Preparation of Scandium Complexes with Benzamidinate Ligands: Synthesis and Reactivity of Alkyl and Hydrido Derivatives

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A range of new scandium complexes incorporating N,N'-bis(trimethylsilyl)benzamidinato ligands has been prepared. Addition of $[PhC(NSiMe_3)_2]Li(TMEDA)$ to $ScCl_3(THF)_3$ in THF gives $[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$ in moderate yield. Alternatively, the use of $[RC(NSiMe_3)_2]Na(Et_2O)_n$ (R = Ph, Tol) gives good yields of the lithium-free halide $[RC(NSiMe_3)_2]_2ScCl(THF)$. The latter is a useful starting material for the preparation of a number of derivatives, including $[PhC(NSiMe_3)_2]_2ScR'$ ($R' = CH_2SiMe_3$, Mes), $[PhC(NSiMe_3)_2]_2ScMe(THF)$, $[TolC(NSiMe_3)_2]_2Sc(BH_4)(THF)$, and $[PhC(NSiMe_3)_2]_2ScNHC_6H_3\text{-}2,6\text{-}Pr^i_2$, which were obtained by salt metathesis reactions from the corresponding alkali-metal reagents. Reaction of $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ with Me_3SiCCH gives the σ-alkyne $[PhC(NSiMe_3)_2]_2ScCCSiMe_3$ and Me_4Si. $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ reacts readily with H_2 to form $\{[PhC(NSiMe_3)_2]_2ScH\}_2$. The hydride reacts with Ph_2C_2 in refluxing benzene to give the mono-insertion product $[PhC(NSiMe_3)_2]_2ScC(Ph){=}C(Ph)H$. Two derivatives have been crystallographically characterized: $[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$ and $\{[PhC(NSiMe_3)_2]_2ScH\}_2$.

Introduction

The use of nitrogen-based donors as supporting ligands in transition-metal chemistry has received considerable attention.[1] For the early transition metals, the focus has been largely on the preparation and reactivity of electrophilic species, some of which function as olefin polymerization catalysts.[2−5] Following our studies[6−8] of N_4-donor sets involving porphyrin ligands, we recently turned our attention to bis(amidinate) ligation for the preparation of early transition metal derivatives.[9] We were attracted to N,N'-bis(trimethylsilyl)benzamidinate due to its ease of preparation and derivatization, solubility properties, and steric bulk. A number of workers have demonstrated the synthetic utility of this ligand for the preparation of inorganic compounds across the periodic table,[10−12] but only recently have detailed investigations into their reactivity been described.[4,9,13−17]

Here we report[18] the synthesis and characterization of a number of scandium benzamidinates. The major starting material for our investigations has been $[PhC(NSiMe_3)_2]_2ScCl(THF)$,[16] which was recently mentioned in a review, and from this a range of derivatives has been prepared.

Results and Discussion

Multigram quantities of $[RC(NSiMe_3)_2]_2ScCl(THF)$ (R = Ph, Tol) were easily obtained by the reaction of $Na[RC(NSiMe_3)_2](Et_2O)_n$ with $ScCl_3(THF)_3$ in THF. Crystallization from Et_2O afforded the product as colorless crystals in reasonable yields (ca. 70%). The related reaction using $[PhC(NSiMe_3)_2]Li(TMEDA)$ (TMEDA = N,N,N',N'-tetramethylethylenediamine) gave $[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$ as colorless crystals in moderate yield. Crystals of the dichloride−lithium adduct suitable for X-ray diffraction studies were grown from hexanes at −10 °C. An ORTEP view of one of the two crystallographically independent molecules is shown in Figure 1. The two independent molecules are virtually identical with a pseudoinversion center between the two. The compound features a planar $Sc(\mu\text{-}Cl)_2Li$ core with the lithium further coordinated to the chelating TMEDA ligand. The amidinate ligands adopt a typical planar coordination geometry to the metal center, with Sc−N bond lengths varying from 2.168(5) to 2.230(5) Å. The Sc−Cl bonds range in length from 2.529(3) to 2.560(3) Å and are similar to the values reported for $(Cp_2ScCl)_2$ (average 2.575 Å).[19] The Cl−Sc−Cl bond angles of 83.37(9) and 84.03(9)° are identical within

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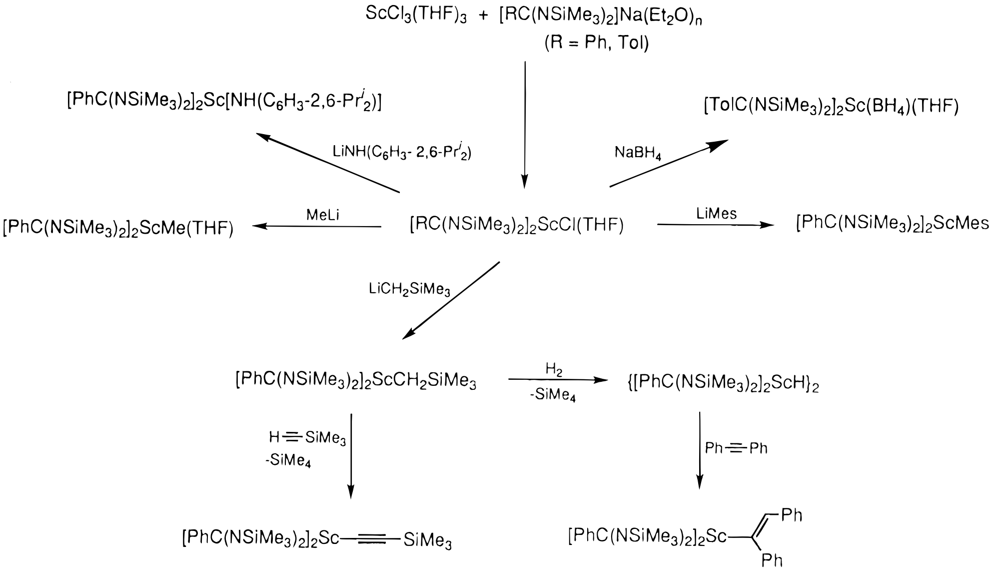
Scheme 1



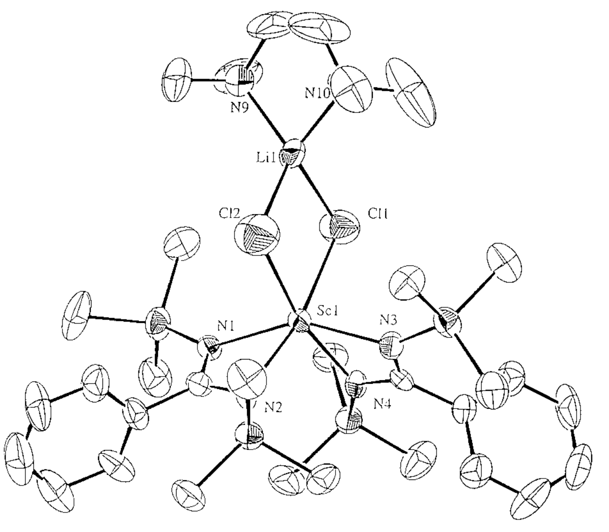


Figure 1. ORTEP view of $[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$ drawn with 50% thermal ellipsoids. Hydrogens were omitted for clarity.

experimental error and are only slightly more acute than that reported[20] for $Cp^*{}_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (84.8(1)°). Coordination about the lithium atoms is roughly tetrahedral with average bond lengths of 2.38 and 2.07 Å for Li−Cl and Li−N bonds, respectively. Bond angles about the lithium atoms are typical with average values of 91.2 and 88.5° for Cl−Li−Cl and N−Li−N angles, respectively.

