Scandium Reduced Arene Complex: Protonation and Reaction with Azobenzene

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Abstract: The reactivity of the reduced anthracene complex of scandium [Li(thf)$_3$][Sc{N(tBu)Xy}$_2$(anth)] (**2-anth-Li**) (Xy = 3,5-Me$_2$C$_6$H$_3$; anth = C$_{14}$H$_{10}$$^{2-}$, thf = tetrahydrofuran) toward Brønsted acid [NEt$_3$H][BPh$_4$] and azobenzene is reported. While a stepwise protonation of **2-anth-Li** with two equivalents of [NEt$_3$H][BPh$_4$] afforded the scandium cation [Sc{N(tBu)Xy}$_2$(thf)$_2$][BPh$_4$] (**3**), reduction of azobenzene gave a thermolabile, anionic scandium reduced azobenzene complex [Li(thf)][Sc{N(tBu)Xy}$_2$(η^2-PhNNPh)] (**4**), which slowly lost one of the anilide ligands to form the neutral scandium azobenzene complex dimer [Sc{N(tBu)Xy}(μ-η^2:η^2-Ph$_2$N$_2$)]$_2$ (**5**).

Exposure of **3** to CO$_2$ produced the scandium carbamate complex [Sc{κ^2-O$_2$CN(tBu)(Xy)}$_2$][BPh$_4$] (**6**) as a result of CO$_2$ insertion into the Sc–N bonds. In an attempt to prepare scandium hydrides, the reaction of **3** with the hydride sources LiAlH$_4$ and Na[BEt$_3$H] led to the terminal aluminum hydride [AlH{N(tBu)Xy}$_2$(thf)] (**7**) and the scandium n-butoxide [Sc{N(tBu)(Xy)}$_2$(μ-OnBu)] (**8**) after Sc/Al transmetalation and nucleophilic ring-opening of THF, respectively. All reported compounds isolated in moderate to good yields were fully characterized.

Introduction

The chemistry of early transition metals is dominated by their high-valent states owing to their highly oxophilic and electropositive nature.[1] In recent years low-valent early transition metal complexes have attracted attention due to their stoichiometric as well as catalytic applications in small molecule activation,[2] reductive coupling[3] and radical reactions.[4] High reactivity and the tendency towards oxidation to their highest oxidation states often makes isolation of these low-valent early transition metal complexes challenging. Specifically, for scandium, the transition metal with the lowest atomic number, only a limited number of complexes in its low valent states are known, with just a few of them isolated and structurally characterized.[5] For instance, the first isolated examples of Sc^{II} complexes [M(L)]][Sc{N(SiMe$_3$)$_2$}$_3$] (M = K and Cs; L = 2.2.2-crypt-and and 18-crown-6) were reported by Evans et al. only in 2017 and were shown to activate CO$_2$ and N$_2$ even at low temperature.[6] General paucity of such low-valent scandium complexes hindered the exploration of their reactivity. The use of transition metal reduced arene complexes to mimic the property of low-valent transition metal complexes is an alternative approach that has been applied in recent years.[7] In

this regard, a series of scandium reduced arene complexes of the general formula [(NN^{fc})Sc]$_2$(μ-RA) (NN^{fc} = (NSitBuMe$_2$)$_2$fc; fc = 1,1'-ferrocenediyl; RA = C$_{10}$H$_8$$^{2-}$ (**I**), C$_{14}$H$_{10}$$^{2-}$ (**II**))[8] and [M(thf)$_n$][Sc{N(tBu)Xy}$_2$(RA)] (M = Li–K; n = 1–6; RA = C$_{10}$H$_8$$^{2-}$ (**2-naph-M**) and C$_{14}$H$_{10}$$^{2-}$ (**2-anth-M**); Xy = 3,5-Me$_2$C$_6$H$_3$)[9] were prepared by Diaconescu et al. and our group. While **I** and **II** were shown to activate P$_4$,[10] C–F bonds,[11] and promote reductive C–C coupling reaction of alkynes[12] and pyridine,[8] **2-anth-Li** endure C–C coupling reaction of nitriles with reduced anthracene ligand.[9] As a continuation of our work, we present here a systematic study on the protonation of the reduced anthracene complex **2-anth-Li** with Brönsted acid to afford a dianilide scandium cation, and the use of **2-anth-Li** as a 2e$^-$ donor reagent in the reduction of azobenzene.

Results and Discussion

A systematic study on the protonation of transition metal complexes of dianionic naphthalene or anthracene ligand has not been reported,[8] prompting us to investigate the protonation of the recently reported scandium reduced anthracene complex [Li(thf)$_3$][Sc{N(tBu)Xy}$_2$(anth)] (**2-anth-Li**) (Xy = 3,5-Me$_2$C$_6$H$_3$; anth = C$_{14}$H$_{10}$$^{2-}$). In our earlier report we have shown that the protonation of **2-anth-Li** with one equivalent of [NEt$_3$H][BPh$_4$] led to the formation of the scandium anthracenyl complex [Sc{N(tBu)Xy}$_2$(C$_{14}$H$_{11}$)(thf)].[9] Here we present a stepwise protonation of **2-anth-Li** with two equivalent of [NEt$_3$H][BPh$_4$] in THF that produced the bis(anilide) scandium cation [Sc{N(tBu)Xy}$_2$(thf)$_2$][BPh$_4$] (**3**) after elimination of 9,10-dihydroanthracene (Scheme 1, Figure S5). After work-up, compound **3** was isolated as a spectroscopically pure, colorless solid in 81% yield (See supporting information (SI), Sec. 2.2). Compound **3** was also obtained in a more efficient way starting from the scandium alkyl complex [Sc{N(tBu)Xy}$_2$(CH$_2$SiMe$_3$)(thf)] (**1-CH$_2$SiMe$_3$**), which was prepared by salt metathesis of [ScCl

