Mono(pentamethylcyclopentadienyl)yttrium Compounds Stabilized by *N,N′*-Bis(Trimethylsilyl)benzamidinate Ligands

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Reaction of YCl_3·3.5THF with Cp*K followed by $[PhC(NSiMe_3)_2]Li·OEt_2$ in THF gives the surprisingly stable yttrium cyclopentadienyl−benzamidinate chloride $\{Cp^*[PhC(NSiMe_3)_2]Y(\mu\text{-}Cl)\}_2$ (**1**). Thermally induced redistribution of the various ligands leading to disproportionation of the molecule was not observed. The dimer does not split easily, e.g., it does not react with THF to give $Cp^*[PhC(NSiMe_3)_2]YCl·THF$. Attempts to produce monomeric derivatives of **1** by substitution of the chloride by alkoxy, amide, or alkyl substituents using salt metathesis methodology were not successful. Reaction of **1** with 2 equiv of MeLi in the presence of TMEDA (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) afforded the structurally characterized $Cp^*[PhC(NSiMe_3)_2]Y(\mu\text{-}Me)_2Li·TMEDA$ (**2**). Compound **2** is a useful precursor for other yttrium pentamethylcyclopentadienyl−benzamidinate derivatives by controlled protolysis: with $HC{\equiv}CCMe_3$ or HOAr it yields $Cp^*[PhC(NSiMe_3)_2]Y(\mu\text{-}C{\equiv}CCMe_3)Li·TMEDA$ (**3**) and $Cp^*[PhC(NSiMe_3)_2]YOAr$ (**4**), respectively.

Introduction

The activity of homogeneous catalysts based on lanthanides and group 3 metals carbyl and hydrido derivatives is profoundly influenced by the ancillary ligand system. While previous work has primarily focused on compounds stabilized by two (substituted) cyclopentadienyl ligands, Cp'_2LnR,[1] there has been increased attention for other spectator ligands whether as alternatives for or in addition to cyclopentadienyls ligands.[1j,2] Recently, we have reported the synthesis and reactivity of bis(*N,N′*-bis(trimethylsilyl)benzamidinato)yttrium complexes, $[PhC(NSiMe_3)_2]_2YR$ (R = alkyl, alkynyl, hydrido).[3] It was shown that replacing the bis(pentamethylcyclopentadienyl) ligand system by two *N,N′*-bis(trimethylsilyl)benzamidinate ligands results in a dramatic decrease of catalytic reactivity of the metal center for C−C bond formation.[3] A theoretical analysis of these results indicated that this drop in catalyic activity probably is due to an increased ionicity of the metal benzamidinate bonding. Therefore it is interesting to investigate mixed-ligand, Cp* benzamidinate, yttrium compounds to see whether or not these complexes would exhibit reactivity intermediate to that of Cp^*_2YR and $[PhC(NSiMe_3)_2]_2YR$.

The number of well-characterized mono(pentamethylcyclopentadienyl)yttrium and -lanthanide derivatives is limited.[1j,2f,4] In general mono(pentamethylcyclopentadienyl) compounds are sterically less crowded than the bis(pentamethylcyclopentadienyl) derivatives and a kinetically stable, well-defined configuration is more difficult to achieve. The choice of the yttrium/lanthanide precursor complex appears to be crucial, because incorporation of salt and solvent molecules, which block further reactivity, is even more frequently observed than in the corresponding bis(pentamethylcyclopentadienyl) systems, Cp^*_2LnR.[4,5]

A major problem, encountered when studying mono(pentamethylcyclopentadienyl)yttrium and -lanthanide complexes, is that they often show ligand exchange which leads to disproportionation.[4b,5a,b] In this respect, organolanthanide complexes resemble main group organometallics like organomagnesium (Schlenk equilib-

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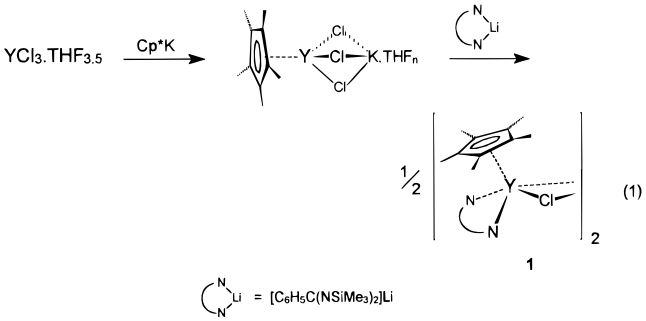
ria with mixtures of RMgX, MgR_2, and MgX_2[6]) and organocalcium compounds (disproportionation of Cp*CaI·2THF to Cp^*_2Ca·2THF and CaI_2·2THF[7]). When the reactivity of mixed-ligand yttrium compounds is to be studied, the complexes should be kinetically sufficiently inert with respect to redistribution of the ancillary ligands under the reaction conditions.

