

Synthesis, structure and reactivity of scandium bis(trimethylsilyl)amido derivatives



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ABSTRACT

The synthesis of scandium complexes supported by two bis(trimethylsilyl)amido ligands and their reactivity to generate a variety of organometallic derivatives is reported. The monomeric scandium complex $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{Cl}$, **1**, and the “ate” complex $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Cl}_2\text{Li}(\text{THF})_3$, **2**, were generated by salt metathesis routes from $\text{ScCl}_3(\text{THF})_3$ and $\text{LiN}(\text{SiMe}_3)_2$. Complex **1** reacts cleanly with MeLi or KCH_2Ph to form the compounds $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{R}$, ($\text{R} = \text{Me}$, **3**; CH_2Ph , **4**), respectively. Upon reaction of **1** with bulky lithium reagents such as $\text{LiCH}_2\text{SiMe}_3$ or TripLi, cyclometalation at scandium occurs to generate the bimetallic species $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\mu\text{-CH}_2)_2\text{Sc}\{\text{N}(\text{SiMe}_3)\text{SiMe}_2\}_2(\text{THF})$, **5**. Finally, the scandium iodide congener $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{I}$, **6**, was produced by reaction of **3** with the iodide transfer reagent $[\text{Et}_3\text{NH}]\text{I}$. Attempts to access a low valent scandium complex, by reduction of **6** with either KC_8 or $[(\text{nacnac})\text{Mg}]_2$, where $\text{nacnac} = (2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)$ failed to afford well-defined low valent organometallic scandium species. All compounds were characterized by single crystal X-ray diffraction studies.

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1. Introduction

Silazane ligands have proven to be popular groups for incorporation into rare earth complexes for well over 40 years. In particular, the use of the bis(trimethylsilyl)amido ligand for preparing remarkable homoleptic three coordinate metal complexes, $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_3$, of both rare earth ($\text{M} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Ho}, \text{Yb}, \text{Lu}$ and Y) [1], and early first row d-block metals ($\text{M} = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}$ and Fe) [2] was initially reported in the 1970s. Later, additional homoleptic bis(trimethylsilyl)amido derivatives of the lanthanides were published [3]. These complexes have proven invaluable in rare earth chemistry as precursors to an incredibly wide array of organometallic complexes via amine elimination protocols [4]. In subsequent years, variants of the bis(trimethylsilyl)amido ligand have emerged, with the 1,1,3,3-tetramethyldisilazane group representing a prominent example of a less sterically demanding alternative. Notably, silazane derivatives of the rare earth metals continue to grow in popularity for use in organometallic chemistry, as they tend to be both thermally robust and straightforward to prepare via commercially available starting materials.

Ligand redistribution is a common problem encountered when substituting ligands in rare earth complexes. Because of this diffi-

culty, the synthesis of mixed ligand complexes of the lanthanides by salt metathesis can be exceedingly challenging. A variety of bis(trimethylsilyl)amido/chloride complexes of the lanthanide series, as well as yttrium, have been previously prepared and found to exist typically as dimers in the solid-state with the generic formula $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2(\mu\text{-Cl})_2]$, where $\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Yb}$ and Y [5]. Such heteroleptic rare earth complexes bearing two silazane ligands and a halide are of great intrinsic value because they can serve as precursors for ligand derivatization via single or double amine elimination with proteo ligands of general form H_2L or HL to yield products $[\text{Ln}(\text{L})_2\text{X}]$ or $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_2\text{X}(\text{L})]$, respectively [5d,6]. Recently, $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2(\mu\text{-Cl})_2]$ was converted into the yttrium phenylacetylide complex $[(\text{PhC}\equiv\text{C})\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_2]$, which was implicated as an intermediate in the catalytic cycloaddition of terminal alkynes to azides to afford 1,5-disubstituted-1,2,3-triazoles [7]. Additionally, upon appropriate activation, mixed amido/halide complexes can also be used as catalysts for the polymerization of olefins [8].

Accordingly, we were interested in extending the chemistry of mixed bis(trimethylsilyl)amido/halide complexes to the smaller rare earth metal scandium in order to explore the organometallic reactivity of such species. In this work, the preparation of a bis(trimethylsilyl)amido/chloride complex of scandium, $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{Cl}$, **1**, is described. Salt metathesis of **1** with various group 1 organometallic reagents resulted in the facile formation of a range of organoscandium derivatives, which have all been

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characterized by single crystal X-ray diffraction. Additionally, we have prepared the mixed bis(trimethylsilyl)amido/iodide derivative and investigated its suitability for reduction chemistry.

2. Results and discussion

2.1. Synthesis of complexes and characterization

Reaction of the tetrahydrofuran adduct of scandium chloride, $\text{ScCl}_3(\text{THF})_3$, with 2 equivalents of $\text{LiN}(\text{SiMe}_3)_2$ in toluene solution resulted in clean formation of the mixed bis(trimethylsilyl)amido chloride complex, $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{Cl}$, (**1**, Scheme 1) in high yield (92%, recrystallized). This complex has previously been reported in a patent as a pre-catalyst for olefin polymerization; however, only limited characterization data was provided and no reaction chemistry beyond olefin polymerization has been published [9]. In particular, any discussion of the solid-state structure of **1** or reactivity to form organometallic derivatives thereof is notably absent from the literature. The ^1H NMR spectrum of complex **1** (benzene- d_6) exhibits a singlet at δ 0.39 (36H) corresponding to two equivalent silazane ligands, in addition to two multiplets at δ 3.98 and 1.17, each integrating to 4H, consistent with one coordinated THF ligand. Single crystals of **1** suitable for an X-ray diffraction experiment were grown from a concentrated toluene solution at -35°C . Complex **1** adopts a monomeric structure in the solid state (Fig. 1), and as suggested by the NMR data, one equivalent of THF is retained as a donor ligand to stabilize the coordinatively unsaturated metal. The scandium center exhibits distorted tetrahedral geometry. Notably, the steric bulk imparted by bis(trimethylsilyl)amido groups sufficiently saturates the metal's coordination sphere such that the molecule exists as a monomer. This species can be readily compared to the mixed amido chloride complex, $[\text{Sc}\{\text{N}(\text{SiHMe}_2)_2\}_2(\text{THF})(\mu\text{-Cl})_2]$ (2.049 Å) and the homoleptic complex $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_3$ (average length = 2.049 Å) [1c]. The Sc–Cl distance is 2.3824(4) Å, which is likewise comparable to other monomeric scandium chloride structures, such as $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2\text{Cl}_2$ [11], which exhibits an average Sc–Cl contact of 2.389 Å.