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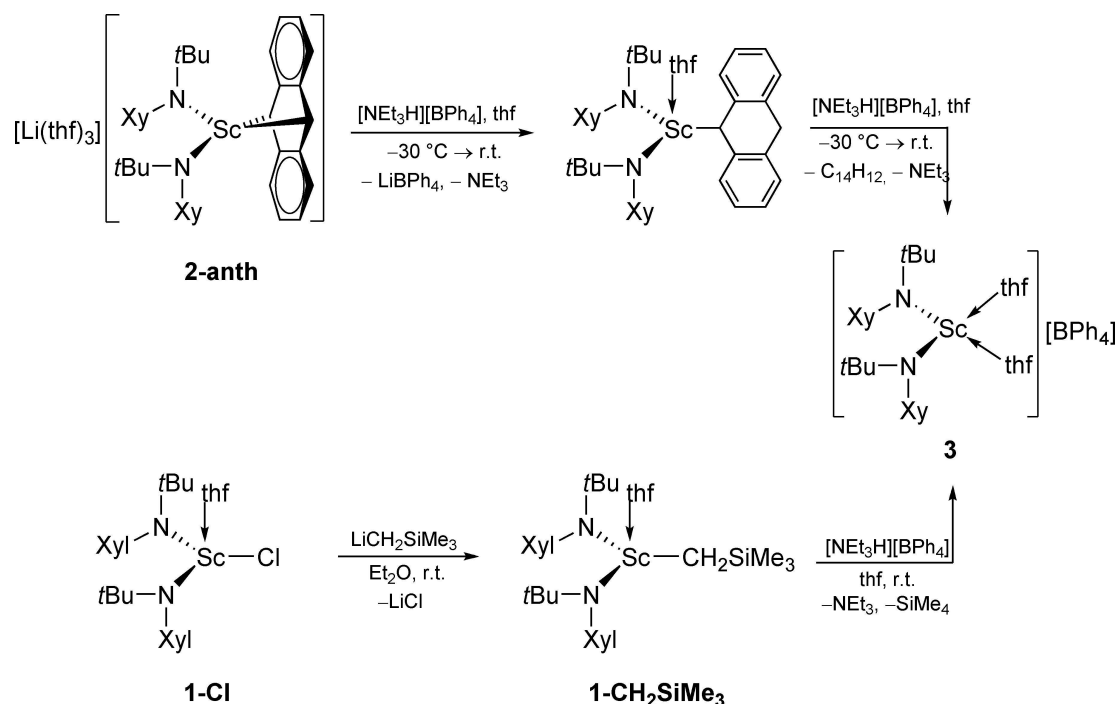
Scheme 1. Synthesis of the scandium alkyl complex **1-CH$_2$SiMe$_3$** and scandium cation **3**.

{N(*t*Bu)Xy}$_2$(thf)] (**1-Cl**) with LiCH$_2$SiMe$_3$ (Scheme 1) and fully characterized by multinuclear magnetic resonance spectroscopy, elemental analysis, and single crystal X-ray diffraction (See SI, Sec. 2.1 and 3). Protonation of **1-CH$_2$SiMe$_3$** with one equivalent of [NEt$_3$H][BPh$_4$] under ambient condition afforded the scandium cation **3** in 88% isolated yield (See SI, Sec. 2.2). Thermally stable compound **3** is highly soluble in THF but insoluble in Et$_2$O, benzene, or aliphatic hydrocarbons.

The molecular structure of **3**, as confirmed by single crystal X-ray diffraction, revealed that the cation is well separated from the BPh$_4$ anion with a closest Sc···H distance of 5.8829(5) Å. Compound **3** represents a rare example of a structurally characterized scandium cation.[13,14] In the solid state the tetra-coordinate scandium atom resides in a distorted tetrahedral environment formed by the two anilide ligands and two THF molecules (Figure 1). The Sc—N distances of 1.9913(16) and 2.0327(18) Å in complex **3** are significantly shorter compared to that of the precursor **2-anth-Li** ($d(\text{Sc-N})_{avg} = 2.126$ Å)[9] or **1-CH$_2$SiMe$_3$** ($d(\text{Sc-N})_{avg} = 2.072$ Å) (Figure S28), indicating an increased N→Sc donation due to the increased positive charge on the scandium atom. Similarly, Sc—O bonds ($d(\text{Sc-O})_{avg} = 2.1418$ Å) in **3** are also shorter compared to that found in **1-CH$_2$SiMe$_3$** ($d(\text{Sc-O}) = 2.190(2)$ Å) (Figure S28).

Further structural information of **3** was obtained from multinuclear magnetic resonance spectroscopy. The ^{1}H and ^{13}C{^{1}H} NMR spectra in [D$_8$]THF corroborate well with the solid-state structure and display a single set of signals in a 2:1 ratio for the anilide ligands and [BPh$_4$]$^-$ anion. The most characteristic spectroscopic feature of compound **3** is the broad ^{45}Sc NMR signal at $\delta = 312$ ppm ($\Delta v_{1/2} = \sim 10000$ Hz, Figure S9) that appears at a higher field when compared to that of the
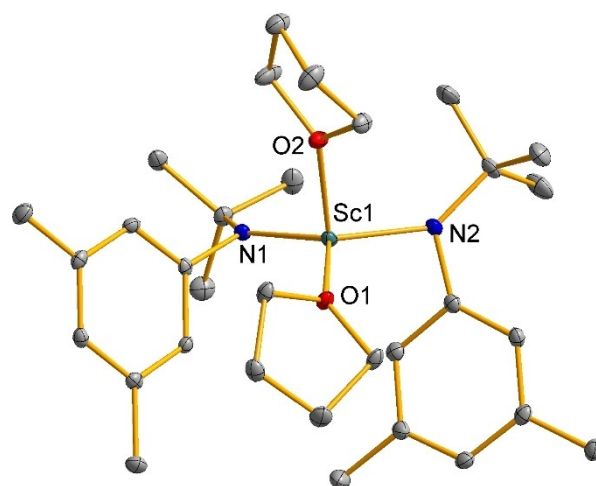
Figure 1. Molecular structure of **3** in the solid state with displacement parameters at 30% probability level. H atoms and [BPh$_4$] anion are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 1.9913(16), Sc1-N2 2.0327(18), Sc1-O1 2.1478(14), Sc1-O2 2.1357(14); N1-Sc1-N2 118.46(7), N1-Sc1-O1 122.76(6), N2-Sc1-O1 113.88(6), N1-Sc1-O2 103.24(6), N2-Sc1-O2 101.96(6), O1-Sc1-O2 86.69(5).