Here we report the synthesis and characterization of several mono(pentamethylcyclopentadienyl)(*N*,*N*′-bis(trimethylsilyl)benzamidinato)yttrium complexes which are resistant to disproportionation. The molecular structure of Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-Me)$_2$Li·TMEDA is described, together with a study of its potential application as a precursor for the synthesis of other Cp*(benzamidinato)yttrium complexes.

Results and Discussion

Synthesis and Characterization of Mono(pentamethylcyclopentadienyl)(benzamidinato)yttrium Compounds, Cp*[PhC(NSiMe$_3$)$_2$]YR. The benzamidinate ligand can conveniently be introduced by treatment of YCl_3·3.5THF with Cp*K followed by [PhC(NSiMe$_3$)$_2$]Li·OEt$_2$ in THF, affording {Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-Cl)}$_2$ (**1**) after extraction with hot toluene (eq 1). When YCl_3·3.5THF was first treated with [PhC(NSiMe$_3$)$_2$]Li·OEt$_2$ followed by Cp*K, a mixture of products was obtained. From this mixture, [PhC(NSiMe$_3$)$_2$]$_2$YCl·THF rather than the mixed-ligand chloride **1** was isolated, indicating that the order of introduction of the ligands is crucial. Complex **1** is moderately soluble in hot toluene and THF. Remarkably, it does not retain salt or solvent molecules, as commonly observed in group 3 metal and lanthanide chemistry. The compound is thermally stable in toluene and THF (both solvents: 12 h, reflux), showing no sign of intermolecular ligand exchange. Apparently, the chloro bridge in **1** is very stable and prevents ligand redistribution and solvation. Unlike {Cp*$_2$Y(μ-Cl)}$_2$, **1** does not react with THF to form the monochloro THF adduct. Spectroscopic data (NMR) show that 1 equiv of toluene is present in the crystal lattice. While slowly released in the solid state at room temperature, the toluene can be quantitatively removed by gently warming (50 °C) *in vacuo*. The ^{1}H and ^{13}C NMR spectra of **1** show one signal for the C$_5$*Me*$_5$ (^{1}H, δ = 2.28 ppm; ^{13}C, δ = 12.0 ppm) and benzamidinate-Si*Me*$_3$ (^{1}H, δ = 0.10 ppm; ^{13}C, δ = 3.1 ppm) groups, suggesting a highly symmetric conformation (or fast dynamic processes involving the benzamidinate ligands).



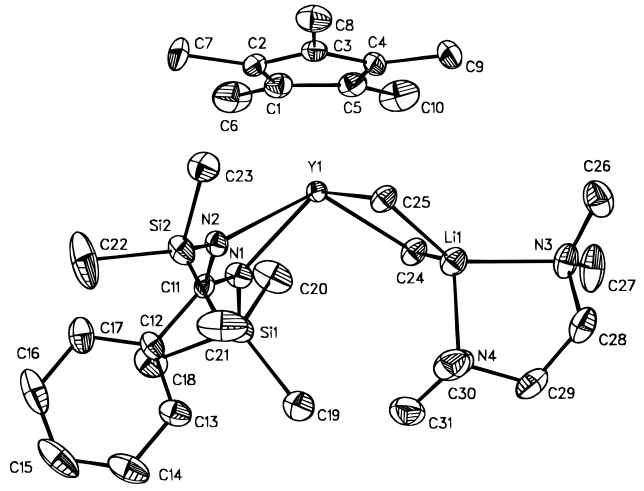
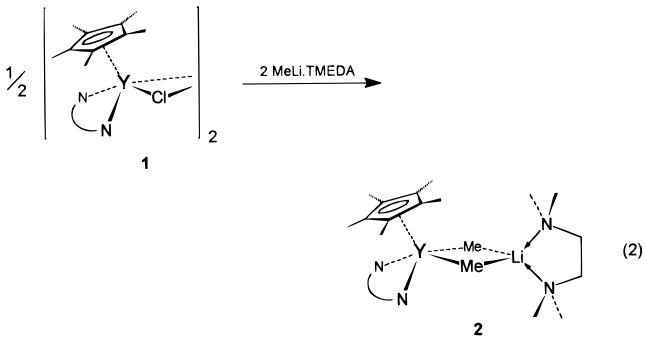


Figure 1. ORTEP drawing of Cp*[C$_6$H$_5$C(NSiMe$_3$)$_2$]Y(μ-Me)$_2$Li·TMEDA (**2**) with 50% probability ellipsoids.

