1 H, *H*C(Si...)$_3$], 0.34, 0.38 [2 × s, 2 × 9 H, Si(C*H*$_3$)$_2$], 0.76 [s, 27 H, C(C*H*$_3$)$_3$], 0.95 (d, $^3J_{HH}$ = 6.2 Hz, 9 H, HCC*H*$_3$), 2.82 (q, $^3J_{HH}$ = 6.2 Hz, 3 H, *H*CCH$_3$). − ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 295 K): δ = 6.1, 7.1 [Si(*C*H$_3$)$_2$], 12.1 [H*C*(Si...)$_3$], 24.5 (HC*C*H$_3$), 27.7 [C(*C*H$_3$)$_3$], 36.0 [s, *C*(CH$_3$)$_3$], 60.5 (H*C*CH$_3$). − ^{29}Si{^{1}H} NMR (79.50 MHz, C_6D_6, 295 K): δ = −1.8. − ^{7}Li{^{1}H} NMR (77.77 MHz, C_6D_6, 295 K): δ = 0.7. $C_{25}H_{58}Li_3N_3Si_3$ (505.84): calcd. C 59.36, H 11.56, N 8.31; found C 58.82, H 11.16, N 7.94.

Preparation of [HC{SiMe$_2$N[(*S*)-3,3-dimethyl-2-butyl]}$_3$ZrCl] (3): To a stirred solution of **2** (0.35 g, 0.70 mmol) in toluene (5 mL) was added solid $ZrCl_4$ (0.38 mg, 1.60 mmol). After treatment in an ultrasonic bath for 24 h at 60 °C the precipitate of LiCl and unreacted $ZrCl_4$ was separated by centrifugation. Storage of the filtrate at −30 °C yielded the zirconium complex **3** as an off-white microcrystalline solid (yield: 0.14 g, 34%). − ^{1}H NMR (400.13 MHz, [D$_8$]toluene, 295 K): δ = −0.48 [s, 1 H, *H*C(Si...)$_3$], 0.28, 0.39 [2 × s, 2 × 9 H, Si(C*H*$_3$)$_2$], 1.03 [s, 27 H, C(C*H*$_3$)$_3$], 1.45 (d, 9 H, $^3J_{HH}$ = 6.2 Hz, HCC*H*$_3$), 2.88 (m, 3 H, *H*CCH$_3$). − ^{13}C{^{1}H} NMR (100.61 MHz, [D$_8$]toluene, 295 K): δ = 1.5 [H*C*(Si...)$_3$], 5.7, 5.9 [Si(*C*H$_3$)$_2$], 27.5 (HC*C*H$_3$), 27.8 [C(*C*H$_3$)$_3$], 36.4 [s, *C*(CH$_3$)$_3$], 62.5 (H*C*CH$_3$). − ^{29}Si{^{1}H} NMR (79.50 MHz, [D$_8$]toluene, 29: δ = 1.1. − IR (toluene): ṽ = 2960 (vs), 2964 (vs), 2871 (s), 1477 (s), 1458 (s), 1254 (vs), 1104 (vs), 1082 (vs), 1011 (m), 951 (vs), 868 (vs), 840 (vs), 815 (vs), 678 (w) cm^{-1}. − $C_{25}H_{58}ClN_3Si_3Zr$ (611.69): calcd. C 49.09, H 9.56, N 6.87; found C 48.66, H 9.45, N 6.99.

Preparation of [HC{SiMe$_2$N(Li)[(*S*)-3,3-dimethyl-2-butyl]}$_3$-LiCl(Et$_2$O)$_3$] (4): To a stirred solution of **2** (0.50 g, 0.99 mmol) in diethyl ether (10 mL) at −20 °C was added [TiCl$_4$(THF)$_2$] (0.33 g, 0.99 mmol). After stirring for four days at room temperature the precipitate was separated by centrifugation. Storage of the dark brown solution at 4 °C yielded colourless crystals of **4** (yield: 0.19 g, 24%). The yield obtained in several runs of this reaction varied between ca. 10% and 30%. Due to facile loss of diethyl ether it was not possible to obtain a correct elemental analysis. − M.p.: 31 °C (dec.). − ^{1}H NMR (400.13 MHz, [D$_8$]toluene, 295 K): δ = −0.75 [s, 1 H, *H*C(Si...)$_3$], 0.32, 0.37 [2 × s, 2 × 9 H, Si(C*H*$_3$)$_2$], 0.77 [s, 27 H, C(C*H*$_3$)$_3$], 0.96 (d, 9 H, $^3J_{HH}$ = 6.2 Hz, HCC*H*$_3$), 1.12 (t, Et$_2$O), 2.82 (q, 3 H, $^3J_{HH}$ = 6.2 Hz, *H*CCH$_3$), 3.28 (q, Et$_2$O). − ^{13}C{^{1}H} NMR (100.61 MHz, [D$_8$]toluene, 295 K): δ = 6.0, 7.0 [Si(*C*H$_3$)$_2$], 12.1 [H*C*(Si...)$_3$], 15.5 (Et$_2$O), 24.5 (HC*C*H$_3$), 27.7 [C(*C*H$_3$)$_3$], 36.0 [s, *C*(CH$_3$)$_3$], 60.6 (H*C*CH$_3$), 65.8 (Et$_2$O). − ^{29}Si{^{1}H} NMR (79.50 MHz, [D$_8$]toluene, 295 K): δ = −1.8. − ^{7}Li{^{1}H} NMR (77.77 MHz, [D$_8$]toluene, 295 K): δ = −2.9, 0.8.