scandium alkyl complex **1-CH$_2$SiMe$_3$** ($\delta(^{45}\text{Sc}) = 464$ ppm, $\Delta v_{1/2} = \sim 10000$ Hz, Figure S4). As expected, the ^{11}B{^{1}H} NMR spectrum shows a sharp singlet at $\delta = -6.5$ ppm for the [BPh$_4$]$^-$ ion (Figure S8).

Previously we have shown that **2-anth-Li** acts as a one-electron donor in the reduction of nitriles.[9] Here we present the reduction of *trans*-azobenzene with **2-anth-Li**, where it acts as a two-electron donor reagent. Thus, the addition of an orange solution of *trans*-azobenzene in THF to **2-anth-Li** at
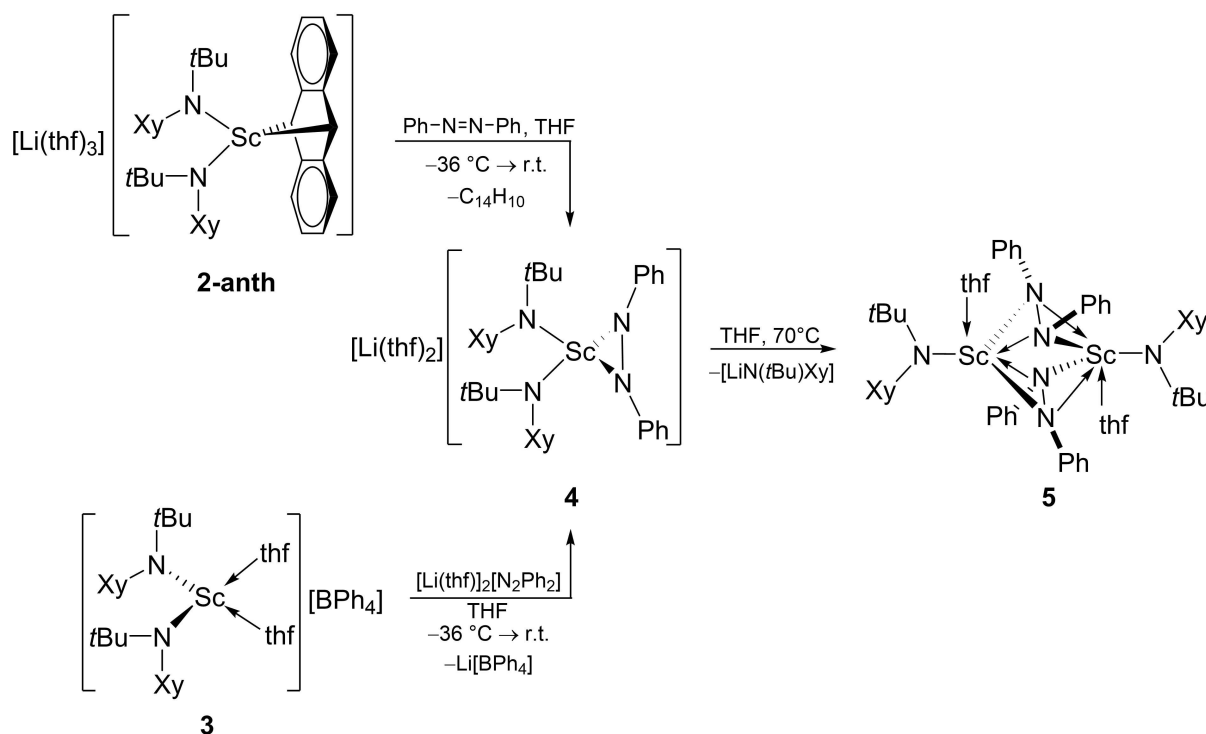
Scheme 2. Synthesis of scandium azobenzene complexes **4** and **5**.

−36 °C led to an immediate reaction as observed by a rapid color change from dark red to light yellow. Monitoring the reaction by ^{1}H NMR spectroscopy confirmed the formation of the reduced azobenzene complex [Li(thf)$_2$][Sc{N(tBu)Xy}$_2$(η^2-PhNNPh)] (**4**) along with free anthracene (Scheme 2, Figure S10). After work-up, **4** was isolated as a colorless solid in 46% yield (See SI, Sec. 2.3). Compound **4** can also be prepared starting from scandium cation **3**. Thus, the reaction of **3** with one equivalent of [Li$_2$N$_2$Ph$_2$] in THF at −36 °C led to a selective formation of **4** along with one equivalent of Li[BPh$_4$] (Scheme 2). Compound **4** was obtained as an analytically pure solid in 51% yield (See SI, Sec. 2.3). Despite its ionic character, **4** is soluble in aliphatic solvents. In the solid-state compound **4** is thermally stable but in solution it slowly but selectively loses one of the anilide ligands (*vide infra*).