As shown in Scheme 1, $[RC(NSiMe_3)_2]_2ScCl(THF)$ compounds (R = Ph, Tol) are good starting materials for the preparation of a wide range of new derivatives. Reaction of $[TolC(NSiMe_3)_2]_2ScCl(THF)$ with $NaBH_4$ in THF, followed by extraction with hexanes, yielded colorless crystals of $[TolC(NSiMe_3)_2]_2Sc(BH_4)(THF)$. IR data are consistent[21] with bidentate coordination of the borohydride ligand, showing absorptions at 2463 and 2388 cm^{-1} assignable to the (A_1, B_1) B−H(terminal) stretches and a broad band with multiple shoulders at 2330 cm^{-1} assignable to the (A_1, B_2) B−H(bridging) stretches.

Reaction of $[PhC(NSiMe_3)_2]_2ScCl(THF)$ with lithium reagents was successful for the preparation of five-coordinate $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$, $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_2Ph$, and $[PhC(NSiMe_3)_2]_2ScMes$ (Mes = 2,4,6-trimethylphenyl). The proton NMR spectrum of $[PhC(NSiMe_3)_2]_2ScMes$, which was easily isolated as colorless crystals from hexanes, shows a broadened signal for the $-SiMe_3$ groups of the amidinate ligands indicative of slow rotation of the amidinate ligands on the NMR time scale. Both $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ and $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_2Ph$ were isolated as colorless crystals from hexamethyldisiloxane (HMDSO) and are exceedingly soluble in hydrocarbon solvents. In contrast to $Cp^*{}_2ScR$ compounds,[22] heating to 60 °C in C_6D_6 led to no reaction. Proton NMR spectroscopy shows signals at δ 0.41 and 0.58 for the α-CH_2 protons of $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ and $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_2Ph$, respectively. These are upfield of related absorptions in other d^0-amidinates such as $[PhC(NSiMe_3)_2]_2TiMe_2$ and $[PhC(NSiMe_3)_2]_2TiCH_2SiMe_3(Cl)$[9] ($\delta$ 1.96 and 3.06, respectively) due to the effect of the highly electropositive scandium. Relative to the analogous $Cp^*{}_2Sc$ compounds, however, the signals are shifted slightly downfield, possibly indicative of a more electron-deficient metal in $[PhC(NSiMe_3)_2]_2Sc$ than that of the $Cp^*{}_2Sc$ fragment.[22] Qualitatively, the steric demands of the $PhC(NSiMe_3)_2$ ligand appears to be intermediate to Cp and Cp* ligands.[9,23] Attempts to prepare the corresponding methyl derivative using MeLi gave instead the six-coordinate $[PhC(NSiMe_3)_2]_2ScMe(THF)$ in good yield.

$[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ reacted with H_2 (1 atm) at room temperature in hexanes or benzene to give 1 equiv of Me_4Si and the hydride $\{[PhC(NSiMe_3)_2]_2ScH\}_2$. This may also be prepared from either $[PhC(NSiMe_3)_2]_2ScMe(THF)$ or $[PhC(NSiMe_3)_2]_2ScMes$, but these reac-

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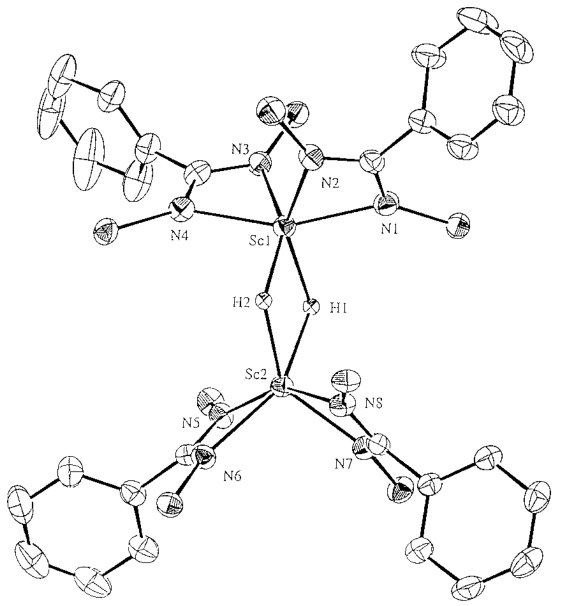

Figure 2. ORTEP view of $\{[PhC(NSiMe_3)_2]_2ScH\}_2$ drawn with 50% thermal ellipsoids. Methyl groups and nonhydridic hydrogens were omitted for clarity.

tions require elevated temperatures (ca. 70 °C) to proceed at reasonable rates. The ^1H NMR spectrum of $\{[PhC(NSiMe_3)_2]_2ScH\}_2$ shows two broad, partially-overlapped peaks for the $-SiMe_3$ groups of the amidinate ligands, once again indicative of a sterically congested metal center. These signals coalesce at 37 °C corresponding to a barrier to ligand rotation of $\Delta G^{\ddagger} = 10(1)$ kcal/mol. We did not detect the hydride resonance in the ^1H NMR presumably due to coupling to the quadrupolar ^{45}Sc ($I = {}^7/_2$). Bercaw and co-workers have reported[22] observing broadened hydride signals in the related $Cp^*{}_2Sc$ system. IR spectroscopy revealed a broad band at 1283 cm^{-1} that is consistent with early metal bridging hydrides.[5,24] This band is absent in the deuteride which showed a new band (partially obscured) at 907 cm^{-1}. Crystals of the hydride for X-ray diffraction studies were prepared by the blanketing of H_2 onto a hexanes solution of $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ at room temperature. An ORTEP view of the molecular structure is shown in Figure 2. Each Sc is coordinated in a distorted octahedral fashion with the bridging hydrides, which were located and refined isotropically, roughly equidistant to both metal centers. The Sc−H bond distances range from 1.87(3) to 2.00(3) Å and are typical of early metal bridging hydride ligands,[25−27] but there are almost no reliable Sc−H bond distances from crystal structure analyses reported in the literature for comparison.[5] Borohydride and dicarbollide derivatives display longer Sc−H bond lengths of 2.03 and 2.18 Å for $[C_5H_3(SiMe_3)_2]_2ScBH_4$[28] and $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$,[29] respectively. The Sc_2H_2 core is planar with H−Sc−H angles of 61(1) and 65(1)° and a Sc−Sc distance of 3.30 Å. Each of the amidinate ligands is coordinated with the Sc atom in the N−C−N plane.

The hydride is quite thermally robust in C_6D_6 solution showing only trace decomposition after heating to 60 °C for 24 h, and no exchange was observed with D_2 (15 psig) under the same conditions. Additionally, the dimeric structure remained intact even after heating in the presence of THF. Ethylene and propylene failed to react at room temperature; however, at 60 °C ethylene is sluggishly polymerized and propene appears to undergo multiple insertions. Heating was also required to initiate the reaction of Me_3SiCCH, where, at 60 °C, multiple products were formed. The absence of H_2 and the presence of several vinylic peaks in the ^1H NMR spectrum are consistent with initial insertion of alkyne into the Sc−H bond; however, no pure product could be isolated. $[PhC(NSiMe_3)_2]_2ScCCSiMe_3$ was also detected by ^1H NMR spectroscopy indicative of competing σ-bond metathesis and insertion pathways.