It was previously documented that compound **1** could be synthesized by reaction of scandium(III) chloride with potassium

hexamethyldisilazide in THF [9]; however, we discovered that the use of THF as a reaction solvent can lead to “ate” complex formation when using lithium hexamethyldisilazide as the source of silylamide ligand. Specifically, we found that reaction of $\text{ScCl}_3(\text{THF})_3$ with 2 equivalents of $\text{LiN}(\text{SiMe}_3)_2$ in THF resulted in formation of the “ate” complex $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Cl}_2\text{Li}(\text{THF})_3$, **2**. When triturated with toluene, complex **2** can be reverted to **1** with loss of both LiCl and THF (Scheme 1).

Recrystallization of the “ate” complex **2** from heptane solution yielded single crystals suitable for analysis by X-ray diffraction. The complex crystallized as a racemic twin in the orthorhombic space group $\text{P}2_12_12_1$ and the molecular structure is depicted in

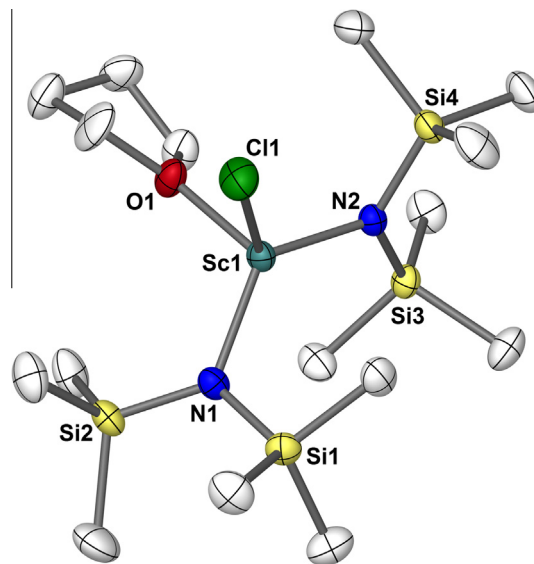


Fig. 1. Thermal ellipsoid plot (50% probability) of $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{Cl}$ (**1**) with hydrogen atoms omitted for clarity.

Table 1
Selected bond distances (Å) and angles ($^\circ$) for compounds **1–4** and **6**.

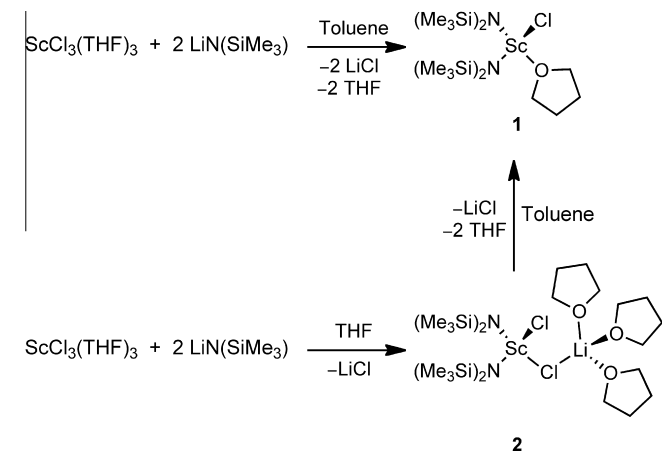
	1	2	3	4	6
Sc1–N1	2.038(1)	2.066(3)	2.061(2)	2.068(1)	2.048(2)
Sc1–N2	2.053(1)	2.064(3)	2.068(2)	2.064(1)	2.017(2)
Sc1–E ^a	2.3824(4)	2.373(1)	2.287(3)	2.269(2)	2.8002(5)
Sc1–O1 ^b	2.1274(9)	–	2.159(2)	2.151(1)	2.123(2)
N1–Si1	1.731(1)	1.718(3)	1.723(2)	1.729(1)	1.733(2)
N1–Si2	1.731(1)	1.726(3)	1.723(2)	1.726(1)	1.738(2)
N2–Si3	1.731(1)	1.714(3)	1.726(2)	1.734(1)	1.733(2)
N2–Si4	1.737(1)	1.725(3)	1.731(2)	1.727(1)	1.736(2)
Sc1–Cl1 ^c	–	2.422(1)	–	–	–
Li1–Cl1 ^c	–	2.413(7)	–	–	–
N1–Sc1–N2	126.06(4)	122.5(1)	122.0(1)	120.9(1)	123.0(1)
N1–Sc1–O1 ^b	109.45(4)	–	114.5(1)	96.15(4)	97.4(1)
N2–Sc1–O1 ^b	97.89(4)	–	100.1(1)	114.23(4)	109.5(1)
O1–Sc1–E ^b	95.79(3)	–	91.6(1)	110.0(1)	93.9(1)
N1–Sc1–E	108.08(3)	110.6(1)	108.7(1)	113.6(1)	120.8(1)
N2–Sc1–E	114.43(3)	106.7(1)	115.6(1)	102.1(1)	106.8(1)
Si1–N1–Si2	121.4(1)	121.3(2)	120.7(1)	119.2(1)	120.9(1)
Si3–N2–Si4	122.8(1)	121.7(2)	121.2(1)	118.8(1)	121.3(1)
Sc1–Cl1–Li1 ^c	–	121.7(2)	–	–	–
N1–Sc1–Cl1 ^c	–	104.1(1)	–	–	–
N2–Sc1–Cl1 ^c	–	108.4(1)	–	–	–
Cl2–Sc1–Cl1 ^c	–	102.9(1)	–	–	–
Sc1–Cl3–Cl4 ^d	–	–	–	105.9(1)	–

^a E corresponds to the atom Cl1 for compound **1**, Cl2 for compound **2**, C17 for compound **3**, C13 for compound **4**, I1 for compound **6**.