Initial attempts to substitute the chloride ligand in **1** with Li-O-2,6-(CMe$_3$)C$_6$H$_3$, MN(SiMe$_3$)$_2$ (M = Li, Na), or alkylating reagents such as MCH(SiMe$_3$)$_2$ (M = Li, K), Li-CH$_2$-2-NC$_5$H$_3$-6-Me, or LiCH$_2$XMe$_3$ (X = Si, C) were unsuccessful. Although reaction occurred with KCH$_2$Ph, it led to a complex product mixture. Only treatment of **1** with 2 equiv of MeLi in the presence of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) gave a well-defined product, Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-Me)$_2$Li·TMEDA (**2**, eq 2). The reason for the observed low reactivity of **1** is assumed to be the (kinetic) stability of the bridging chloride unit. Apparently, only the smaller MeLi approaches the chloride bridge closely enough to react. Furthermore, TMEDA seems to be essential to stabilize the alkyl complex since reaction of **1** with MeLi (1, 2 equiv, pentane, ether, toluene, THF) in the absence of TMEDA invariably resulted in complex product mixtures. As observed for **1**, the ^{1}H and ^{13}C NMR spectra of **2** show single resonances for both the C$_5$*Me*$_5$ (^{1}H, δ = 2.42 ppm; ^{13}C, δ = 12.1 ppm) and benzamidinate-Si*Me*$_3$ (^{1}H, δ = 0.11 ppm; ^{13}C, δ = 3.7 ppm) groups. In contrast to the analogous Cp*$_2$Y(μ-Me)$_2$Li·2OEt$_2$ (δ = −1.80 ppm)[1a] and [PhC(NSiMe$_3$)$_2$]$_2$Y(μ-Me)$_2$Li·TMEDA (^{1}H, δ −0.48 ppm; ^{13}C, δ = 10.1 ppm),[3b] the μ-C*H*$_3$ resonance (^{1}H, δ = −0.91 ppm; ^{13}C, δ = 13.5 ppm) appears as a broad singlet.



A low-temperature X-ray diffraction determination of the molecular structure of **2** was carried out. An ORTEP drawing of **2** is shown in Figure 1, and important bond lengths and angles are listed in Table 1. The yttrium is coordinated by one pentamethylcyclopenta-

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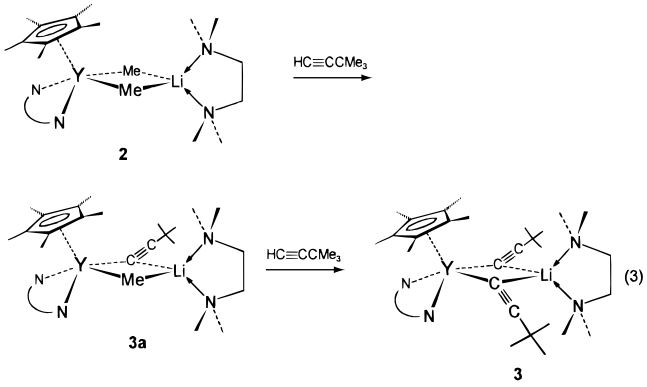
Table 1. Selected Distances and Angles for Cp*[$C_6H_5C(NSiMe_3)_2$]Y(μ-Me)$_2$Li·TMEDA (2)

		Distances (Å)	
Y(1)−C(ring)$_{av}$	2.678(3)	Y(1)−C(25)	2.493(3)
Y(1)−Cent	2.392(3)	N(1)−C(11)	1.338(4)
Y(1)−N(1)	2.423(3)	N(2)−C(11)	1.329(4)
Y(1)−N(2)	2.414(2)	C(24)−Li(1)	2.175(6)
Y(1)−C(24)	2.480(3)	C(25)−Li(1)	2.191(6)
		Angles (deg)	
C(11)−Y(1)−C(24)	106.85(10)	Y(1)−C(24)−Li(1)	81.61(18)
C(11)−Y(1)−C(25)	109.28(10)	Y(1)−C(25)−Li(1)	81.02(18)
Cent−Y(1)−C(24)	108.91(10)	N(1)−Y(1)−C(24)	86.88(10)
Cent−Y(1)−C(25)	107.46(10)	N(2)−Y(1)−C(25)	89.15(10)
Cent−Y(1)−C(11)	127.97(10)	C(24)−Y(1)−C25)	89.67(11)
Cent−Y(1)−N(1)	120.09(10)	N(1)−Y(1)−N(2)	56.75(8)
Cent−Y(1)−N(2)	120.74(10)	N(1)−C(11)−N(2)	119.1(3)
N(1)−C(11)−C(12)−C(13)	87.0(4)		