Reaction of $\{[PhC(NSiMe_3)_2]_2ScH\}_2$ with the internal alkyne Ph_2C_2 in refluxing benzene cleanly gives yellow crystals of the single insertion product, $[PhC(NSiMe_3)_2]_2ScC(Ph){=}C(Ph)H$, in 40% isolated yield. In contrast, reaction of $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ with Me_3SiCCH in C_6D_6 was found to give exclusively the σ-bond metathesis product $[PhC(NSiMe_3)_2]_2ScCCSiMe_3$, which we formulate as a monomeric species in solution on the basis of a single sharp $-SiMe_3$ signal for the amidinate ligands in the ^1H NMR. This is in contrast to the dimeric $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}CCH)\}_2$, which was recently reported[13] by Teuben. Further equivalents of the alkyne reacted with the acetylide at 60 °C, yielding an uncharacterized mixture of products. Details of the reactions of the hydride and alkyl derivatives with ethylene and higher olefins will be presented separately.[30]

In summary, the scandium chloride $[PhC(NSiMe_3)_2]_2ScCl(THF)$ has been shown to be a good starting material for the preparation of a wide range of new alkyl, amido, and borohydride derivatives. The alkyl derivatives react with dihydrogen under mild conditions to yield the dimeric hydride with the liberation of RH. Reaction of alkyl and hydride derivatives with terminal and internal alkynes reveals competing insertion and σ-bond metathesis pathways.

Experimental Section

General Considerations. Standard Schlenk-line and glovebox techniques were used throughout.[31] Tetrahydrofuran (THF), diethyl ether, hexamethyldisiloxane (HMDSO), and hexanes were dried over 4-Å molecular sieves and then distilled from sodium/benzophenone under nitrogen. Dichloromethane (from sieves) was distilled from CaH_2 under nitrogen. C_6D_6 was predried over 4-Å molecular sieves, degassed with three freeze−pump−thaw cycles, and vacuum transferred from sodium/benzophenone. H_2 and D_2 were used directly from cylinders without purification. The compounds $ScCl_3(THF)_3$,[32,33] $Li[RC(NSiMe_3)_2](TMEDA)$,[34] $Na[RC(NSiMe_3)_2]$

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(R = Ph, Tol),[23,35,36] $LiCH_2SiMe_3$,[37] and $LiCH_2SiMe_2Ph$[37] were prepared according to literature procedures. $(Et_2O)LiMes$ was prepared by the addition of n-BuLi to the aryl bromide in Et_2O. $LiNHC_6H_3$-2,6-Pr^i_2 was prepared by addition of the amine to n-butyllithium in hexanes. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperatures. Chemical shifts (δ) are given relative to residual protium in the deuterated solvent at 7.15 (C_6D_6). IR samples were prepared as Nujol mulls and taken between KBr plates unless stated otherwise. Elemental analyses and mass spectral data were determined within the College of Chemistry, University of California, Berkeley, CA. Single-crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley, CA.

$[TolC(NSiMe_3)_2]_2ScCl(THF)$. Tetrahydrofuran (75 mL) was added to $ScCl_3(THF)_3$ (3.10 g, 8.43 mmol) and $Na[TolC(NSiMe_3)_2](Et_2O)$ (6.32 g, 16.9 mmol) in a 250-mL round-bottomed flask forming an orange, slightly cloudy solution. After the solution was stirred overnight, the volatiles were removed under reduced pressure. The resulting orange-red solid was extracted with Et_2O (90 mL) and filtered through a pad of Celite on a fritted disk. Concentration to 15 mL followed by cooling to −40 °C gave the product as colorless crystals (2.85 g, 47.8%). Mp: 160−170 °C. ^1H NMR (C_6D_6, 300 MHz): δ 7.21 (d, J = 8.0 Hz, 4 H), 6.89 (d, J = 7.9 Hz, 4 H), 4.32 (m, 4 H), 2.03 (s, 6 H), 1.46 (m, 4 H), 0.18 (s, 36H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 183.3, 139.7, 138.1, 128.8, 126.5, 73.1, 25.5, 21.2, 2.6. IR: 1658 (w), 1613 (w), 1444 (s, br), 1393 (m), 1245 (m), 1166 (w), 1110 (w), 1010 (w), 986 (m), 845 (s, br), 759 (m), 644 (w), 467 (m) cm^{-1}. Anal. Calcd for $C_{32}H_{58}ClN_4OScSi_4$: C, 54.32; H, 8.26; N, 7.92. Found: C, 54.18; H, 8.25; N, 7.86.

$[PhC(NSiMe_3)_2]_2ScCl(THF)(Et_2O)_n$. A 250-mL round-bottomed flask was loaded with $ScCl_3(THF)_3$ (4.47 g, 12.2 mmol) and $Na[PhC(NSiMe_3)_2](Et_2O)_{1.25}$ (9.22 g, 24.3 mmol). Tetrahydrofuran (125 mL) cooled to −50 °C was added forming a colorless suspension. After the mixture had stirred overnight at room temperature, the volatiles were removed under reduced pressure and the resulting white solid was extracted with Et_2O (125 mL). Filtration through a Celite pad on a fritted disk followed by concentration to 25 mL and cooling to −40 °C yielded the product as colorless crystals. Et_2O content was determined by ^1H NMR spectroscopy. Total yield from two crops: 6.7 g, 74%. ^1H NMR (C_6D_6, 300 MHz): δ 7.28−7.22 (m, 4H), 7.08−7.00 (m, 6H), 4.28 (m, 4H), 3.27 (q, 1.9H), 1.45 (m, 4H), 1.11 (t, 2.8H), 0.14 (s, 36H).

$[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$. In a 100-mL round-bottomed flask, THF (40 mL) cooled to −40 °C was added to $[PhC(NSiMe_3)_2]Li(TMEDA)$ (2.10 g, 5.44 mmol) and $ScCl_3(THF)_3$ (1.00 g, 2.72 mmol) forming a white slurry. The mixture was stirred overnight at room temperature giving a clear, slightly yellow solution. The volatiles were removed under reduced pressure affording a white solid. Extraction with Et_2O (70 mL) followed by filtration through a Celite pad on a fritted disk gave a clear, pale yellow solution. Concentration of the solution to 35 mL followed by cooling to −40 °C produced the product as small colorless crystals (1.1 g, 52%). Mp: 210−228 °C. ^1H NMR (C_6D_6, 300 MHz): δ 7.40−7.35 (m, 4 H), 7.08−7.00 (m, 6 H), 2.10 (s, 12 H), 1.70 (s, 4 H), 0.28 (s, 36 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 181.7, 141.8, 127.7, 127.5, 126.5, 57.0, 46.0, 2.4. IR: 1292 (w), 1259 (w), 1242 (m), 986 (m), 844 (s, br), 785 (w), 763 (m), 731 (w), 702 (m), 604 (w), 494 (m) cm^{-1}. Anal. Calcd for $C_{32}H_{62}Cl_2LiN_6ScSi_4$: C, 50.17; H, 8.16; N, 10.97. Found: C, 50.12; H, 8.38; N, 10.96.