^b The listed parameter pertains only to compounds **1**, **3**, **4**, and **6**.

^c The listed parameter pertains only to compound **2**.

^d The listed parameter pertains only to compound **4**.



Scheme 1. Synthesis of mixed bis(trimethylsilyl)amido chloride complexes of scandium.

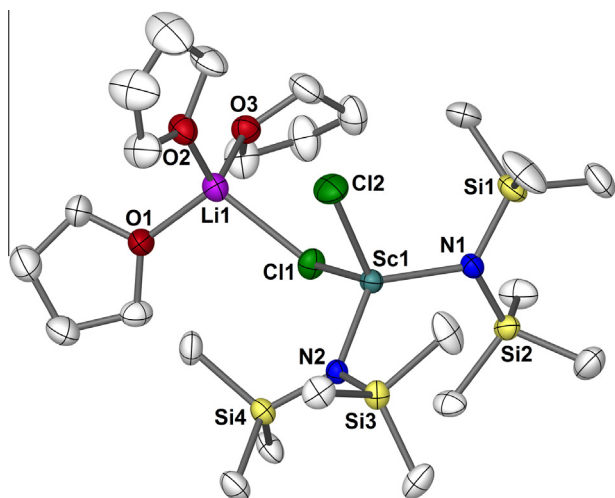


Fig. 2. Thermal ellipsoid plot (50% probability) of $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Cl}_2\text{Li}(\text{THF})_3$ (**2**), with hydrogen atoms omitted for clarity.

Fig. 2 as a thermal ellipsoid plot. Similar to **1**, complex **2** is monomeric in the solid state with a four-coordinate scandium center. Both Sc–N contacts (2.066(3) and 2.064(3) Å) are slightly elongated relative to that in **1** (Table 1). As expected, the terminal Sc–Cl2 bond length (2.373(1) Å) is shorter than that to the bridging chloride ligand. Bond distances of 2.422(1) Å (Sc1–Cl1) and 2.413(7) Å (Li1–Cl1) were measured for the chloride ligand bridging Sc and Li; the Sc1–Cl1–Li1 bond angle is 121.6(2)°.

Reaction of **1** with the reagents MeLi or KCH_2Ph in toluene at ambient temperature yielded the expected organometallic derivatives $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{Me}$, **3**, and $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{CH}_2\text{Ph}$, **4**, respectively (Scheme 2). Both complexes are monomeric in the solid state with one THF molecule retained as a Lewis base donor. The ^1H NMR spectrum of **3** (benzene- d_6) exhibits a singlet integrating to 3H at δ 0.141, corresponding to the methyl ligand. The silazane ligands resonate as a singlet at δ 0.39 and the THF donor gives rise to multiplets at δ 3.84 and 1.14. Similarly, the ^1H NMR spectrum of complex **4** (cyclohexane- d_{12}) showed signals consistent with one benzyl ligand; the expected aromatic signals were observed in the range from δ 6.60–6.98 while the methylene protons resonate as a singlet at δ 2.20. Signals from the other groups were as expected: a singlet (δ 0.22) that integrated as 36H corresponds to equivalent bis(trimethylsilyl)amido functionalities and two multiplets at δ 3.87 and 1.79 are consistent with one coordinated THF ligand.

Both complexes **3** and **4** were characterized by single crystal X-ray diffraction experiments. Single crystals of both complexes were obtained from concentrated toluene solutions at -35°C and the molecular structures are depicted as thermal ellipsoid plots in Figs. 3 and 4, respectively. Complexes **3** and **4** are both monomeric in the solid state and feature four-coordinate scandium centers

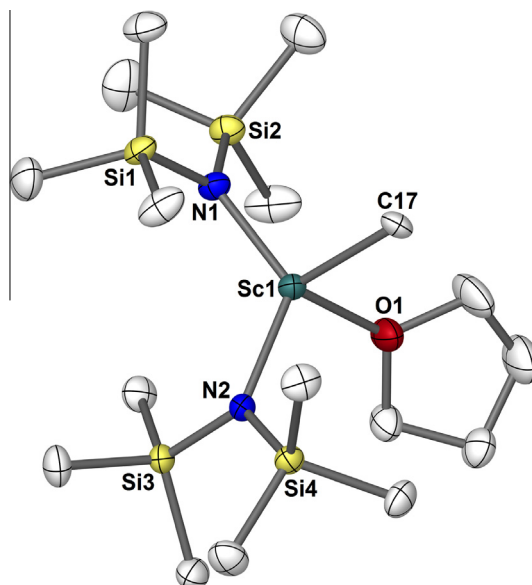


Fig. 3. Thermal ellipsoid plot (50% probability) of $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{Me}$ (**3**) with hydrogen atoms omitted for clarity.