dienyl, one chelating benzamidinate, and two methyl ligands. The latter bridge yttrium and lithium. The complex can be described as a four-legged piano stool, with yttrium in the center (Cent−Y(1)−N(1) = 120.09-(10)°, Cent−Y(1)−N(2) = 120.74(10)°, Cent−Y(1)−C(24) = 108.91(10)°, Cent−Y(1)−C(25) = 107.46(10)°). The structure is similar to that of the previously described Cp[PhC(NSiMe$_3$)$_2$]ZrCl$_2$ and Cp[PhC(NSiMe$_3$)$_2$]TiMe$_2$.[8] It exhibits *pseudo-*C_s symmetry where the two methyl groups are related by an imaginary plane of symmetry bisecting the Me−Y−Me angle. As expected, the benzamidinate group forms an almost planar four-membered ring with yttrium (torsion angle N(2)−Y(1)−N(1)−C(11) = −5.94(19)°), with the benzamidinate phenyl ring almost perpendicular to it (the acute dihedral angle between the N(1)−C(11)−N(2) and C(11)−C(12)−C(13) planes being 87.0(4)°). Compared to [*p*-MeOC$_6$H$_4$C-(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ (Y−N$_{av}$ = 2.338(4) Å)[3b] and {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-R)}$_2$ (R = H, Y−N$_{av}$ = 2.356(3) Å; R = C≡CH, Y−N$_{av}$ = 2.366(4) Å),[3a,b] the Y−N distances are notably longer (Y(1)−N(1) = 2.423(3) Å, Y(1)−N(2) = 2.414(2) Å), which may be a result of the lower electrophilicity of the metal center in the systems.[3] The N(1)−C(11) (1.338(4) Å) and N(2)−C(11) (1.329(4) Å) bonds are identical to those in bis(benzamidinato)-yttrium derivatives and indicate effective charge delocalization in the N−C−N fragment.[9] The distance between the Cp*(cent)−Y(1) (2.392(3) Å) is normal and is comparable to values observed for other mono- and bis-Cp*Y derivatives (2.363(3)−2.420(6) Å).[10] The Y−C(Me) bond distances of 2.480(3) and 2.493(3) Å are comparable to the Y−C bond in Cp*$_2$YCH(SiMe$_3$)$_2$ (2.468(7) Å)[10a] and are considerably shorter than in {Cp$_2$Y(μ-Me)}$_2$ (2.553(10), 2.537(9) Å).[10c] where presumably steric congestion of the metal center is the reason for the long Y−C bond.

Protolysis Reactions of Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-Me)$_2$Li·TMEDA (2). Because the alkyl ligands of compound **2** are susceptible to controlled protolysis under mild conditions, **2** is potentially a useful precursor for a range of derivatives. Specifically, the reaction of **2** with 2 equiv of 3,3-dimethyl-but-1-yne, HC≡CCMe$_3$, selectively yields Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-C≡CCMe$_3$)$_2$-Li·TMEDA (**3**, eq 3). During the reaction, the intermediate Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-Me)(μ-C≡CCMe$_3$)Li·-TMEDA (**3a**) could be identified by two inequivalent benzamidinate-Si(C*H*$_3$)$_3$ resonances (δ = 0.18, 0.10 ppm) in the ^{1}H NMR spectrum. The observation of **3a** supports stepwise substitution of the methyl groups of **2**. The structure of complex **3** is comparable to [PhC-(NSiMe$_3$)$_2$]$_2$Y(μ-C≡CCMe$_3$)$_2$Li·TMEDA,[3c] Cp*$_2$Y(μ-C≡CCMe$_3$)$_2$Li·THF,[11a] and Cp*$_2$Sm(μ-C≡CPh)K.[11b] Analogous to **1** and **2**, in the ^{1}H and ^{13}C NMR spectra of **3**, single resonances are observed for C$_5$(*CH*$_3$)$_5$ (^{1}H, δ = 2.53 ppm; ^{13}C, δ = 13.0 ppm) and PhC(NSi(*CH*$_3$)$_3$)$_2$ (^{1}H, δ = 0.16 ppm; ^{13}C, δ = 4.0 ppm), suggesting a symmetric structure in solution. The C≡CC(*CH*$_3$)$_3$ groups appear as singlets (^{1}H, δ = 1.29 ppm; ^{13}C, δ = 32.5 ppm), whereas the doublet resonance of the acetylide α-carbon (δ = 120.5 ppm, $^1J_{Y-C}$ = 8 Hz) indicates a monomeric structure for **3**. The yttrium coupling at the alkynyl α-carbon is small compared to the corresponding one in [PhC(NSiMe$_3$)$_2$]$_2$Y(μ-C≡CCMe$_3$)$_2$Li·TMEDA ($^1J_{Y-C}$ = 15 Hz) and in the dimeric acetylides {[PhC(NSiMe$_3$)$_2$]$_2$Y-(μ-C≡CR)}$_2$ (R = H, alkyl, Ph, SiMe$_3$: 20−21 Hz).[3c]



Whereas with HC≡CCMe$_3$ the anionic structure is preserved, reaction of **2** with 2 equiv of 2,6-di-*tert*-butylphenol yielded the neutral Cp*[PhC(NSiMe$_3$)$_2$]-YOAr (**4**, OAr = 2,6-OC$_6$H$_3$(CMe$_3$)$_2$, eq 4). Competitive protolysis of the Cp* or benzamidinate ligand is not observed, indicating the high kinetic stability of these