$[PhC(NSiMe_3)_2]_2ScMe(THF)$. In a 100-mL round-bottomed flask, $[PhC(NSiMe_3)_2]_2ScCl(THF)(Et_2O)_{0.4}$ (1.50 g, 2.11 mmol) and Et_2O (45 mL) were combined forming a clear colorless solution. MeLi (2.11 mmol, 1.42 M in Et_2O) was added dropwise causing white precipitate to form. After the mixture was stirred overnight, the volatiles were removed under reduced pressure to give a colorless residue, which was extracted with hexanes (50 mL) and filtered through a pad of Celite on a fritted disk. Concentration to 10 mL and cooling to −40 °C yielded the product as small colorless crystals (1.0 g, 65%). Recrystallization from Et_2O afforded analytically pure product. Mp: 113−126 °C. ^1H NMR (C_6D_6, 400 MHz): δ 7.25−7.20 (m, 4H), 7.10−7.00 (m, 6H), 4.17 (m, 4H), 1.50 (m, 4H), 0.12 (s, 36H), 0.03 (s, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 182.4, 142.9, 128.1, 126.4, 72.0, 25.5, 2.6. IR: 1434 (s), 1403 (s), 1255 (sh), 1246 (s), 1169 (w), 1094 (w), 1073 (w), 1020 (m), 1010 (m), 1001 (m), 984 (s), 917 (m), 845 (s, br), 785 (m), 761 (s), 732 (m), 701 (m), 683 (w), 604 (w), 498 (m) cm^{-1}. Anal. Calcd for $C_{31}H_{57}N_4OScSi_4$: C, 56.49; H, 8.72; N, 8.50. Found: C, 56.24; H, 8.79; N, 8.78.

$[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$. Toluene (20 mL) was added to a 100-mL round-bottomed flask containing $[PhC(NSiMe_3)_2]_2ScCl(THF)(Et_2O)_{0.8}$ (0.750 g, 1.01 mmol) and $LiCH_2SiMe_3$ (95.0 mg, 1.01 mmol) forming a cloudy colorless solution. After the solution was stirred overnight, the volatiles were removed under reduced pressure. The remaining cloudy oil was extracted with hexanes (25 mL) and filtered through a pad of Celite on a fritted disk. The solvent was then removed under reduced pressure and HMDSO (15 mL) was added forming a clear colorless solution. Concentration to 0.5 mL and cooling to −40 °C failed to induce crystallization. Crystalline product was obtained by concentrating the HMDSO solution to a sticky oil and leaving it at room temperature overnight (0.35 g, 53%). Subsequent batches of product were crystallized by the addition of a seed crystal. Mp: 106−108 °C. ^1H NMR (C_6D_6, 400 MHz): δ 7.20−7.17 (m, 4H), 7.08−6.80 (m, 6H), 0.47 (s, 9H), 0.41 (s, 2H), 0.12 (s, 36H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 184.7, 141.3, 128.8, 128.2, 126.7, 4.7, 2.7. IR: 1432 (s), 1402 (s), 1248 (m), 1168 (w), 1074 (w), 1032 (w), 1002 (w), 986 (m), 918 (w), 945 (s, br), 761 (m), 721 (w), 701 (w), 504 (m) cm^{-1}. Anal. Calcd for $C_{30}H_{57}N_4ScSi_5$: C, 54.66; H, 8.72; N, 8.50. Found: C, 54.54; H, 8.78; N, 8.35.

$[PhC(NSiMe_3)_2]_2ScCH_2SiMe_2Ph$. To a 100-mL round-bottomed flask was added $[PhC(NSiMe_3)_2]_2ScCl(THF)$ (0.500 g, 0.674 mmol), $LiCH_2SiMe_2Ph$ (0.105 g, 0.674 mmol), and toluene (20 mL) forming a cloudy colorless solution. After the solution was stirred overnight, the volatiles were removed under reduced pressure. The resulting oily solid was extracted with hexanes (40 mL) and filtered through a pad of Celite on a fritted disk. The volatiles were again removed under reduced pressure, and HMDSO (15 mL) was added. Concentration to 3 mL followed by cooling to −40 °C yielded product as small colorless crystals (0.26 g, 53%). Mp: 102−103 °C. ^1H NMR (C_6D_6, 400 MHz): δ 7.88 (dd, J = 1.4, 8.0 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1 H), 7.20−7.15 (m, 4H), 7.05−6.96 (m, 6H), 0.68 (s, 6H), 0.58 (s, 2H), 0.07 (s, 36H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 184.7, 146.1, 141.2, 134.1, 128.9, 128.1, 127.2, 126.7, 3.6, 2.7.

$[PhC(NSiMe_3)_2]_2ScMes$. Toluene (25 mL) was added to a 100-mL round-bottomed flask containing $[PhC(NSiMe_3)_2]_2ScCl(THF)$ (0.500 g, 0.674 mmol) and $(Et_2O)LiMes$ (0.135 g, 0.674 mmol) forming a white suspension. After the mixture was stirred overnight, the volatiles were removed under reduced pressure. The resulting white solid was extracted with hexanes (40 mL) and filtered. Concentration of the clear colorless filtrate to 8 mL followed by cooling to −40 °C yielded the product as small colorless crystals. Two crops yielded 0.24 g (51%). Mp: 167−168 °C. ^1H NMR (C_6D_6, 400 MHz): δ 7.25 (br, 4 H), 7.07−6.98 (m, 6H), 6.91 (s, 2H), 2.90 (s, 6H), 2.27 (s, 3H), 0.03 (br, 36H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 184.1, 142.0, 141.2, 135.6, 128.8, 126.4 (br), 125.8, 25.1, 21.7, 2.6. IR: 1592 (w), 1424 (s, br), 1247 (m), 1170 (w), 1034 (w), 1011 (w), 1002 (w), 986 (m), 914 (w), 843 (s, br), 790 (w), 761 (m), 720 (w), 704 (w), 685 (w), 604 (w), 546 (w), 506 (m) cm^{-1}. Anal.

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Table 1. Crystal Data and Collection Parameters

	$\{[PhC(NSiMe_3)_2]_2ScH\}_2$	$[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$
formula	$C_{52}H_{94}N_8Sc_2Si_8$	$C_{64}H_{124}Cl_4Li_2N_{12}Sc_2Si_8$
fw	1145.97	1532.06 (two indep. molecules)
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
temp (°C)	−150	−102
a (Å)	16.279(3)	15.418(4)
b (Å)	19.852(4)	16.526(4)
c (Å)	21.025(4)	18.900(4)
V (Å^3)	6780(3)	4470(3)
α (deg)	90	102.72(2)
β (deg)	93.80(1)	106.18(1)
γ (deg)	90	93.75(2)
Z	4	2
d_{calc} (g/cm^3)	1.12	1.06
diffractometer	Siemens SMART	Siemens SMART
radiation	Mo Kα	Mo Kα
monochromator	graphite	graphite
detector	CCD area detector	CCD area detector
scan type, deg	ω, 0.3	ω, 0.3
frame collcn time (s)	30	30
reflcns measd	hemisphere	hemisphere
2θ range (deg)	3−46.5	3.1−46.5
μ (mm^{-1})	0.38	0.16
T_{min}, T_{max}	0.828, 0.879	0.854, 0.946
cryst dimens (mm)	0.40 × 0.30 × 0.20	0.40 × 0.15 × 0.20
no. of reflcns measd	21 515	17 854
no. of unique reflcns	9501	12 321
no. of observns ($I > 3\sigma$)	7771	9755
no. of parameters	639	829
R_{int} (%)	3.12	4.42
R (%)	4.11	9.94
$R_{w\,(\%)}$	6.85	9.51
GOF	2.41	7.51

Table 2. Selected Data for $[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$