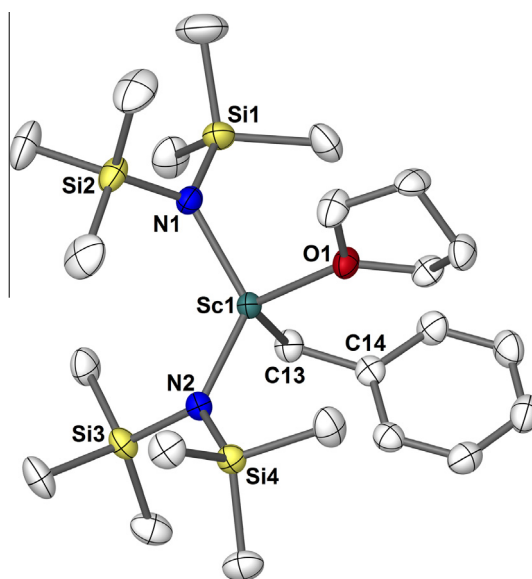
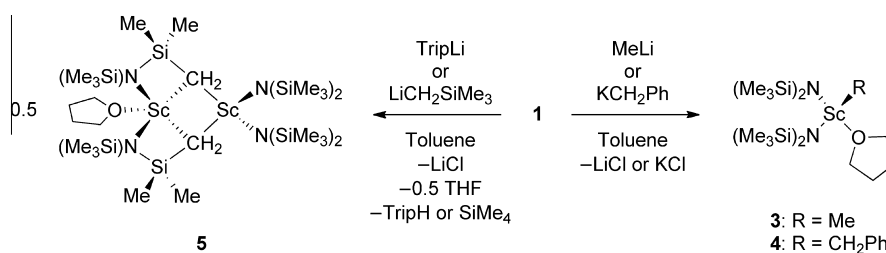


Fig. 4. Thermal ellipsoid plot (50% probability) of $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{CH}_2\text{Ph}$ (**4**) with hydrogen atoms omitted for clarity.

with distorted tetrahedral geometry. The Sc–N bond lengths in both complexes are comparable to one another (**3**: 2.060(2), 2.067(1); **4**: 2.064(1), 2.068(1) Å; Table 1). Typical Sc–C contacts



Scheme 2. Synthesis of bis(trimethylsilyl)amido supported organoscandium complexes.

are also found in both species: in **3**, the methyl group (C17) is 2.285(2) Å from scandium. The η^1 -bound benzyl group in complex **4** exhibits a Sc–CH₂ length of 2.269(2) Å, and a Sc1–C13–C14 bond angle of 105.9(1)°. The next closest contact of the benzyl ligand with scandium is via the *ipso* carbon (C14) with a separation of 3.027(1) Å; this distance is outside of the typical range expected for Sc–C bonds and does not suggest a significant bonding interaction between Sc and C14.

In contrast to the clean formation of the methyl and benzyl derivatives **3** and **4** by salt metathesis of **1** with methyl lithium and benzyl potassium, respectively, when **1** was reacted with bulkier organolithium reagents, the formation of an unusual doubly cyclometalated bimetallic complex, Sc{N(SiMe₃)₂}₂(μ-CH₂)₂Sc{N(SiMe₃)SiMe₂}₂(THF), **5**, was observed. In **5**, two silazane ligands have undergone deprotonation of the γ -methyl C–H groups to afford a doubly cyclometalated species. Complex **5** can be accessed by reaction of **1** with either 2,4,6-triisopropylphenyllithium (TripLi) or LiCH₂SiMe₃ (Scheme 2). It is presumed that in both cases the reaction proceeds through the expected metathesis product (Sc{N(SiMe₃)₂}₂(THF)R, where R = Trip or CH₂SiMe₃) with loss of LiCl; however, due to the bulky nature of these organometallic ligands, the complex then decomposes by intra- and intermolecular cyclometalative C–H bond activation to afford the bimetallic complex **5**, with loss of RH [12]. This notion is supported by the fact that when the benzyl derivative **4** was heated to 80 °C in benzene-*d*₆, the *in situ* formation of cyclometalated compound **5** and toluene was observed by ¹H NMR spectroscopy.

The molecular structure of **5** was unambiguously established by single crystal X-ray diffraction and is depicted in Fig. 5 as a thermal ellipsoid plot. The complex adopts an asymmetric bimetallic configuration with two cyclometalated carbon atoms bridging two scandium centers. One scandium (Sc1) is four-coordinate and tetrahedral, while the other (Sc2) is pentacoordinate and exhibits distorted trigonal bipyramidal geometry. The tetrahedral geometry of Sc1 is comprised of two silazane ligands bound via nitrogen (N1 and N2) and two bridging cyclometalated carbon atoms (C27 and C28). The trigonal bipyramidal Sc2 bears a THF ligand, and a silazane group bound via both nitrogen (N3) and cyclometalated carbon atoms (C27), in the equatorial positions. Another silazane group (N4) and the remaining cyclometalated carbon atom (C28) occupy the apical sites. Intriguingly, the cyclometalated carbons (C27 and C28) bridge both scandium ions; however, it is notable

Table 2
Selected bond distances (Å) and angles (°) for compound **5**.

N1–Si1	1.736(2)	N3–Si5	1.725(2)
N1–Si2	1.725(2)	N3–Si6	1.727(2)
N2–Si3	1.731(2)	N4–Si7	1.713(2)
N2–Si4	1.737(2)	N4–Si8	1.710(2)
Sc1–C27	2.288(2)	Sc2–C27	2.370(2)
Sc1–C28	2.318(2)	Sc2–C28	2.442(2)
Sc1–N1	2.081(2)	Sc2–N3	2.028(2)
Sc1–N2	2.092(2)	Sc2–N4	2.066(2)
Sc2–O1	2.164(1)		
N1–Sc1–N2	123.5(1)	C28–Sc1–C27	95.2(1)
Si1–N1–Si2	121.8(1)	Si5–N3–Si6	125.8(1)
Si3–N2–Si4	115.6(1)	Si7–N4–Si8	125.3(1)
N1–Sc1–C28	109.7(1)	N2–Sc1–C28	114.1(1)
N1–Sc1–C27	105.9(1)	N2–Sc1–C27	103.9(1)
N4–Sc2–C28	165.5(1)	N3–Sc2–C27	123.7(1)
O1–Sc2–N3	112.7(1)	C27–Sc2–O1	121.2(1)
Sc1–C27–Sc2	88.5(1)	Sc1–C28–Sc2	86.1(1)

that both originate from the silylamido ligands on Sc2, while the silazane ligands bound to Sc1 remain intact.