The reduced azobenzene complex **4** was fully characterized by multinuclear magnetic resonance spectroscopy and elemental analysis. In addition, the molecular structure was confirmed by X-ray diffraction on a suitable single crystal obtained upon storing a saturated solution of **4** in diethyl ether/*n*-pentane mixture at room temperature. The molecular structure revealed a contact ion pair with the tricoordinate, planar lithium ion ($\Sigma\angle$Li = 359.4°) connected to the anionic fragment through bonding with one of the nitrogens of reduced azobenzene ligand (d(Li1-N1) = 1.961(7)) and anilide ligands (d(Li1-N3) = 2.126(8)) (Figure 2). Compound **4** represents the second example of a structurally characterized reduced azobenzene complex of scandium, just after the recently reported cyclopentadienyl complex [K(crypt)][(η^5-C$_5$Me$_5$)(C(tBu){N(iPr)}$_2$)Sc(η^2-N$_2$Ph$_2$)] (crypt = [2.2.2]-cryptand).[15] As expected, the dianionic azoben-
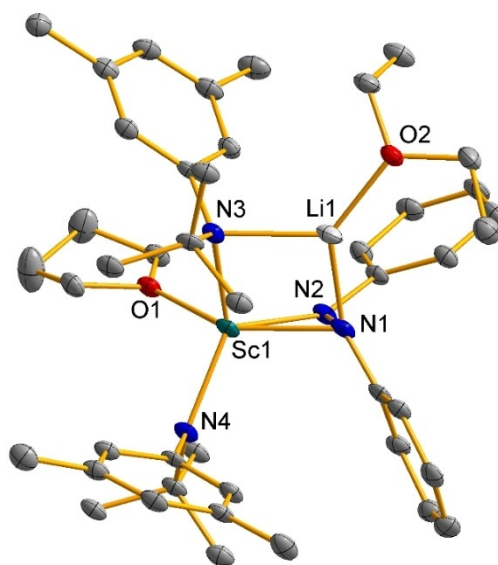

Figure 2. Molecular structure of **4** in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.150(3), Sc1-N2 2.038(3), Sc1-N3 2.206(3), Sc1-N4 2.055(3), Sc1-O1 2.207(3), N1-N2 1.469(4), Li1-N1 1.961(7), Li1-N3 2.126(8), Li1-O2 1.912(6); N1-Sc1-N2 40.96(11), N3-Sc1-N4 131.24(10), N1-Sc1-N3 89.84(11), N1-Sc1-N4 110.40(12), N2-Sc1-N3 107.28(11), N2-Sc1-N4 117.10(12), N3-Sc1-O1 93.85(10), N4-Sc1-O1 96.02(10), N1-Li1-N3 97.6(3).

zene ligand is bonded to the penta-coordinate scandium(III) center in an η^2-fashion and behaves as a π-donor ligand, as evident from the torsion angle C$_{Ph}$–N1-N2-C$_{Ph}$ of −91.4(4)°.[16] Due to the coordination of one of the nitrogen atoms of the

azobenzene ligand with the lithium cation, the Sc–N bond distances (d(Sc1-N1) = 2.150(3) Å, d(Sc1-N2) = 2.038(3) Å) differ significantly from each other. For the same reason, the Sc–N bond distances (d(Sc1-N3) = 2.206(3) Å, d(Sc1-N4) = 2.055(3) Å) of the anilide ligands also differ markedly from each other. Such an elongation of the Sc–N bonds for the tetra-coordinate nitrogen atoms (N1 and N3) compared to that of the tri-coordinate nitrogen atoms (N2 and N4) can be explained by the higher coordination number and a decreased N→Sc donation. The N1-N2 bond distance of 1.469(4) Å in the reduced azobenzene ligand is significantly longer than that of free azobenzene (d(N=N) = 1.249(4) Å),[17] but compares well with the N–N distance of the reported scandium azobenzene complex [K(crypt)][(η^5-C$_5$Me$_5$)(C(tBu){N(iPr)}$_2$)Sc(N$_2$Ph$_2$)] (d(N–N) = 1.4727(15) Å).[15]

Further structural information of **4** in solution was obtained by multinuclear magnetic resonance spectroscopy in [D$_8$]THF. In contrast to the C_1-symmetric structure in the solid-state, the ^{1}H NMR spectrum of **4** at 296 K indicates a more symmetric structure (C_s), as confirmed by a single set of signals both for the phenyl and the xylyl groups (Figure S11). Such a higher symmetry in solution suggests a fluxional structure at room temperature. At 253 K, the ^{1}H and the ^{13}C{^{1}H} NMR spectra display two sets of signals for the *ortho*- and *meta*-CH of the phenyl groups and broadening of the signals corresponding to tBu and *para*-CH of the xylyl groups, implying a lower symmetry at low temperatures. The ^{45}Sc NMR spectrum of **4** in [D$_8$]THF at 253 °K displays a very broad signal at δ = 349 ppm ($\Delta v_{1/2}$ = ~ 35000 Hz, Figure S15), which is at a slightly lower field compared to that of the scandium cation **3** (δ = 312 ppm, $\Delta v_{1/2}$ = ~ 10000 Hz). The ^{7}Li{^{1}H} NMR spectrum of **4** displays a sharp

signal at δ −0.5 ppm for the lithium cation (Figure S14) and the value appears slightly upfield shifted compared to that of LiCl in [D$_8$]THF (δ = 0.5 ppm).