Bond Distances (Å)			
Sc1−Cl1	2.557(3)	Sc1−N4	2.196(5)
Sc1−Cl2	2.545(3)	Li1−Cl1	2.38(1)
Sc1−N1	2.230(5)	Li1−Cl2	2.35(1)
Sc1−N2	2.182(5)	Li1−N9	2.13(1)
Sc1−N3	2.199(5)	Li1−N10	2.04(1)
Bond Angles (deg)			
Cl1−Sc1−Cl2	83.37(9)	N2−Sc1−Cl1	167.2(1)
N1−Sc1−N2	62.8(2)	N2−Sc−Cl2	91.6(2)
N3−Sc1−N4	62.2(2)	Li1−Cl1−Sc1	92.0(3)
N1−Sc1−N3	151.1(2)	Li1−Cl2−Sc1	92.9(3)
N2−Sc1−N4	97.3(2)	Cl1−Li1−Cl2	91.5(4)
N2−Sc1−Cl1	167.2(1)	N9−Li1−N10	87.7(5)
N2−Sc1−Cl2	91.6(2)	N9−Li1−Cl1	118.0(6)
N4−Sc1−Cl1	89.8(1)	N9−Li1−Cl2	127.3(5)
N4−Sc1−Cl2	167.3(2)	N10−Li1−Cl1	117.6(5)
N1−Sc1−Cl1	105.9(1)	N10−Li1−Cl2	117.5(6)
N1−Sc1−Cl2	95.7(2)		

Table 3. Selected Data for $\{[PhC(NSiMe_3)_2]_2ScH\}_2$

Bond Distances (Å)			
Sc1−H1	1.92(3)	Sc2−H1	2.00(3)
Sc1−H2	1.87(3)	Sc2−H2	1.98(3)
Sc1−N1	2.219(3)	Sc2−N5	2.235(3)
Sc1−N2	2.192(3)	Sc2−N6	2.225(3)
Sc1−N3	2.205(3)	Sc2−N7	2.187(3)
Sc1−N4	2.236(3)	Sc2−N8	2.224(3)
Sc1−Sc2	3.3077(8)		
Bond Angles (deg)			
H1−Sc1−H2	65(1)	N2−Sc1−N4	105.1(1)
H1−Sc1−N1	86(1)	H2−Sc1−N1	110(1)
H1−Sc1−N2	141(1)	H2−Sc1−N2	103(1)
H1−Sc1−N3	106(1)	H2−Sc1−N3	147(1)
H1−Sc1−N4	112(1)	H2−Sc1−N4	90(1)
N1−Sc1−N2	62.2(1)	H1−Sc2−H2	61(1)
N1−Sc1−N3	100.8(1)	N5−Sc2−N8	154.4(1)
N1−Sc1−N4	157.6(1)	N6−Sc2−N7	103.8(1)
N2−Sc1−N3	102.1(1)		

Calcd for $C_{35}H_{57}N_4ScSi_4$: C, 60.82; H, 8.31; N, 8.11. Found: C, 60.63; H, 8.41; N, 7.89.

$\{[PhC(NSiMe_3)_2]_2ScH\}_2$. In a 100-mL Schlenk tube, the addition of hexanes (10 mL) to $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ (0.50 g, 0.76 mmol) formed a clear colorless solution. The flask was evacuated briefly and then backfilled with H_2 (ca. 5 psig). After remaining undisturbed overnight, analytically pure product was isolated as colorless crystals (0.34 g, 79%). Mp: 199−205 °C (dec with gas evolution). ^1H NMR (C_6D_6, 300 MHz): δ 7.60−7.40 (br, 4H), 7.18−6.90 (br), 0.32 (br, 18H), 0.15 (br, 18H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 185.4, 142.3, 128.6, 126.6, 4.3, 3.0. IR: 1447 (s, br), 1434 (s, br), 1283 (m, br), 1260 (m, sh), 1246 (m), 1168 (w), 1030 (w), 1002 (m, sh), 985 (s), 932 (w), 845 (s, br), 786 (w), 761 (m), 745 (w), 723 (w), 698 (m), 604 (w), 496 (m) cm^{-1}. IR (CaF_2, C_6D_6): 3061 (w), 2954 (m), 2896 (w), 1435 (s, br), 1406 (s, br), 1290 (m, br), 1260 (m, sh), 1246 (s), 1162 (w), 1074 (w), 1030 (w), 1002 (m, sh), 985 (s), 942 (m), 933 (m) cm^{-1}. Anal. Calcd for $C_{52}H_{94}N_8Sc_2Si_8$: C, 54.50; H, 8.27; N, 9.78. Found: C, 54.13; H, 8.39; N, 9.48.

$[PhC(NSiMe_3)_2]_2ScC(Ph){=}C(Ph)H$. To a 100-mL round-bottomed flask containing $\{[PhC(NSiMe_3)_2]_2ScH\}_2$ (0.166 g, 0.145 mmol) and Ph_2C_2 (51.6 mg, 0.290 mmol) was added benzene (20 mL) forming a clear colorless solution. The solution was heated to reflux forming a clear yellow solution. After the solution was stirred overnight, the volatiles were removed under reduced pressure. The resulting yellow solid was extracted with hexanes (35 mL) and filtered. Concentration of the clear yellow filtrate to 15 mL followed by cooling to −10 °C afforded the product as clear yellow crystals. Two crops yielded 87 mg (40%). Mp: 214-231 °C. ^1H NMR (C_6D_6, 400 MHz): δ 7.67−7.60 (m, 4H), 7.45−7.35 (m, 4H), 7.28 (s, 1H), 7.20−7.16 (m, 2H), 7.14−7.07 (m, 4H), 7.05−6.96 (m, 6H), 0.03 (s, 36H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 184.1, 152.5, 145.2, 141.0, 138.4, 129.2, 128.7, 128.5, 128.1, 127.4, 127.1, 126.5, 126.0, 124.6, 2.3. IR: 1590 (w), 1421 (m), 1245 (m), 1168 (w), 1074 (w), 1032 (w), 1002 (w), 987 (m), 920 (w), 840 (s, br), 784 (w), 761 (m), 723 (m), 702 (m), 506 (m) cm^{-1}. Anal. Calcd for $C_{40}H_{57}N_4ScSi_4$: C, 63.95; H, 7.65; N, 7.46. Found: C, 63.81; H, 7.71; N, 7.61.