The contacts between the scandium and metalated carbon atoms vary slightly within the complex (Table 2). Those bonded to Sc1 are marginally shorter (Sc1–C27 = 2.288(2) Å and Sc1–C28 = 2.318(2) Å) than those to Sc2 (Sc2–C27 = 2.370(2) Å and Sc2–C28 = 2.442(2) Å). This difference is likely due to the different geometries enforced at each metal center. The cyclometalated silazane ligands in **5** form planar four-membered metallacycles comparable to those in related rare earth complexes [13], as well as transition metal [14] and actinide [15] complexes possessing cyclometalated silazane ligands.

2.2. Attempted reduction chemistry

Access to the scandium iodide species Sc{N(SiMe₃)₂}₂(THF)I, **6**, was achieved by reaction of the scandium methyl complex **3** with [Et₃NH]I in methylene chloride (Scheme 3). Complex **6** has previously been described as a reagent in scandium reduction chemistry; however, neither synthetic details nor full characterization data were documented [16]. The ¹H NMR spectrum of **6** is similar to that of **1**, with one signal at δ 0.42 (36H) corresponding to the silazane ligands, and two multiplets at δ 4.10 and 1.16, consistent with one coordinated molecule of THF. Single crystals of complex **6** suitable for X-ray diffraction analysis were grown from a concentrated toluene solution at –35 °C and the molecular structure is displayed in Fig. 6. The structure features tetrahedral geometry comparable to that observed in complex **1**, with two silazane ligands, one iodide, and a THF donor. The Sc–N bond lengths of 2.048(2) and 2.017(2) Å, and Sc–I distance of 2.8002(5) Å fall within normal parameters.

In a preliminary effort to prepare a low valent scandium species, complex **6** was reacted with KC₈ (10 equivalents) in toluene solution. This resulted in the formation of a red oil as the major product; however, despite extensive efforts we were unable to unambiguously establish the identity of this compound or the nature of the scandium oxidation state with certainty. Isolation and characterization of this species is the focus of an investigation currently in progress in our lab. The formation of a colored (red)

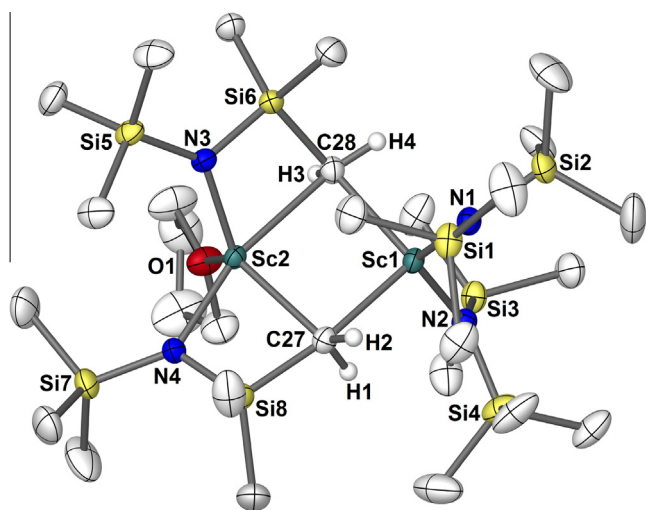
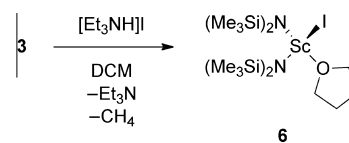


Fig. 5. Thermal ellipsoid plot (50% probability) of Sc{N(SiMe₃)₂}₂(μ-CH₂)₂Sc{N(SiMe₃)SiMe₂}₂(THF) (**5**) with hydrogen atoms (except H1, H2, H3 and H4) omitted for clarity.



Scheme 3. Synthesis of Sc{N(SiMe₃)₂}₂(THF)I.

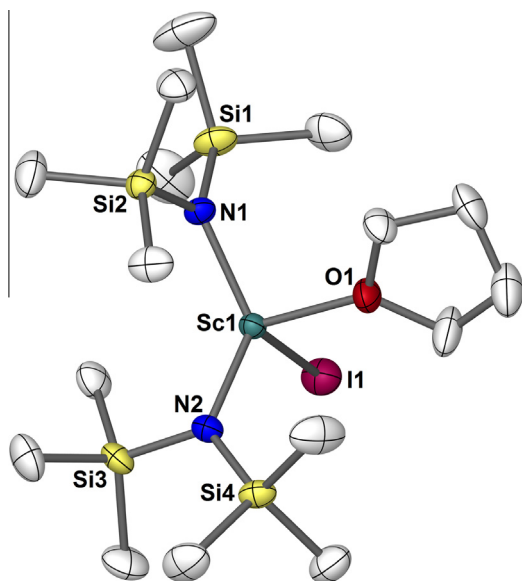


Fig. 6. Thermal ellipsoid plot (50% probability) of $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{I}$ (**6**) with hydrogen atoms omitted for clarity.

product may be indicative of a low valent scandium or mixed valent ($\text{Sc}^{1+}/\text{Sc}^{3+}$) complex [17], especially compared to the Sc^{3+} complexes **1–6** described herein, which, as expected, are colorless. Notably, the major product from this reaction exhibited a significant downfield shift of the silazane ligand resonances (δ 0.64) in the ^1H NMR spectrum (benzene-*d*₆) compared to that of the starting material, **6** at δ 0.42. No THF resonances were evident in the ^1H NMR spectrum and all attempts to crystallize the product failed, suggesting a possible oligomeric or polymeric species. In contrast to reduction attempts of **6** using KC_8 , reduction of **6** with the Mg (I) dimer, [nacnacMg]₂ [18], resulted in ligand redistribution that afforded the homoleptic complex $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_3$ as well as scandium metal, which deposited on the reaction glassware as a mirror. Due to these results, the bis(trimethylsilyl)amido ligand does not appear to provide sufficient steric bulk to stabilize a highly reactive low valent scandium species. It has been demonstrated previously that bulky multidentate ligands can drastically facilitate the stabilization and isolation of otherwise hard to access and highly reactive low valent metal complexes [19]. In this vein, we are working toward preparing a family of scandium dialkyl complexes supported by a bis(pyrazolyl)carbazole ligand [20], (CzPz)ScR₂, from which, we expect analogous reduction chemistry may yield more stable complexes that can be isolated and fully characterized.