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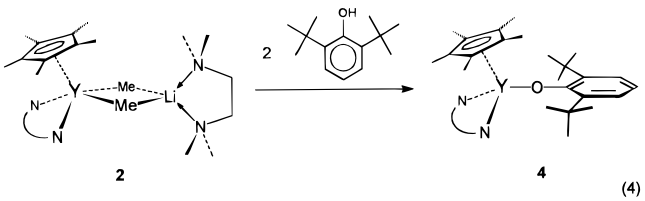
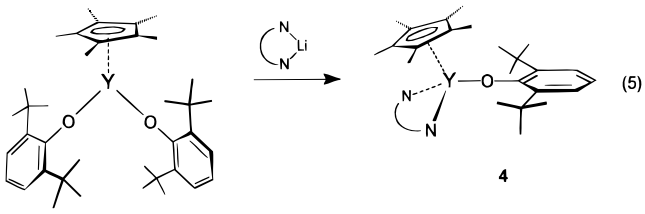


2 4 (4)

ligands. Compound **4** is extremely soluble in hexane. Evaporation of the solvent leaves a colorless, sticky oil, which did not solidify on standing at room temperature. Attempts to purify **4** by sublimation or vacuum distillation failed due to thermal decomposition. Compound **4** can also be prepared directly by treatment of Cp*Y[OAr]$_2$ with [PhC(NSiMe$_3$)$_2$]Li·OEt$_2$ in toluene (eq 5).



4 (5)

Again, purification is hindered due to the extremely high solubility of **4**. Because (neutral) yttrium alkyl complexes are normally more soluble than their aryloxide congeners, no attempts to alkylate **4** were undertaken.

Conclusions

This study shows that mixed-ligand compounds Cp*[PhC(NSiMe$_3$)$_2$]YX are accessible through stepwise ligand introduction, starting from YCl$_3$·3.5THF , although the order of introduction of ancillary ligands appears to be crucial. The reaction of Cp*Y[OAr]$_2$ (OAr = 2,6-OC$_6$H$_3$(CMe$_3$)$_2$) with the lithium benzamidinate salt [PhC(NSiMe$_3$)$_2$]Li·OEt$_2$ offers an alternative strategy for the preparation of mixed-ligand yttrium complexes such as Cp*[PhC(NSiMe$_3$)$_2$]YOAr. The chloride {Cp*[PhC(NSiMe$_3$)$_2$]YCl}$_2$ (**1**) is sufficiently inert with respect to redistribution of the various ligands. It also resists reaction with Lewis bases such as THF. Substitution of the chloride ligands in **1** is difficult: even powerful alkylation reagents such as MCH(SiMe$_3$)$_2$ (M = Li, K) do not seem to react with **1**. The kinetic stability of this dimeric chloro derivative considerably hampers the development of this chemistry by chloride metathesis of **1**. So far, only the methyl complex, Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-Me)$_2$Li·TMEDA (**2**), has been shown to be accessible. Nevertheless, compound **2** provides a useful a useful starting material for further reactivity studies, since the methyl substituents are susceptible to controlled protolysis by HC≡CR and H−OR under mild conditions.

Experimental Section

General Comments. All compounds are extremely oxygen- and moisture-sensitive. Manipulations were therefore carried out under nitrogen using glovebox (Braun MB-200) and Schlenk-line techniques. Solvents were distilled from Na (toluene), K (THF), or Na/K alloy (pentane, hexane, benzene, benzene-d_6, THF-d_8) and stored under nitrogen. YCl$_3$·3.5THF was prepared by continuous extraction of anhydrous YCl$_3$[12] with THF. Cp*Y[OAr]$_2$[5] and [PhC(NSiMe$_3$)$_2$]Li·OEt$_2$[13] were prepared according to literature procedures. NMR spectra were recorded on a Varian VXR 300 (^{1}H NMR at 300 MHz, ^{13}C NMR at 75.4 MHz) spectrometer at 30 °C. ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances. IR spectra were recorded on a Mattson-4020 Galaxy FT-IR spectrophotometer.