Table 4. Positional Parameters and Equivalent Isotropic Displacement Coefficients for $[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$

atom	*x*	*y*	*z*	*B*(eq) (Å^2)	atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Sc1	0.21294(8)	0.21765(8)	0.01476(6)	2.23(4)	C21	0.3727(4)	0.2810(4)	−0.1084(4)	2.5(2)
Sc2	0.80857(8)	0.29148(7)	0.48359(6)	2.15(4)	C22	0.3400(6)	0.2790(6)	−0.1857(4)	4.5(3)
Cl1	0.3493(2)	0.2635(2)	0.1350(1)	5.40(8)	C23	0.3970(8)	0.3036(6)	−0.2229(5)	6.1(4)
Cl2	0.1837(2)	0.0961(2)	0.0712(2)	7.4(1)	C24	0.4863(7)	0.3275(7)	−0.1879(7)	6.2(5)
Cl3	0.6673(2)	0.2474(2)	0.3669(1)	5.71(9)	C25	0.5200(5)	0.3323(6)	−0.1123(6)	5.5(4)
Cl4	0.8296(2)	0.4185(2)	0.4330(2)	7.1(1)	C26	0.4639(5)	0.3084(5)	−0.0730(5)	4.1(3)
Si1	0.0762(1)	0.3504(1)	0.1167(1)	3.53(7)	C27	0.4897(8)	0.1049(7)	0.199(1)	11.5(7)
Si2	0.0272(1)	0.1116(1)	−0.1560(1)	3.18(7)	C28	0.3786(7)	−0.0140(6)	0.1634(6)	6.2(4)
Si3	0.3579(1)	0.0969(1)	−0.0879(1)	3.27(7)	C29	0.410(1)	0.072(1)	0.2867(7)	13(1)
Si4	0.2661(1)	0.4180(1)	−0.0223(1)	3.03(7)	C30	0.367(1)	0.114(1)	0.3239(8)	14(1)
Si5	0.7590(1)	0.0835(1)	0.5113(1)	2.86(6)	C31	0.3335(8)	0.2584(8)	0.3418(5)	7.2(5)
Si6	0.6640(1)	0.4004(1)	0.5928(1)	3.39(7)	C32	0.2186(7)	0.1480(7)	0.3040(6)	6.6(4)
Si7	0.9944(1)	0.3756(1)	0.6579(1)	3.01(6)	C33	0.8756(6)	0.0608(4)	0.5158(5)	4.3(3)
Si8	0.9400(1)	0.1780(1)	0.3639(1)	3.06(7)	C34	0.6798(5)	0.0323(5)	0.4144(4)	3.8(3)
N1	0.1005(3)	0.2846(3)	0.0416(3)	2.5(2)	C35	0.7251(6)	0.0314(5)	0.5795(4)	4.3(3)
N2	0.0788(3)	0.1846(3)	−0.0703(3)	2.9(2)	C36	0.6994(7)	0.4971(5)	0.5701(5)	5.1(3)
N3	0.2968(3)	0.1782(3)	−0.0604(3)	2.7(2)	C37	0.5381(6)	0.3719(6)	0.5409(6)	6.6(4)
N4	0.2668(3)	0.3123(3)	−0.0325(3)	2.6(2)	C38	0.6826(7)	0.4261(6)	0.6979(5)	5.4(4)
N5	0.7600(3)	0.1917(3)	0.5275(3)	2.5(2)	C39	0.7157(4)	0.2409(4)	0.5624(3)	2.7(2)
N6	0.7276(3)	0.3218(3)	0.5626(3)	2.3(2)	C40	0.6453(5)	0.2092(4)	0.5961(4)	3.2(2)
N7	0.9443(4)	0.3175(3)	0.5643(3)	2.4(2)	C41	0.5617(5)	0.1689(5)	0.5512(4)	3.9(3)
N8	0.9191(3)	0.2317(3)	0.4467(3)	2.3(2)	C42	0.5002(6)	0.1390(6)	0.5825(5)	5.1(3)
N9	0.3047(4)	0.1750(5)	0.2965(4)	4.3(3)	C43	0.5218(6)	0.1473(7)	0.6589(5)	5.6(4)
N10	0.4025(5)	0.0720(4)	0.2099(4)	4.5(3)	C44	0.6075(6)	0.1830(5)	0.7052(4)	4.8(3)
N11	0.6043(4)	0.4421(4)	0.2961(3)	3.2(2)	C45	0.6704(5)	0.2154(5)	0.6741(4)	3.9(3)
N12	0.6973(4)	0.3333(4)	0.2080(3)	3.8(2)	C46	0.9645(7)	0.4824(6)	0.6602(5)	6.1(4)
C1	0.1685(6)	0.3527(6)	0.2050(4)	4.7(3)	C47	0.9409(6)	0.3315(7)	0.7189(4)	5.7(4)
C2	0.0681(6)	0.4579(6)	0.1044(5)	4.9(3)	C48	1.1185(5)	0.3819(6)	0.6946(4)	4.9(3)
C3	−0.0314(6)	0.3146(7)	0.1332(5)	5.9(4)	C49	1.0281(5)	0.1045(5)	0.3812(4)	4.1(3)
C4	−0.0928(5)	0.1177(6)	−0.2046(4)	4.7(3)	C50	0.9804(7)	0.2547(6)	0.3167(4)	5.3(4)
C5	0.0923(5)	0.1289(5)	−0.2214(4)	4.0(3)	C51	0.8344(6)	0.1125(6)	0.3012(4)	5.2(3)
C6	0.0330(6)	0.0061(5)	−0.1382(5)	5.1(3)	C52	0.9774(5)	0.2713(4)	0.5142(3)	2.5(2)
C7	0.0439(4)	0.2346(5)	−0.0220(4)	3.0(2)	C53	1.0770(4)	0.2636(4)	0.5291(4)	2.9(2)
C8	−0.0581(4)	0.2333(5)	−0.0387(4)	3.4(2)	C54	1.1133(5)	0.2044(5)	0.5631(5)	4.6(3)
C9	−0.1016(5)	0.2966(5)	−0.0644(5)	4.6(3)	C55	1.2116(6)	0.2001(6)	0.5751(5)	6.1(4)
C10	−0.1989(6)	0.2901(7)	−0.0784(6)	6.2(4)	C56	1.2598(7)	0.253(1)	0.5517(6)	7.9(5)
C11	−0.2419(6)	0.2245(8)	−0.0608(7)	7.2(5)	C57	1.2187(6)	0.3114(7)	0.5150(5)	5.4(4)
C12	−0.1976(6)	0.1668(6)	−0.0322(7)	6.1(4)	C58	1.1313(5)	0.3180(5)	0.5054(4)	4.2(3)
C13	−0.1078(5)	0.1677(5)	−0.0216(5)	4.2(3)	C59	0.5193(6)	0.4022(6)	0.3080(6)	6.0(4)
C14	0.4803(6)	0.1153(5)	−0.0256(5)	4.9(3)	C60	0.6229(5)	0.5271(5)	0.3427(5)	4.3(3)
C15	0.3055(6)	−0.0007(5)	−0.0756(5)	4.3(3)	C61	0.5939(6)	0.4419(6)	0.2185(5)	4.9(3)
C16	0.3557(6)	0.0786(6)	−0.1900(5)	5.0(3)	C62	0.6060(6)	0.3563(6)	0.1724(5)	5.0(3)
C17	0.1491(6)	0.4357(5)	−0.0671(5)	4.9(3)	C63	0.7007(7)	0.2433(6)	0.1713(5)	6.2(4)
C18	0.3424(7)	0.4738(5)	−0.0646(5)	5.3(4)	C64	0.7684(6)	0.3845(7)	0.1954(6)	6.1(4)
C19	0.3080(6)	0.4697(5)	0.0812(4)	4.1(3)	Li1	0.3071(8)	0.1490(8)	0.1818(6)	3.3(4)
C20	0.3099(4)	0.2567(4)	−0.0670(3)	2.5(2)	Li2	0.7009(9)	0.3671(7)	0.3226(6)	3.5(4)

$\{[PhC(NSiMe_3)_2]_2ScD\}_2$. The procedure for the preparation of $\{[PhC(NSiMe_3)_2]_2ScH\}_2$ was followed except H_2 was replaced by D_2. IR: 1446 (s, br), 1404 (s, br), 1260 (m, sh), 1246 (s), 1169 (w), 1074 (w), 1002 (m, sh), 984 (s), 907 (s, br), 840 (s, br), 786 (m), 761 (m), 745 (m), 723 (m), 701 (m), 664 (w), 605 (w), 515 (m), 491 (m) cm^{-1}. IR (CaF_2, C_6D_6): 3061 (w), 2954 (m), 2896 (w), 1434 (s, br), 1405 (s, br), 1260 (m, sh), 1246 (s), 1162 (w), 1074 (w), 1002 (m, sh), 984 (s), 932 (m), 916 (s), 908 (s), 904 (s) cm^{-1}.