Compound **4** is thermolabile in solution under ambient conditions. The ^{1}H NMR spectroscopy of a [D$_8$]THF solution of **4** revealed that the decomposition slowly but selectively leads to the neutral scandium azobenzene dimer [Sc{N(tBu)Xy}(μ-η^2:η^2-Ph$_2$N$_2$)(thf)]$_2$ (**5**) after elimination of [LiN(tBu)Xy] (Scheme 2). Compound **5** was prepared on a synthetic scale by heating a [D$_8$]THF solution of **4** for 8 h at 70 °C and isolated, after work-up, as an analytically pure, colorless solid in 62% yield (see SI, Sec. 2.4). The elimination of an anilide ligand from a metal center under ambient conditions is quite unusual, though it was observed before under strongly reducing conditions.[9,18] Unlike the precursor **4**, compound **5** is sparingly soluble in THF at room temperature and a thermally stable solid under complete exclusion of air.

The molecular structure of **5** was confirmed by single crystal X-ray diffraction. Compound **5** represents the first example of a dimeric scandium reduced azobenzene complex. Such dimeric complexes were mainly observed for lanthanides,[19] and except La,[20] similar complexes have never been isolated for other transition metals. This observation suggests that group 3 metals behave like lanthanides. The molecular structure of **5** revealed a centrosymmetric molecule with a very short Sc···Sc distance (3.0313(9) Å) between two hexacoordinate scandium centers (Figure 3). The reduced azobenzene ligands unsymmetrically bind the scandium centers, as evident from a short and a long Sc–N bond. The short Sc1-N1 bond distance of 2.0781(18) Å is appropriate for a Sc-N$_{amide}$ bond and compares well with that of the anionic complex **4** (d(Sc–N)$_{avg}$ = 2.094 Å) as well as its own
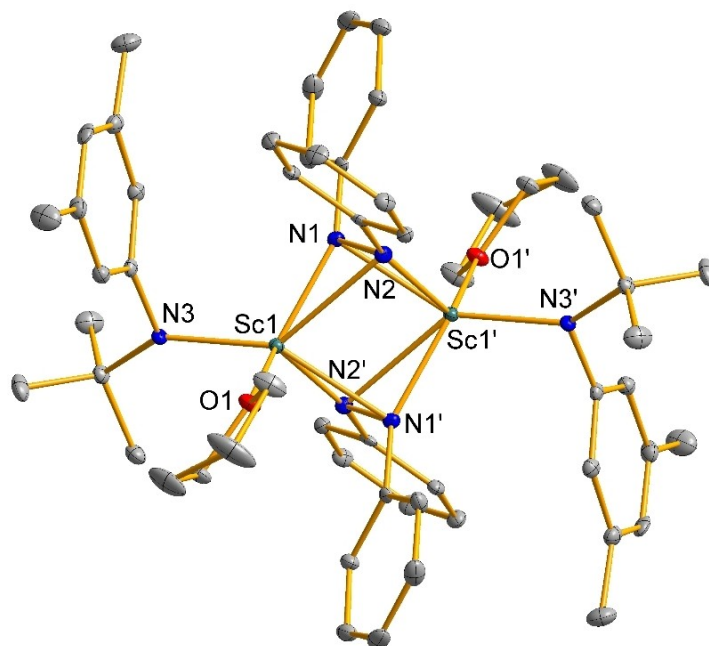
Figure 3. Molecular structure of **5** in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.0781(18), Sc1-N2 2.5155(19), Sc1-N3 2.042(2), Sc1-O1 2.1953(16), N1-N2 1.457(2); N1-Sc1-N2 35.39(7), N1-Sc1-N3 110.86(7), N2-Sc1-N3 137.05(7), O1-Sc1-N1 127.98(7), O1-Sc1-N2 96.49(6), O1-Sc1-N3 93.97(7), Sc1-N1-Sc1' 86.98(7), Sc1-N2-Sc1' 81.90(6).

Sc1-N3 bond (2.042(2) Å). On the other hand, the Sc1-N2 bond distance of 2.5155(19) Å is significantly higher (21%) than the Sc1-N1 bond distance and characteristic for a Sc-N$_{amine}$ bond.[21] The N—N bond distance of 1.457(2) Å of the azobenzene ligands is comparable to that of the precursor **4** (d(N—N) = 1.469(4) Å) and also comparable with that of the lanthanide complexes of reduced azobenzene dimer.[19,20] The long N—N bond along with the bond angles around each tetra-coordinate nitrogen atom clearly supports their sp^3 hybridization.

The solution structure of compound **5** is consistent with the solid-state structure, as confirmed by the multinuclear magnetic resonance spectroscopy in [D$_8$]THF that revealed a single set of signals for the anilide and the azobenzene ligands. Akin to precursor **4**, the resonance corresponding to the *ortho*-CH signal of the aryl groups of **5** appears as a broad signal in the region δ = 6.30–6.55 ppm (Figure S16), indicating a hindered rotation around N-C$_{ph}$ bond. Several attempts to observe a ^{45}Sc NMR signal remained unsuccessful due to the low solubility of **5** in [D$_8$]THF.

The reaction of a THF solution of **3** with CO$_2$ led to the selective formation of the scandium dicarbamate complex [Sc{κ^2-O$_2$CN(*t*Bu)(Xy)}$_2$(thf)$_3$][BPh$_4$] (**6**) after insertion of CO$_2$ into the Sc—N bonds (Scheme 3). The insertion of CO$_2$ into the TM-N$_{amide}$ (TM = transition metal) bond is well-known[22] and such a CO$_2$ insertion into the TM-N$_{anilide}$ bond was also observed in few cases.[23] The formation of a scandium carbamate complex through CO$_2$ insertion into the Sc—N bond was never observed. Compound **6** was isolated as an analytically pure, colorless solid in 92% yield. (see SI, Sec. 2.5).