Preparation of {Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-Cl)}$_2$·2(toluene) (1). YCl$_3$·3.5THF (1.8 g, 40.2 mmol) was added to a suspension of Cp*K (6.2 g, 35.5 mmol) in THF (250 mL) at room temperature. The reaction mixture was stirred overnight, after which [PhC(NSiMe$_3$)$_2$]Li·OEt$_2$ (13.5 g, 39.2 mmol) was added. After the solution was stirred for an additional 1 h, the solvent was removed *in vacuo* and the residue extracted with hot toluene (200 mL). Concentration and cooling to −30 °C yielded **1** (4.0 g, 6.5 mmol, 18%) as colorless crystals. Concentration and cooling to −30 °C of the mother liquor yielded another crop of **1** (4.2 g, 6.8 mmol, 19%) as a white microcrystalline material. The ^{1}H and ^{13}C NMR spectra of **1** showed the presence of toluene, apparently in the crystal lattice. IR (KBr/Nujol, cm^{-1}): 2953 (vs), 2924 (vs), 2855 (vs), 1460 (s), 1398 (s), 1377 (s), 1258 (m), 1246 (m), 1005 (m), 995 (m), 837 (s), 781 (w), 760 (m), 733 (w), 712 (w), 704 (w), 490 (w). ^{1}H NMR (benzene-d_6, δ): 7.10 (m, 10H, Ar), 2.28 (s, 15 H, C$_5$(CH_3)$_5$), 2.11 (s, 3H, PhCH_3), 0.10 (s, 18H, PhC(NSi(CH_3)$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, δ): 184.1 (s, Ph*C*(NSiMe$_3$)$_2$), 141.4 (s, Ar), 129.1 (s, Ar), 128.3 (s, Ar), 126.5 (s, Ar), 125.5 (s, Ar), 120.2 (s, *C*$_5$Me$_5$), 21.2 (s, PhCH_3), 12.0 (s, C$_5$(CH_3)$_5$), 3.1 (s, PhC(NSi(CH_3)$_3$)$_2$). The product slowly lost toluene from the crystal lattice. To obtain a satisfactory elemental analysis, it was gently warmed (50 °C) *in vacuo* to remove all the toluene. Anal. Calcd (found) for (C$_{23}$H$_{38}$ClN$_2$Si$_2$Y)$_2$: C, 52.81 (52.34); H, 7.32 (7.26); Y, 17.00 (16.71).

Preparation of Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-Me)$_2$Li·TMEDA (2). An ethereal solution (50 mL) of **1** (1.6 g, 2.6 mmol) and TMEDA (0.8 mL, 5.2 mmol) was cooled to −80 °C and treated with MeLi (3.8 mL, 5.2 mmol). During warming to room temperature, salt precipitated. After the mixture was stirred for an additional 1 h, the volatiles were removed *in vacuo* and the residue was extracted with ether (40 mL). Cooling to −30 °C yielded **2** (1.1 g, 1.7 mmol, 66%) as large cube-shaped crystals. IR (KBr/Nujol, cm^{-1}): 2949 (vs), 2918 (vs), 2724 (sh), 1460 (vs), 1377 (s), 1354 (s), 1312 (w), 1287 (w), 1242 (m), 1159 (w), 1125 (w), 1063 (w), 1034 (w), 1020 (w), 1003 (m), 990 (m), 949 (w), 918 (w), 835 (s), 785 (m), 756 (s), 735 (s), 725 (s), 704 (m), 679 (w), 486 (w), 438 (w). ^{1}H NMR (benzene-d_6, δ): 7.10 (m, 5H, Ar), 2.42 (s, 15H, C$_5$(CH_3)$_5$), 1.94 (s, 12H, TMEDA-CH_3), 1.62 (s, 4H, TMEDA-CH_2), 0.11 (s, 18H, PhC(NSi(CH_3)$_3$)$_2$), −0.91 (br-s, 6H, μ-CH_3). ^{13}C NMR (benzene-d_6, δ): 183.0 (s, Ph*C*(NSiMe$_3$)$_2$), 143.4 (s, Ar), 128.2 (d, Ar, $^1J_{C-H}$ = 158 Hz), 127.4 (d, Ar, $^1J_{C-H}$ = 160 Hz), 126.1 (d, Ar, $^1J_{C-H}$ = 165 Hz), 115.7 (s, *C*$_5$Me$_5$), 56.4 (t, TMEDA-*C*H$_2$, $^1J_{C-H}$ = 130 Hz), 46.1 (q, TMEDA-*C*H$_3$, $^1J_{C-H}$ = 135 Hz), 13.5 (br-s, μ-*C*H$_3$), 12.1 (q, C$_5$(*C*H$_3$)$_5$, $^1J_{C-H}$ = 125 Hz), 3.7 (q, PhC(NSi(*C*H$_3$)$_3$)$_2$, $^1J_{C-H}$ = 118

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Hz). Anal. Calcd (found) for $C_{31}H_{60}LiN_4Si_2Y$: C, 58.10 (58.14); H, 9.44 (9.36); Y, 13.87 (13.82).

NMR Tube Reaction of 2 with HC≡CCMe$_3$. An NMR tube charged with **2** (10 mg, 0.016 mmol) in benzene-d_6 (1 mL) was treated with 3,3-dimethyl-but-1-yne (5 μL, 0.04 mmol). Following the reaction by ^{1}H NMR spectroscopy showed the gradual decrease of resonances of **2** and increase of resonances which can be attributed to the intermediate Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-Me)(μ-C≡CCMe$_3$)Li·TMEDA (**3a**) and the final product Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-C≡CCMe$_3$)$_2$Li·TMEDA (**3**). After several hours at room temperature, the ^{1}H NMR spectrum showed only resonances of **3** and unreacted HC≡CCMe$_3$. Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-Me)(μ-C≡CCMe$_3$)-Li·TMEDA (**3a**): ^{1}H NMR (benzene-d_6, δ) 7.08 (m, 5H, Ar), 2.48 (s, 15H, C$_5$(CH_3)$_5$), 2.06 (s, 12H, TMEDA-CH_3), 1.84 (d, 2H, TMEDA-CH_2, $^2J_{H-H}$ = 11 Hz), 1.62 (d, 2H, TMEDA-CH_2, $^2J_{H-H}$ = 11 Hz), 1.28 (s, 9H, C≡CC(CH_3)$_3$), 0.18 (s, 9H, PhC(NSi(CH_3)$_3$)$_2$), 0.10 (s, 9H, PhC(NSi(CH_3)$_3$)$_2$), −0.93 (br s, 3H, CH_3).