$[TolC(NSiMe_3)_2]_2Sc(BH_4)(THF)$. Tetrahydrofuran (30 mL) was added to $[TolC(NSiMe_3)_2]_2ScCl(THF)$ (0.50 g, 0.71 mmol) and $NaBH_4$ (0.080 g, 2.1 mmol) in a 100-mL round-bottomed flask forming a cloudy colorless solution. After the solution was stirred overnight, the volatiles were removed under reduced pressure. The resulting white residue was extracted with hexanes (50 mL) and filtered through a pad of Celite on a fritted disk. Concentration to 10 mL followed by cooling to −40 °C gave the product as large colorless crystals (0.30 g, 62 %). Mp: 160−161 °C dec. ^1H NMR (C_6D_6, 400 MHz): δ 7.17 (d, $J = 8.0$ Hz, 4 H), 6.89 (dd, $J = 0.6$, 8.3 Hz, 4 H), 4.15 (m, 4 H), 2.03 (s, 6 H), 1.44 (m, 4 H), 0.15 (s, 36 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 182.9, 139.5, 138.1, 128.7, 126.5, 72.7, 25.4, 21.2, 2.7. IR: 2463 (w), 2388 (w), 2349 (w), 2230 (w), 1612 (w), 1433 (s, br), 1400 (s, sh), 1244 (s), 1168 (w), 1110 (w), 1008 (m, sh), (987 (s), 843 (s, br), 760 (m), 733 (m), 685 (w), 644 (w), 633 (w), 603 (w), 463 (m) cm^{-1}. Anal. Calcd for $C_{32}H_{62}BN_4OScSi_4$: C, 55.95; H, 9.10; N, 8.16. Found: C, 55.83; H, 9.05; N, 7.96.

$[PhC(NSiMe_3)_2]_2ScNHC_6H_3\text{-}2,6\text{-}Pr^i{}_2$. To a 100-mL round-bottomed flask containing $[PhC(NSiMe_3)_2]_2ScCl(THF)(Et_2O)_{0.8}$ (2.00 g, 2.70 mmol) and $LiNHC_6H_3\text{-}2,6\text{-}Pr^i$ (0.490 g, 2.70 mmol) was added toluene (40 mL) forming a cloudy, dirty yellow solution. After the solution was stirred overnight, the volatiles were removed under reduced pressure. The remaining yellow-orange solid was extracted with hexanes (75 mL) and filtered through a pad of Celite on a fritted disk. Concentration to 20 mL and cooling to −40 °C yielded the product as large colorless crystals. Total yield from two crops: 1.5 g, 74% Mp: 162−163 °C. ^1H NMR (C_6D_6, 400 MHz): δ 7.30−7.25 (m, 4H), 7.20 (d, $J = 7.6$ Hz, 2H), 7.05−7.00 (m, 6H), 6.92 (t, $J = 7.6$ Hz, 1H), 5.86 (br, 1H), 3.40 (sept, $J = 6$ 8 Hz, 2H), 1.54 (d, $J = 6.8$ Hz, 12H), 0.04 (s, 36H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 184.8, 150.5, 141.5, 133.8, 128.9, 128.3, 126.6, 123.0, 117.1, 30.3, 24.0, 2.4. IR: 1736 (w), 1590 (w), 1447 (s), 1430 (s), 1334 (w), 1263 (m), 1247 (m), 1170 (w), 1008 (w), 984 (m), 916 (w), 843 (s, br), 786 (w), 761 (m), 746 (w), 701 (w), 574 (w), 505 (m) cm^{-1}. Anal. Calcd for $C_{38}H_{66}N_5ScSi_4$: C, 60.83; H, 8.87; N, 9.33. Found: C, 60.71; H, 8.81; N, 9.31.

Reaction of $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ with Me_3SiCCH. To a serum-capped NMR tube containing $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ (9.0 mg, 14 μmol) and benzene-d_6 was added Me_3SiCCH (1.9 μL, 14 μmol) forming a clear colorless

Table 5. Positional Parameters and Equivalent Isotropic Displacement Coefficients for {[PhC(NSiMe$_3$)$_2$]$_2$ScH}$_2$