3. Conclusions

The synthesis and characterization of a variety of scandium complexes supported by two bis(trimethylsilyl)amido ligands is described. The developed complexes, which represent valuable starting materials for subsequent functionalization by salt metathesis and alkane and amine elimination routes, include scandium bis(trimethylsilyl)amido complexes possessing chloride (**1**), methyl (**3**), benzyl (**4**) and iodide (**6**) ligands. Attempts to prepare derivatives containing bulkier CH_2SiMe_3 or Trip groups resulted in intra- and inter-molecular cyclometalative C–H bond activation of the γ -methyl groups of the silazane ligand, resulting in formation of a doubly cyclometalated species, **5**. Preliminary attempts to prepare low valent scandium complexes from **6**, supported by the bis(trimethylsilyl)amido ligand, have met with limited success.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere with the rigorous exclusion of oxygen and water using standard glove box (MBraun) or high vacuum line techniques, unless specified otherwise. The solvents pentane, heptane, benzene, toluene and THF were dried and purified using a solvent purification system (MBraun) and stored in evacuated 500 mL bombs over either “titanocene” indicator (pentane, heptane, benzene and toluene) or sodium benzophenone ketyl (THF). Deuterated solvents (benzene-*d*₆, toluene-*d*₈ and cyclohexane-*d*₁₂) were dried over sodium benzophenone ketyl, degassed via three freeze–pump–thaw cycles, distilled under vacuum and stored in glass bombs under argon. Unless otherwise specified, all solvents required for air-sensitive manipulations were introduced directly into the reaction flasks by vacuum transfer with condensation at -78°C . Samples for NMR spectroscopy were recorded on a 300 MHz Bruker Avance II (Ultraschield) spectrometer (^1H 300.13 MHz, $^{13}\text{C}\{^1\text{H}\}$ 75.47 MHz) and referenced relative to SiMe_4 through the residual solvent resonance(s) for ^1H and $^{13}\text{C}\{^1\text{H}\}$. All NMR spectra were recorded at ambient temperature (295 K) unless specified otherwise. Elemental analyses were performed using an Elementar Americas Vario MicroCube instrument. The reagents $\text{ScCl}_3(\text{THF})_3$ [21], $\text{K}(\text{CH}_2\text{Ph})$ [22], and TripLi [23], were prepared according to literature procedures. A solid sample of MeLi was obtained by removal of diethyl ether from a 1.6 M solution purchased from Sigma–Aldrich. A solid sample of $\text{LiCH}_2\text{SiMe}_3$ was obtained by removal of pentane from a 1.0 M solution purchased from Sigma–Aldrich. All deuterated solvents were purchased from Cambridge Isotope Laboratories. All other reagents were obtained from Sigma–Aldrich or Alfa Aesar and used as received.

4.2. Synthesis of compounds

4.2.1. $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Cl}(\text{THF})$ (**1**)

To an intimate mixture of $\text{LiN}(\text{SiMe}_3)_2$ (7.02 g, 42.0 mmol) and $\text{ScCl}_3(\text{THF})_3$ (7.72 g, 21.0 mmol) toluene (65 mL) was added via vacuum transfer with condensation at -95°C . The solution was allowed to slowly warm to ambient temperature and was stirred for 14.5 h during which time a white precipitate formed. The volatiles were removed *in vacuo* to give a white residue that was then brought into a glove box. The product was extracted into toluene and filtered to remove LiCl. The filtrate was concentrated under vacuum and left at -35°C to crystallize. White crystals were collected by filtration, washed with heptane and dried under reduced pressure. Yield: 9.11 g (92%). ^1H NMR (benzene-*d*₆): δ 3.98 (m, 4H, OCH_2), 1.17 (m, 4H, OCH_2CH_2), 0.39 (s, 36H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene-*d*₆): δ 75.1 (OCH_2), 24.9 (OCH_2CH_2), 5.3 ($\text{Si}(\text{CH}_3)_3$). Anal. Calc. for $\text{C}_{16}\text{H}_{44}\text{ClN}_2\text{OScSi}_4$: C, 40.60; H, 9.37; N, 5.92. Found: C, 40.22; H, 8.97; N, 5.81%.

4.2.2. $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Cl}_2\text{Li}(\text{THF})_2$ (**2**)

A 100 mL round-bottomed flask attached to a swivel frit apparatus was charged with $\text{LiN}(\text{SiMe}_3)_2$ (2.90 g, 17.32 mmol) and $\text{ScCl}_3(\text{THF})_3$ (3.18 g, 8.66 mmol). The flask was cooled to -78°C and THF (50 mL) was added by vacuum transfer. The cloudy yellow solution was allowed to slowly warm to ambient temperature and then stirred for 17 h. The solvent was removed under vacuum and the residue was reconstituted in pentane and filtered to remove LiCl. The collected solid was then washed thoroughly with pentane, and all volatiles were removed from the filtrate to leave the product as a white solid. Yield: 4.62 g (81%). Further manipulation of the material (especially dissolution in toluene or benzene solvents)

caused rapid loss of LiCl and THF from the complex and reversion to **1**. Because of this, characterization of complex **2** by solution NMR spectroscopy was not possible. Furthermore, upon drying the material thoroughly under vacuum, loss of THF was also evident, resulting in an unsatisfactory elemental combustion analysis of **2**. Upon recrystallization of **2** from heptane at $-35\text{ }^{\circ}\text{C}$, a mixture of crystals of **2** and **1** were obtained. Due to the different crystal habits of **2** and **1**, it was possible to carefully select crystals of **2** under a microscope (over those of **1**) for characterization by single crystal X-ray diffraction. The crystals of complex **1** formed by this manner were positively identified by X-ray diffraction unit cell determination.