Preparation of Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-C≡CCMe$_3$)$_2$Li·TMEDA (3). A solution of **2** (1.4 g, 2.2 mmol) in ether (40 mL) was treated with 0.6 mL (4.8 mmol) of 3,3-dimethyl-but-1-yne at room temperature. After 16 h, the volatiles were removed *in vacuo* and the residue was dissolved in ether (30 mL). Concentration and cooling to −30 °C gave **3** (1.1 g, 1.4 mmol, 71%) as colorless crystals. IR (KBr/Nujol, cm^{-1}): 2955 (vs), 2922 (vs), 2359 (w), 2029 (w), 1460 (s), 1400 (m), 1377 (s), 1360 (m), 1310 (w), 1290 (m), 1238 (s), 1200 (w), 1159 (w), 1003 (m), 991 (m), 991 (m), 951 (w), 839 (s), 783 (w), 758 (m), 731 (m), 700 (w), 482 (w), 426 (w). ^{1}H NMR (benzene-d_6, δ): 7.07 (m, 5H, Ar), 2.53 (s, 15H, C$_5$(CH_3)$_5$), 2.22 (s, 12H, TMEDA-CH_3), 1.96 (s, 4H, TMEDA-CH_2), 1.29 (s, 18H, C≡CC(CH_3)$_3$), 0.16 (s, 18H, PhC(NSi(CH_3)$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ): 182.1 (s, Ph*C*(NSiMe$_3$)$_2$), 143.3 (s, Ar), 128.2 (d, Ar, $^1J_{C-H}$ = 159 Hz), 127.7 (d, Ar, $^1J_{C-H}$ = 163 Hz), 127.4 (d, Ar, $^1J_{C-H}$ = 160 Hz), 120.5 (d, Y−*C*(≡CCMe$_3$), $^1J_{Y-C}$ = 8 Hz), 117.6 (s, *C*$_5$Me$_5$), 57.0 (t, TMEDA-*C*H$_2$, $^1J_{C-H}$ = 133 Hz), 47.6 (q, TMEDA-*C*H$_3$, $^1J_{C-H}$ = 134 Hz), 32.5 (q, C≡CC(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 28.5 (s, C≡C*C*Me$_3$), 13.0 (q, C$_5$(*C*H$_3$)$_5$, $^1J_{C-H}$ = 125 Hz), 4.0 (q, PhC(NSi(*C*H$_3$)$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd (found) for $C_{41}H_{72}LiN_4Si_2Y$: C, 63.70 (63.80); H, 9.39 (9.46); Y, 11.50 (11.55).

Preparation of Cp*[PhC(NSiMe$_3$)$_2$]YOAr (OAr = 2,6-OC$_6$H$_3$(CMe$_3$)$_2$) (4). Method a. A solution of **2** (0.7 g, 1.1 mmol) in ether (40 mL) was treated with 2,6-di-*tert*-butyl-phenol (0.45 g, 2.2 mmol). The reaction mixture was stirred for 1 h, after which the solvent was removed *in vacuo*. The residue was extracted with pentane (40 mL). Evaporation of the solvent yielded **4** (0.4 g, 0.6 mmol, 52%) as a colorless oil.

Method b. A hexane (40 mL) solution of Cp*Y(OAr)$_2$ (1.7 g, 2.7 mmol) was treated with [PhC(NSiMe$_3$)$_2$]Li·OEt$_2$ (0.9 g, 2.6 mmol). The reaction mixture was heated to reflux, upon which salt precipitated. The mixture was then stirred overnight at room temperature. After filtration, the solvent was removed *in vacuo* leaving **4** as a colorless oil. Isolated yield: 0.6 g (0.9 mmol, 32%). ^{1}H NMR (benzene-d_6, δ): 7.25 (m, 2H, Ar), 7.0 (m, 6H, Ar), 2.12 (s, 15H, C$_5$(CH_3)$_5$), 1.60 (s, 18H, C(CH_3)$_3$), 0.01 (s, 18H, PhC(NSi(CH_3)$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, δ): 136.9 (s, Ar), 132.2 (s, Ar), 128.6 (s, Ar), 126.4 (s, Ar), 125.2 (s, Ar), 125.0 (s, Ar), 117.2 (s, *C*$_5$Me$_5$), 35.0 (s, *C*Me$_3$), 32.1 (s, C(*C*H$_3$)$_3$), 11.7 (s, C$_5$(*C*H$_3$)$_5$), 4.5 (s, PhC(NSi(*C*H$_3$)$_3$)$_2$).