atom	x	y	z	B(eq) (Å^2)	atom	x	y	z	B(eq) (Å^2)
Sc1	0.37422(4)	0.28771(3)	0.38524(3)	1.83(3)	C19	0.6392(2)	0.2307(2)	0.5166(2)	4.2(2)
Sc2	0.49959(3)	0.30103(3)	0.26834(3)	1.75(3)	C20	0.4240(2)	0.2146(2)	0.4826(1)	2.3(1)
Si1	0.19572(6)	0.26197(5)	0.26952(4)	2.43(4)	C21	0.4569(2)	0.1685(2)	0.5345(2)	2.7(1)
Si2	0.29385(6)	0.42208(5)	0.48146(5)	3.04(4)	C22	0.4938(3)	0.1081(2)	0.5176(2)	4.4(2)
Si3	0.28053(6)	0.13845(5)	0.46017(4)	2.60(4)	C23	0.5287(4)	0.0666(2)	0.5646(3)	6.8(3)
Si4	0.56030(6)	0.29786(5)	0.50139(4)	2.44(4)	C24	0.5261(4)	0.0838(3)	0.6275(3)	7.0(3)
Si5	0.59041(6)	0.12918(4)	0.30279(5)	2.52(4)	C25	0.4883(3)	0.1420(2)	0.6450(2)	5.1(2)
Si6	0.70306(6)	0.38820(5)	0.25655(4)	2.58(4)	C26	0.4531(2)	0.1849(2)	0.5975(2)	3.3(2)
Si7	0.46005(6)	0.22305(5)	0.11160(4)	2.51(4)	C27	0.4876(2)	0.1057(2)	0.3284(2)	3.4(2)
Si8	0.42397(6)	0.47327(4)	0.23102(4)	2.25(4)	C28	0.6674(3)	0.1025(2)	0.3677(2)	4.2(2)
N1	0.2511(2)	0.2976(1)	0.3344(1)	2.3(1)	C29	0.6128(2)	0.0771(2)	0.2322(2)	3.3(2)
N2	0.2901(2)	0.3636(1)	0.4197(1)	2.4(1)	C30	0.7218(2)	0.4381(2)	0.3311(2)	3.6(2)
N3	0.3533(2)	0.2014(1)	0.4483(1)	2.2(1)	C31	0.8059(2)	0.3625(2)	0.2300(2)	3.9(2)
N4	0.4664(2)	0.2693(1)	0.4671(1)	2.2(1)	C32	0.6553(2)	0.4421(2)	0.1916(2)	3.3(2)
N5	0.5871(2)	0.2153(1)	0.2863(1)	2.1(1)	C33	0.6508(2)	0.2575(2)	0.2807(1)	2.1(1)
N6	0.6339(2)	0.3220(1)	0.2686(1)	2.2(1)	C34	0.7371(2)	0.2309(2)	0.2888(2)	2.4(1)
N7	0.4618(2)	0.2881(1)	0.1673(1)	2.2(1)	C35	0.7837(2)	0.2400(2)	0.3461(2)	3.3(2)
N8	0.4488(2)	0.3901(1)	0.2148(1)	2.1(1)	C36	0.8615(2)	0.2116(2)	0.3552(2)	4.4(2)
C1	0.0824(2)	0.2559(2)	0.2775(2)	3.6(2)	C37	0.8929(2)	0.1748(2)	0.3061(2)	4.5(2)
C2	0.2173(2)	0.3096(2)	0.1963(2)	3.4(2)	C38	0.8489(2)	0.1674(2)	0.2491(2)	4.1(2)
C3	0.2329(2)	0.1744(2)	0.2603(2)	3.3(2)	C39	0.7706(2)	0.1949(2)	0.2401(2)	3.2(2)
C4	0.2126(3)	0.4884(3)	0.4766(3)	6.8(3)	C40	0.4146(3)	0.1486(2)	0.1485(2)	3.7(2)
C5	0.3963(3)	0.4637(2)	0.4788(2)	4.3(2)	C41	0.5680(3)	0.2057(2)	0.944(2)	3.9(2)
C6	0.2900(3)	0.3740(3)	0.5577(2)	5.1(2)	C42	0.3977(3)	0.2377(2)	0.0351(2)	4.8(2)
C7	0.2314(2)	0.3453(2)	0.3757(1)	2.3(1)	C43	0.4375(2)	0.5334(2)	0.1634(2)	2.7(1)
C8	0.1473(2)	0.3769(2)	0.3724(2)	2.5(1)	C44	0.3161(2)	0.4758(2)	0.2542(2)	3.3(2)
C9	0.0906(2)	0.3572(2)	0.4160(2)	3.7(2)	C45	0.4919(2)	0.5022(2)	0.3008(2)	3.4(2)
C10	0.0120(3)	0.3857(2)	0.4108(2)	4.8(2)	C46	0.4435(2)	0.3537(2)	0.1616(1)	2.1(1)
C11	−0.0092(2)	0.4332(2)	0.3650(2)	4.5(2)	C47	0.4210(2)	0.3839(2)	0.0973(1)	2.1(1)
C12	0.0475(2)	0.4524(2)	0.3234(2)	3.8(2)	C48	0.4825(2)	0.3948(2)	0.0554(2)	3.0(2)
C13	0.1245(2)	0.4243(2)	0.3267(2)	3.0(2)	C49	0.4608(2)	0.4203(2)	−0.0052(2)	3.6(2)
C14	0.2956(2)	0.0671(2)	0.4054(2)	3.4(2)	C50	0.3802(2)	0.4334(2)	−0.0246(2)	3.4(2)
C15	0.2805(3)	0.1042(2)	0.5425(2)	4.9(2)	C51	0.3186(2)	0.4227(2)	0.0168(2)	3.0(2)
C16	0.1780(2)	0.1771(2)	0.4440(2)	3.3(2)	C52	0.3395(2)	0.3984(2)	0.0780(1)	2.6(1)
C17	0.5481(2)	0.3423(2)	0.5782(2)	3.3(2)	H(1)	0.409(2)	0.250(1)	0.307(1)	1.6(6)
C18	0.6042(2)	0.3569(2)	0.4443(2)	3.1(2)	H(2)	0.452(2)	0.340(2)	0.345(2)	3.4(8)

solution. After 30 min, NMR spectroscopic analysis showed complete conversion to the products. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.08−7.03 (m, 4H), 6.99−6.94 (m, 6H), 0.30 (s, 9H), 0.18 (s, 36H), −0.01 (s, 9H).

X-ray Crystallography. Table 1 lists a summary of crystallographic data for both structurally characterized compounds.

{[PhC(NSiMe$_3$)$_2$]$_2$ScH}$_2$. Crystals suitable for X-ray diffraction studies were prepared by the blanketing of H_2 onto an hexanes solution of [PhC(NSiMe$_3$)$_2$]$_2$ScCH$_2$SiMe$_3$ at room temperature. Within 2 h, colorless prisms started forming at the interface. A large crystal was cut to appropriate size and mounted[38] on a glass capillary using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART diffractometer/CCD area detector,[39] centered in the beam, and cooled to −150 °C by a nitrogen-flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrix and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected using a 30-s scan time per frame. The raw data were integrated (XY spot spread = 1.60°; Z spot spread = 0.60°) using SAINT.[40] Data analysis and absorption correction were performed using Siemens XPREP.[41] The unit cell parameters and systematic absences indicated the primitive monoclinic cell $P2_1/n$ (No. 14).[42] The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied.

The 21 515 reflections measured ($\theta = 0{-}45°$) were averaged ($R_{\text{int}} = 3.12\%$) yielding 9501 unique reflections. The structure was solved and refined with the teXsan[43] software package using direct methods[44] and expanded using Fourier techniques.[45] All non-hydrogen atoms were refined anisotropically. The hydride hydrogens were located in a difference Fourier and were refined isotropically. All remaining hydrogens were assigned idealized positions and included in structure factor calculations but were not refined. The final residuals for the 639 variables refined against the 7771 data for which $F^2 > 3\sigma(F^2)$ were $R = 4.11\%$, $R_w = 6.85\%$, and GOF = 2.41.[46] The quantity minimized by the least squares program was $\sum_w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p-factor,[46] used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used,[47] and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[48] The

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[46] $R = [\sum||F_o| - |F_c||]/\sum|F_o|$, $R_w = \{[\sum_w(|F_o| - |F_c|)^2]/\sum_w F_o{}^2\}^{1/2}$, and GOF $= \{[\sum_w(|F_o| - |F_c|)^2]/(n_o - n_v)\}^{1/2}$, where n_o is the number of observations, n_v the number of variable parameters, and the weights w were given by $w = 1/\sigma^2(F_o)$, with $\sigma(F_o{}^2) = [\sigma_o{}^2(F_o{}^2) + (pF_o{}^2)^2]^{1/2}$, where $\sigma^2(F_o)$ is calculated as above from $\sigma(F_o)^2$ and where p is the factor used to lower the weight of intense reflections.

positional and thermal parameters for all non-hydrogen atoms are given in Table 5.

$[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$. While attempting to undertake X-ray structural investigations of a borohydride derivative prepared from $[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$ and $LiBH_4$, we determined the crystal structure of the unreacted dichloride. The crystal was grown from hexanes at −10 °C. A crystal was selected, mounted, centered, and cooled to −102 °C in the manner described above. Data collection, integration, processing, and absorption correction were carried out as described above. The unit cell was determined to be primitive triclinic with space group $P\bar{1}$ (No. 2). The 17 854 reflections measured ($\theta = 0-45°$) were averaged ($R_{int} = 4.42\%$) yielding 12 321 unique reflections. The structure was solved and refined with the teXsan software package using direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were assigned idealized positions and included in structure factor calculations but were not refined. The final residuals for the 829 variables refined against the 9755 data for which $F^2 > 3\sigma(F^2)$ were $R = 9.94\%$, $R_w = 9.51\%$, and GOF = 7.51.[46] The positional and thermal parameters of all non-hydrogen atoms are given in Table 4.

Supporting Information Available: ORTEP diagrams and tables of positional parameters, thermal parameters, and bond distances and angles (51 pages). Ordering information is given on any current masthead page.

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(47) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(48) Cromer, D. T.; Waber, J. T. *Ibid.*, Table 2.3.1.