4.2.3. $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Me}(\text{THF})$ (**3**)

To a flask charged with **1** (0.794 g, 1.68 mmol) and MeLi (0.0382 g, 1.74 mmol) 15 mL of toluene was added at ambient temperature. The cloudy colorless solution was stirred at ambient temperature for 2 h and then filtered through a bed of Celite. The filtrate was concentrated under vacuum and left at $-35\text{ }^{\circ}\text{C}$ overnight to crystallize. The white crystals were collected by filtration, washed with cold pentane and dried under vacuum. Yield: 0.637 g (84%). ^1H NMR (benzene- d_6): δ 3.84 (m, 4H, OCH_2), 1.14 (m, 4H, OCH_2CH_2), 0.39 (s, 36H, $\text{Si}(\text{CH}_3)_3$), 0.14 (s, 3H, ScCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6): δ 73.1 (OCH_2), 30.1 (ScCH_3), 24.8 (OCH_2CH_2), 5.4 ($\text{Si}(\text{CH}_3)_3$). *Anal. Calc.* for $\text{C}_{17}\text{H}_{47}\text{N}_2\text{OScSi}_4$: C, 45.09; H, 10.46; N, 6.19. Found: C, 44.81; H, 10.16; N, 6.27%.

4.2.4. $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2\text{CH}_2\text{Ph}(\text{THF})$ (**4**)

Toluene (10 mL) was added to a solid mixture of **1** (0.356 g, 0.752 mmol) and KCH_2Ph (0.107 g, 0.822 mmol) at ambient temperature to give a pale cloudy orange solution. The mixture was stirred at ambient temperature for 1 h until the reaction appeared complete as evidenced by the loss of the red colored KCH_2Ph . The cloudy solution was filtered through a bed of Celite that was then washed with a further 2 mL toluene. The combined filtrates were

concentrated under vacuum and left at $-35\text{ }^{\circ}\text{C}$ overnight to crystallize. The crystals were collected by filtration, washed with cold pentane and dried under vacuum. Yield: 0.0795 g (20%). ^1H NMR (cyclohexane- d_{12}): δ 6.98–6.89 (ov m, 4H, *ortho*- & *meta*-CH), 6.60 (tt, $^3J_{\text{HH}} = 6.7\text{ Hz}$, $^4J_{\text{HH}} = 1.8\text{ Hz}$, ^1H , *para*-CH), 3.87 (m, 4H, OCH_2), 2.20 (s, 2H, ScCH_2Ph), 1.79 (m, 4H, OCH_2CH_2), 0.22 (s, 36H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6): δ 150.6 (*ipso*-C), 128.6 (*meta*-CH), 125.9 (*ortho*-CH), 119.7 (*para*-CH), 73.6 (OCH_2), 59.8 (br s, ScCH_2Ph), 24.6 (OCH_2CH_2), 5.4 ($\text{Si}(\text{CH}_3)_3$). *Anal. Calc.* for $\text{C}_{23}\text{H}_{51}\text{N}_2\text{OScSi}_4$: C, 52.22; H, 9.72; N, 5.30. Found: C, 52.48; H, 9.75; N, 5.15%.

4.2.5. $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\mu\text{-CH}_2)_2\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})$ (**5**)

A solution of **1** (0.255 g, 0.539 mmol) and $\text{LiCH}_2\text{SiMe}_3$ (0.0544 g, 0.578 mmol) in toluene (10 mL) was stirred at ambient temperature for 2.5 h. The cloudy colorless solution was filtered through a fine porosity frit and the colorless filtrate was then concentrated under reduced pressure. The liquor was left at $-35\text{ }^{\circ}\text{C}$ to generate large prisms which were collected via filtration, washed with cold pentane, and dried under vacuum. Yield: 0.131 g (61%). ^1H NMR (benzene- d_6): δ 3.93 (m, 4H, OCH_2), 1.25 (m, 4H, OCH_2CH_2), 0.425 (br ov s, $\Delta\nu_{1/2} = 20\text{ Hz}$, 52 H, $\text{Si}(\text{CH}_3)_2\text{CH}_2 + \text{Si}(\text{CH}_3)_2\text{CH}_2 + \text{N}\{\text{Si}(\text{CH}_3)_2\}$), 0.312 (ov s, 18H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6): δ 73.2 (OCH_2), 52.2 ($\text{Si}(\text{CH}_3)_2\text{CH}_2$), 24.8 (OCH_2CH_2), 6.5 ($\text{Si}(\text{CH}_3)_2\text{CH}_2$), 6.3 ($\text{N}\{\text{Si}(\text{CH}_3)_2\}$), 5.2 ($\text{Si}(\text{CH}_3)_3$). *Anal. Calc.* for $\text{C}_{28}\text{H}_{78}\text{N}_4\text{OSc}_2\text{Si}_8$: C, 41.96; H, 9.81; N, 6.99. Found: C, 41.85; H, 9.64; N, 6.83%.

4.2.6. $\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_2\text{I}(\text{THF})$ (**6**)

Methylene chloride (20 mL) was added to a flask containing **3** (0.515 g, 1.14 mmol) and Et_3NHI (0.246 g, 1.14 mmol). The mixture was stirred at ambient temperature for 1 h to give a clear and colorless solution. All volatiles were removed under vacuum to afford a white solid. In a glove box, the residue was taken up in toluene (5 mL) and filtered through a bed of Celite to remove trace

Table 3
Summary of X-ray crystallography data collection and structure refinement for compounds **1**–**6**.