The solid-state structure of **6**, as determined by single crystal X-ray diffraction, revealed a seven-coordinate scandium center bonded to two κ^2-coordinated carbamate ligands (O$_2$CN-(*t*Bu)(Xy)) and three THF molecules in a distorted pentagonal bipyramidal coordination geometry (Figure 4). Compound **6** is the first example of a structurally characterized dicarbamate complex of scandium. While the four oxygen atoms of the two carbamate ligands and a THF molecule reside in the pentagonal plane (O—Sc—O bond angle range between 61.22(5) and 82.19(6)°), the other two oxygen atoms from the remaining THF molecules occupy the axial positions (∠O5-Sc1-O7 = 175.61(6)°). The large deviation of the O—Sc—O bond angles from the ideal 72° of the pentagonal plane arises from the small bite angle of the carbamate ligands. As expected, the Sc—O bond distances between the Sc and the κ^2-coordinated, anionic carbamate ligands are nearly the same and appear in the range of 2.1407(13)–2.1625(12) Å, those are only marginally shorter than the Sc—O distances (d(Sc-O$_{THF}$)$_{avg}$ = 2.1744 Å) of the THF molecules.

Further structural information of **6** in solution was obtained by multinuclear magnetic resonance spectroscopy measured in
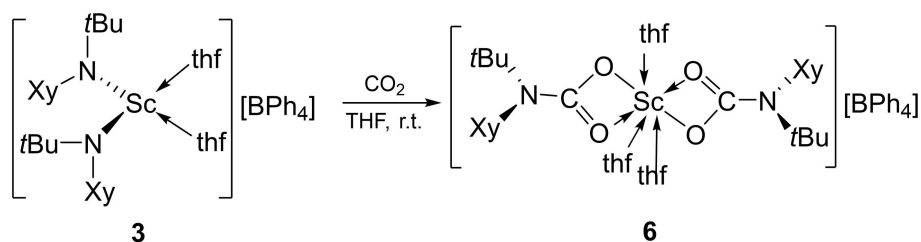
Scheme 3. Reaction of scandium cation **3** with CO$_2$.

Figure 4. Molecular structure of **6** in the solid state with displacement parameters at 30% probability level. H atoms and [BPh$_4$] anion are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-O1 2.1407(13), Sc1-O2 2.1625(12), Sc1-O3 2.1571(12), Sc1-O4 2.1468(12), Sc1-O5 2.1622(14), Sc1-O6 2.1951(12), Sc1-O7 2.1659(14), C1-N1 1.354(2), C2-N2 1.353(2); O1-Sc1-O2 61.22(5), O3-Sc1-O4 61.27(6), O5-Sc1-O6 91.54(5), O5-Sc1-O7 175.61(6), O1-Sc1-O4 82.19(6), O2-Sc1-O6 78.59(6), O3-Sc1-O6 76.85(5).
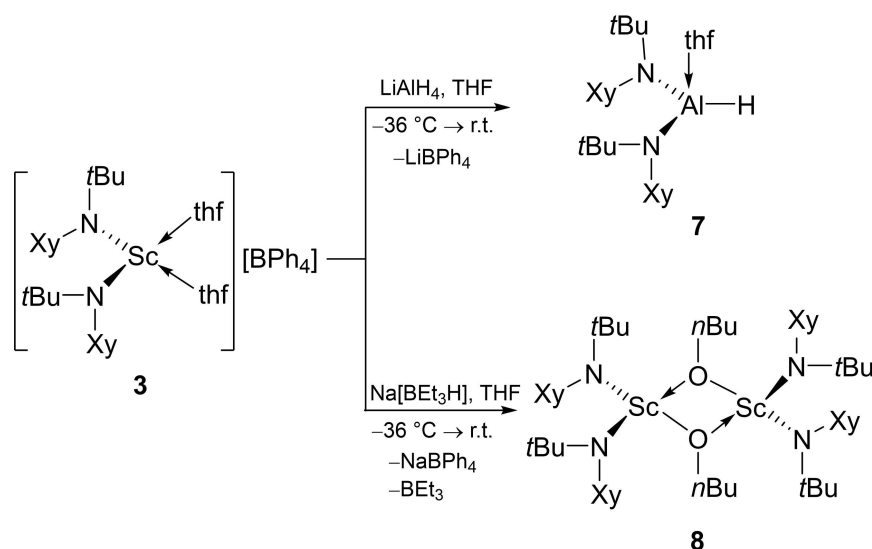
Scheme 4. Reaction of scandium cation **3** with hydride.

[D$_8$]THF at 296 K. The ^{1}H and ^{13}C{^{1}H} NMR spectra shows a single set of signals for the carbamate ligands (Figure S18 and S19), indicating a symmetric structure in solution, as found in the solid-state. The most characteristic signal in the ^{13}C{^{1}H} NMR spectrum is that of the O$_2$C carbon atoms of the carbamate ligands at $\delta = 170.6$ ppm that compares well with the value found in group 4 metal carbamate complexes.[24] The ^{45}Sc NMR spectrum of **6** displays relatively a sharp signal at $\delta = 67$ ppm ($\Delta v_{1/2} = \sim 1100$ Hz) that is significantly upfield shifted compared to the value found for the precursor **3** ($\delta = 312$ ppm). As expected, the ^{11}B{^{1}H} NMR spectrum gave a sharp signal at $\delta = -6.5$ ppm for the [BPh$_4$]$^-$ ion.

Molecular scandium hydrides are rare but constitute an important class of homogeneous olefin hydrogenation and polymerization catalysts.[25] This inspired us to attempt the synthesis of scandium hydride by reacting scandium cation **3** with hydride reagents. Reactions of **3** with hydride sources such as LiAlH$_4$ and Na[BEt$_3$H], however, did not give any scandium hydrides "[ScH{N(tBu)(Xy)}$_2$(thf)]". The addition of LiAlH$_4$ to **3** in THF at $-30°$C resulted in the aluminum hydride [AlH{N-(tBu)(Xy)}$_2$(thf)] (**7**) after transmetalation of scandium with aluminum (Scheme 4). After work-up, compound **7** was isolated as an analytically pure, colorless crystals in 55% yield (see SI, Sec. 2.6). A similar transmetalation reaction was also used before to synthesize aryl-substituted aluminum hydride [Mes*$_2$AlH] starting from the corresponding gallium and indium hydride [Mes*$_2$MH] (Mes* = C$_6$H$_2$-2,4,6-tBu$_3$; M = Ga, In) and LiAlH$_4$.[26] The formation of such an aluminum hydride from any transition metal complex through transmetalation is quite unusual.[27] The fate of scandium remained undetermined.