X-ray Crystallographic Study of 1,2 and 4: Data of **1** were collected using a Siemens P4 diffractometer at a temperature of 301(2) K with oil-coated crystals mounted in Lindemann tubes. Data of **2**

Table 1. Crystal data and structure refinement for **1**, **2** and **4**

	1	2	4
Molecular formula	$C_{25}H_{61}N_3Si_3$	$C_{25}H_{58}Li_3N_3Si_3$	$C_{37}H_{88}ClLi_4N_3O_3Si_3$
M_r	488.04	505.83	770.58
Temperature	301(2) K	193(2) K	193(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic	Trigonal
Space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$R3$ (no. 146)
Z	4	4	6
Unit cell dimensions	a = 10.106(4) Å b = 16.461(5) Å c = 20.268(6) Å	a = 9.0263(6) Å b = 17.2032(17) Å c = 21.0887(16) Å	a = 17.0152(8) Å c = 30.264(3) Å
Volume	3372(2) Å^3	3274.7(5) Å^3	7588.1(8) Å^3
$D_{calcd.}$	0.961 g cm^{-3}	1.026 g cm^{-3}	1.012 g cm^{-3}
Absorption coefficient	0.156 mm^{-1}	0.161 mm^{-1}	0.178 mm^{-1}
F(000)	1096	1120	2556
Crystal size	0.38 × 0.38 × 0.38 mm	0.50 × 0.30 × 0.30 mm	0.40 × 0.40 × 0.40 mm
Scan method	$\theta/2\theta$-scan	ω/θ-scan	ω/θ-scan
θ range for data collection	2.01 to 22.00°	2.27 to 24.96°	2.02 to 24.47°
Limiting indices	$-10 \le h \le 10$, $-17 \le k \le 17$, $-21 \le l \le 21$	$-10 \le h \le 1$, $-20 \le k \le 2$, $-25 \le l \le 2$	$-19 \le h \le 1$, $-1 \le k \le 19$, $-35 \le l \le 3$
Reflections collected	4730	4141	3686
Independent reflections ($R_{int.}$)	4138 (0.0472)	3892 (0.0135)	3165 (0.0320)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4138/0/280	3892/105/365	3165/25/311
$T_{max/min}$	-/-	0.9994/0.9201	0.9995/0.9701
Goodness-of-fit on F^2	0.910	1.036	1.047
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0562, wR_2 = 0.0996	R_1 = 0.0380, wR_2 = 0.0883	R_1 = 0.0531, wR_2 = 0.1303
R indices (all data)	R_1 = 0.1462, wR_2 = 0.1293	R_1 = 0.0468, wR_2 = 0.0948	R_1 = 0.0668, wR_2 = 0.1391
Absolute structure parameter	0.3(2)	−0.34(13)	−0.02(14)
Largest diff. peak and hole	0.181 and −0.232 e Å^{-3}	0.246 and −0.218 e Å^{-3}	0.299 and −0.236 e Å^{-3}

and **4** were collected using an Enraf−Nonius CAD4 diffractometer at a temperature of 193(2) K with oil-coated shock-cooled crystals[21] mounted on the top of a glass pin under nitrogen. Crystal data and experimental details for the crystals of **1**, **2** and **4** are given in Table 1. All data for the structures **2** and **4** were corrected for absorption using Ψ-scans. No absorption correction was applied for structure **1**. The structures were solved by direct methods (SHELXS-97) and refined on F^2 (SHELXL-97).[22]

In the case of **2** one methyl and one *tert*-butyl group of a ligand arm were found to be 50:50 disordered and refined with anisotropic displacement parameters. In the case of **4**, disorder of all coordinated diethyl ether molecules in a 75:25 ratio was found and refined with isotropic displacement parameters. No hydrogen atoms could be calculated for C5S′ of a disordered Et_2O molecule. In the final cycles of refinement all non-hydrogen atoms of **1**, **2** and **4** were assigned anisotropic displacement parameters. The amino hydrogen atoms of **1** were found in a final difference Fourier transformation analysis, all other hydrogen atoms were included in idealized positions riding on the parent atoms and were assigned isotropic displacement parameters of 1.2 U_{eq} (CH, CH_2) and 1.5 U_{eq} (CH_3) of the parent atom.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-156281 (**1**), -156282 (**2**) and -156283 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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