	1	2	3	4	5	6
Formula	$\text{C}_{16}\text{H}_{44}\text{ClN}_2\text{OScSi}_4$	$\text{C}_{24}\text{H}_{60}\text{Cl}_2\text{LiN}_2\text{O}_3\text{ScSi}_4$	$\text{C}_{17}\text{H}_{47}\text{N}_2\text{OScSi}_4$	$\text{C}_{23}\text{H}_{51}\text{N}_2\text{OScSi}_4$	$\text{C}_{28}\text{H}_{78}\text{N}_4\text{OSc}_2\text{Si}_8$	$\text{C}_{16}\text{H}_{44}\text{IN}_2\text{OScSi}_4$
FW (g mol $^{-1}$)	473.30	659.90	452.89	528.98	801.58	564.75
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
<i>a</i> (Å)	8.4120(9)	12.2536(18)	11.8745(5)	13.0375(8)	11.6266(10)	8.5363(12)
<i>b</i> (Å)	11.7049(12)	16.857(3)	19.1099(8)	18.6230(11)	18.8789(16)	10.1688(14)
<i>c</i> (Å)	15.823(2)	18.921(3)	12.2345(5)	13.2799(8)	21.6936(18)	17.838(3)
α ($^{\circ}$)	106.3480(10)	90	90	90	90	79.9030(10)
β ($^{\circ}$)	93.7160(10)	90	98.3237(4)	100.5570(10)	92.7640(10)	89.776(2)
γ ($^{\circ}$)	108.0690(10)	90	90	90	90	70.8500(10)
<i>V</i> (Å 3)	1401.3(3)	3908.2(10)	2747.0(2)	3169.7(3)	4756.1(7)	1437.7(3)
<i>Z</i>	2	4	4	4	4	2
<i>D</i> _{calc} (g cm $^{-3}$)	1.122	1.122	1.095	1.108	1.119	1.305
μ (mm $^{-1}$)	0.537	0.472	0.451	0.400	0.511	1.504
Crystal size (mm 3)	$0.60 \times 0.39 \times 0.26$	$0.60 \times 0.14 \times 0.12$	$0.32 \times 0.31 \times 0.20$	$0.69 \times 0.25 \times 0.20$	$0.58 \times 0.14 \times 0.13$	$0.41 \times 0.12 \times 0.08$
θ ($^{\circ}$)	1.93–27.47	1.62–27.10	1.99–27.10	1.91–27.10	1.88–27.10	2.16–27.10
<i>N</i>	15449	43286	30772	35363	53192	15941
<i>N</i> _{ind}	6315	8609	6064	6990	10487	6256
Data/restraints/parameters	6315/3/266	8609/0/380	6064/0/239	6990/9/320	10487/0/426	6256/0/238
Goodness-of-fit (GOF) on F^2	1.029	1.006	1.048	1.037	1.017	1.057
<i>R</i> ₁ ($I > 2\sigma(I)$) ^a	0.0245	0.0520	0.0345	0.0301	0.0359	0.0306
<i>wR</i> ₂ ($I > 2\sigma(I)$) ^b	0.0701	0.0940	0.0946	0.0797	0.0852	0.0741
<i>R</i> ₁ (all data) ^a	0.0280	0.1092	0.0438	0.0393	0.0534	0.0365
<i>wR</i> ₂ (all data) ^b	0.0730	0.1139	0.1015	0.0859	0.0939	0.0775
Abs. structure parameter	–	0.39(4)	–	–	–	–
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ (e Å $^{-3}$)	0.311; –0.184	0.305; –0.232	0.548; –0.282	0.274; –0.186	0.391; –0.272	1.828; –1.110

Notes:

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|.$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2 \}^{1/2}.$$

amounts of excess Et₃NHl. The filtrate was concentrated to 3 mL and left at –35 °C to crystallize. The mother liquor was decanted off, leaving white needles that were washed with a minimal amount of cold pentane and dried thoroughly under reduced pressure. Yield: 0.487 g (76%). ¹H NMR (benzene-*d*₆): δ 4.10 (m, 4H, OCH₂), 1.16 (m, 4H, OCH₂CH₂), 0.42 (s, 36H, Si(CH₃)₃). ¹³C{¹H} NMR (benzene-*d*₆): δ 75.8 (OCH₂), 24.5 (OCH₂CH₂), 5.4 (Si(CH₃)₃). Anal. Calc. for C₁₆H₄₄IN₂O₂Si₄: C, 34.03; H, 7.85; N, 4.96. Found: C, 33.94; H, 7.55; N, 5.07%.

4.3. X-ray crystallography

Recrystallization of compounds **1**, **3**, **4**, **5** and **6** from concentrated toluene solutions at –35 °C and **2** from heptane at –35 °C afforded single crystals suitable for X-ray diffraction. Crystals were coated in hydrocarbon oil under an argon atmosphere and mounted onto a glass fiber. Data were collected at –100 °C using a Bruker SMART APEX II diffractometer (Mo K α radiation, λ = 0.71073 Å) outfitted with a CCD area-detector and a KRYO-FLEX liquid nitrogen vapor cooling device. A data collection strategy using ω and φ scans at 0.5° steps yielded full hemispherical data with excellent intensity statistics. Unit cell parameters were determined and refined on all observed reflections using APEX2 software [24]. Data reduction and correction for Lorentz polarization were performed using SAINT-Plus software [25]. Absorption corrections were applied using SADABS [26]. The structures were solved by direct methods and refined by the least squares method on F^2 using the SHELXTL software suite [27]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and isotropically refined as riding models to their parent atoms, except in the case of **5**, where the hydrogen atoms attached to metalated carbons (H1, H2, H3, H4) were allowed to refine freely based on electron density from the Fourier map and were held isotropic. Details of the data collection and refinement are given in Table 3. Special considerations were required in the refinement of disordered moieties in the structures of **1** and **4**. In both structures, the THF ligand was disordered over two positions (**1**: 50%/50%; **4**: 53%/47%). Some geometric and displacement restraints were applied in the disorder refinement of **1** and **4** in order to obtain reasonable bond distances and angles.

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Appendix A. Supplementary data

CCDC 1403276–1403281 contain the supplementary crystallographic data for compounds **1–6**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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