The monomeric structure of **7** in the solid-state was confirmed by single crystal X-ray diffraction analysis (Figure 5). The molecular structure revealed an expected distorted tetrahedral geometry around the tetra-coordinate aluminum center. The Al1-H1 bond distance of 1.52(2) Å compares well with that of the above-mentioned three-coordinate, terminal aluminum
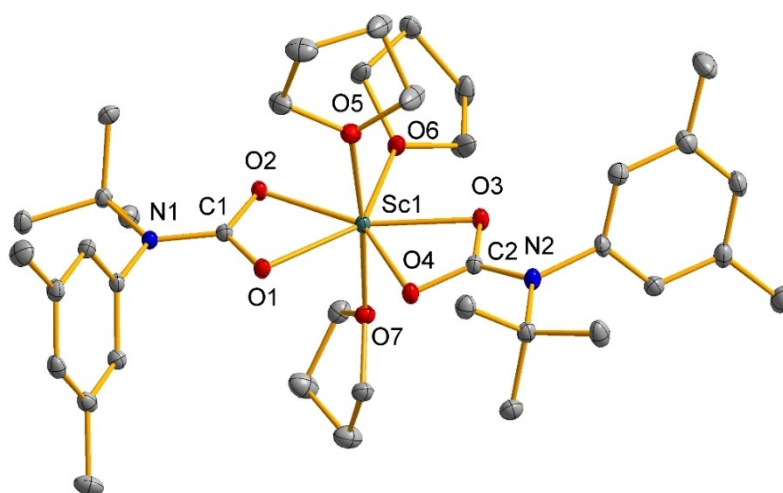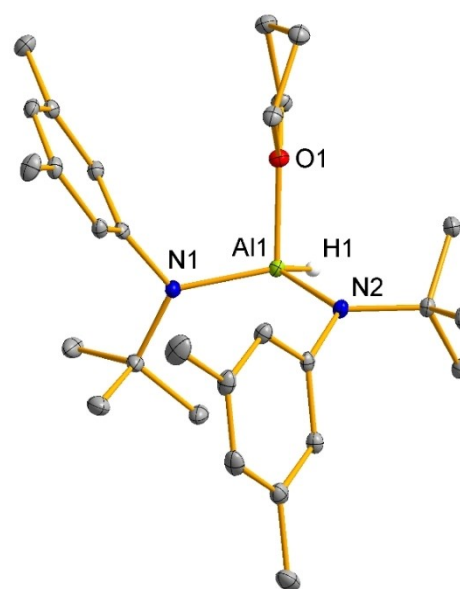

Figure 5. Molecular structure of **7** in the solid state with displacement parameters at 30% probability level. H atoms (except Al bonded H) are omitted for clarity. Selected interatomic distances (Å) and angles (°): Al1-N1 1.8437(15), Al1-N2 1.8223(15), Al1-O1 1.9083(13), Al1-H1 1.52(2); N1-Al1-N2 117.25(8), N1-Al1-O1 105.12(6), N2-Al1-O1 101.78(6).

hydride [Mes*$_2$AlH] (d(Al–H) = 1.53(4) Å)[26a] or with the Al–H distance found (d(Al–H) = 1.49(2) Å) in the recently reported four-coordinate, terminal aluminum hydride [(NON)AlH] (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxanthene).[28] The Al–N bond distances (1.8437(15) and 1.8223(15) Å) are in the expected range for a bond between an Al(III) and an amide ligand.[29]

Compound **7** was also characterized by ^{1}H and ^{13}C{^{1}H} NMR and solid-state IR spectroscopy. Apart from a single set of signals for THF and the anilide ligands, the ^{1}H NMR spectrum of **7** shows a characteristic very broad signal for Al-H at $\delta =$

4.66 ppm ($\Delta v_{1/2} = \sim 125$ Hz) due to the quadrupolar effect of ^{27}Al nucleus (Figure S22). This was confirmed by the ^{27}Al decoupled ^{1}H NMR spectrum that displays a sharp singlet for the Al–H. The Al–H signal of **7** appears at a similar position that has been observed in the previously reported compounds containing terminal Al–H, such as [Mes*$_2$AlH] ($\delta = 5.72$ ppm) or [(NON)AlH] ($\delta = 4.99$ ppm).[28] The solid-state IR spectrum of **7** using KBr pellet shows an intense band at $v = 1773$ cm^{-1}, characteristic of the Al–H stretching vibration (Figure S24).

To avoid the transmetalation reaction, we decided to use Na[BEt$_3$H] as the hydride source. When Na[BEt$_3$H] was added to the scandium cation **3** in THF at $-36\,°$C an immediate reaction occurs, as confirmed by an *in situ* ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum shows a clean conversion of the starting materials into a possible scandium hydride, which at r.t. slowly ring-opens the coordinated THF to form the scandium *n*-butoxide complex [Sc{N(*t*Bu)(Xy)}$_2$(μ-O*n*Bu)] (**8**) (Scheme 4). Compound **8** was isolated as an analytically pure, colorless solid in 58% crystalline yield (see SI, sec. 2.7). The formation of the THF ring-opened product **8** from the scandium cation **3** presumably occurs via nucleophilic attack of a hydride to the C$^\alpha$ atom of the activated THF molecule at the Lewis acidic scandium center. Such nucleophile-assisted ring-opening of THF at the Lewis acidic group 3 metal center was also observed earlier.[30] For instance, the formation of a similar THF ring-opened product [(η^5-C$_5$Me$_5$)Sc(BH$_4$){μ-O(CH$_2$)$_3$CH$_3$}]$_2$ was also observed when [Sc(BH$_4$)$_3$(THF)$_{1.5}$] was treated with K[C$_5$Me$_5$] in THF.[31]

Compound **8** was fully characterized using multinuclear magnetic resonance spectroscopy and elemental analysis. In addition, the molecular structure was confirmed by single crystal X-ray diffraction, which revealed a centrosymmetric, dimeric structure with the *n*-butoxide groups bridging the scandium centers (Figure 6). The tetracoordinate scandium centers reside in a distorted tetrahedral coordination environment and form a perfectly planar Sc$_2$O$_2$ core, as evidence by the Sc1–O1–Sc1'–O1' torsion angle of 0.00(6)°. The Sc–N bonds in **8** are marginally elongated (d(Sc–N)$_{avg} = 2.0504$ Å) compared to those in the scandium cation **3** (d(Sc–N)$_{avg} = 2.012$ Å), indicating a weaker N→Sc donation in the former complex due to the presence of an anionic *n*-butoxide group in comparison to the neutral THF ligand in **3**. The shorter Sc–O bonds (d(Sc–O)$_{avg} = 2.0782$ Å) in **8** than those found in **3** (d(Sc–O)$_{avg} = 2.1418$ Å) are also consistent with the stronger coordination of the *n*-butoxide groups to the scandium centers.

The solution NMR spectra of **8** in [D$_6$]benzene at 296 K are also consistent with the solid state structure. Apart from a single set of signals for the aniline ligand, the ^{1}H NMR spectrum of **8** displays a triplet at $\delta = 0.95$ ppm and three multiplets at $\delta = 1.08, 1.62$ and 3.50 ppm for the CH$_3$ and CH$_2$ protons of the *n*-butoxide groups, respectively. In the ^{45}Sc NMR spectrum, the scandium nucleus of **8** appears as a very broad signal at $\delta = 347$ ppm ($\Delta v_{1/2} = \sim 35000$ Hz), which is only marginally downfield shifted compared to that found in the precursor **3** (312 ppm; $\Delta v_{1/2} = \sim 10000$ Hz).

Conclusion

In summary, the stepwise protonation of [Li(thf)$_3$][Sc{N(*t*Bu)Xy}$_2$(anth)] (**2-anth-Li**) producing the corresponding scandium anthracenyl and the cationic scandium complex support the description of **2-anth-Li** as an adduct of "[Sc^{III}{N(*t*Bu)Xy}$_2$]$^+$" and "[C$_{14}$H$_{10}$]$^{2-}$". The elimination of the anilide ligand from **4** to give
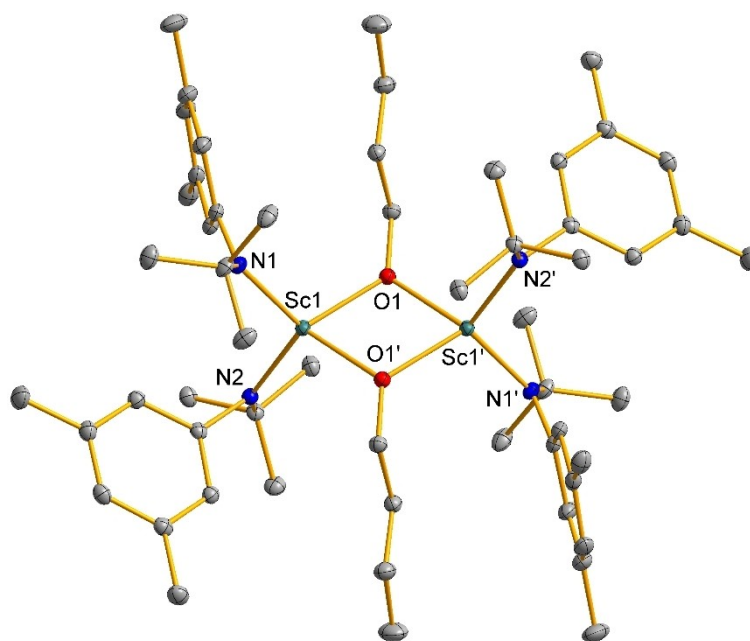
Figure 6. Molecular structure of **8** in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.0788(11), Sc1-N2 2.022(1), Sc1-O1 2.0869(9), Sc1'-O1 2.0695(9); N1-Sc1-N2 111.49(5), N1-Sc1-O1 121.11(4), N2-Sc1-O1 107.27(5), N1-Sc1-O1' 111.82(4), N2-Sc1-O1' 124.55(4).

the scandium azobenzene dimer not only indicates more ionic, weaker Sc-N$_{amide}$ bonds but also this formation shows that scandium behaves like lanthanides when compared with the formation of analogous dimeric azobenzene complexes through cyclopentadienyl ligand elimination reactions. The low Sc-N$_{amide}$ bond strength was also evidenced from the CO_2 insertion reaction of the scandium cation that gave a scandium dicarbamate complex. Finally, attempts to add hydride to the scandium cation did not give the desired scandium hydride but resulted in Sc/Al transmetalation as well as nucleophile-assisted THF ring-opening reaction. The present work demonstrates that the scandium reduced arene complexes serve as precursors for new structural motifs of scandium.

Experimental Section

Crystallographic data: Deposition numbers CCDC 2091773-2091779 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre.

Notes

The authors declare no competing financial interest.

Conflict of Interest

The authors declare no conflict of interest.

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