X-ray Crystallographic Analysis of Cp*[PhC(NSiMe$_3$)$_2$]Y(μ-Me)$_2$Li·TMEDA (2). A suitable colorless polyfacial crystal was glued on top of a glass fiber in a drybox and transferred into the cold nitrogen stream of the low-temperature unit[14] mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a MicroVAX-2000 computer. Unit cell parameters and orientation matrix were determined from a least-squares treatment of the SET4 setting angles[15] of 22 reflections in the range $15.23^o < \theta < 20.63^o$. The unit cell was identified as triclinic, space group $P\bar{1}$. Reduced cell calculations did not indicate any higher metric lattice symmetry,[16] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[17] The intensity of three standard reference reflections, monitored every 3 h of X-ray exposure time, showed no significant fluctuations during data collection. A 360° Ψ-scan for a reflection close to axial ($\bar{2}\bar{2}2$) showed a variation in intensity of less than 13% about the mean value. Intensity data were corrected for Lorentz and polarization effects and scale variation but not for absorption. Standard deviation $\sigma(I)$ in the intensities were increased according to an analysis of the excess variance of the reference reflection: Variance was calculated on the basis of counting statistics and the term (P^2I^2) where P (=0.023) is the instability constant[18] as derived from the excess variance in the reference reflections. Equivalent reflections were averaged and stated observed if satisfying the $I \geq 2.5\sigma(I)$ criterion of observability. The structure was solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[19] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms refined with block-diagonal least-squares procedures (CRYLSQ)[20] minimizing the function $Q = \sum_{\mathbf{h}}[w(|F_o| - k|F_c|)^2]$. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms which coordinates were included in the refinement. Final refinement on F_o by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the nonhydrogen atoms and isotropic thermal displacement parameters for the hydrogen atoms converged at R_F = 0.040 (wR = 0.045). Unit weights were used throughout the refinement. A final difference Fourier map did not show any significant residual features. Crystal data and experimental details of the structure determination are compiled in Table 2. The final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for the non-hydrogen atoms are given

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Table 2. Details of the X-ray Structure Determination of Cp*[$C_6H_5C(NSiMe_3)_2$]Y(μ-Me)$_2$Li·TMEDA (2)

formula	$C_{31}H_{60}N_4Si_2Y$
M_r	640.86
cryst system	triclinic
space group	$P\bar{1}$
a, Å	10.415(1)
b, Å	12.010(1)
c, Å	15.937(1)
α, deg	88.150(6)
β, deg	86.041(9)
γ, deg	69.01(1)
V, Å^3	1856.7(3)
D_{calc}, g·mol^{-3}	1.146
Z	2
F(000)	688
μ(Mo, $K\bar{\alpha}$), cm^{-1}	16.65
cryst size, mm	0.25 × 0.32 × 0.38
wavelength (Mo $K\bar{\alpha}$), Å	0.710 73 (graphite monochromator)
T, K	130
θ range: min, max, deg	1.28, 27.5
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.80 + 0.34 \tan\theta$
data set	h, −13 → 13; k, −15 → 15; l, 0 → 20
tot. data	8802
unique data	8494
obsd data ($I \geq 2.5\sigma(I)$)	6738
no. of refined params	592
final agreement factors	
$R_F = \sum(\|\|F_o\| - \|F_c\|\|)/\sum\|F_o\|$	0.040
$wR = [\sum(w(\|F_o\| - \|F_c\|)^2)/\sum w\|F_o\|^2]^{1/2}$	0.045
weighting scheme	1
$S = [\sum w(\|F_o\| - \|F_c\|)^2/(m - n)]^{1/2}$ [a]	1.372(12)
resid electron density in final diff Fourier map, e/Å^3	−1.14, 1.12
max(shift/σ) final cycle	0.1934
av(shift/σ) final cycle	0.6749 × 10^{-2}

[a] m = no. of observations; n = no. of variables

in Table 3. Scattering factors were taken from Cromer and Mann.[21] Anomalous dispersion factors taken from Cromer and Liberman.[22] All calculations were carried out on the HP9000/735 computer at the University of Groningen with the program packages Xtal,[23] PLATON,[24] and ORTEP.[25]

Table 3. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Displacement Parameters for Non-hydrogen Atoms for Cp*[$C_6H_5C(NSiMe_3)_2$]Y(μ-Me)$_2$Li·TMEDA (2).

atom	x	y	z	U_{eq} (Å^2)[a]
Y(1)	0.19948(3)	0.17528(2)	0.24427(2)	0.0155(1)
Si(1)	0.26814(10)	0.25689(8)	0.46732(5)	0.0249(3)
Si(2)	0.24517(10)	0.46401(8)	0.15249(6)	0.0254(3)
N(1)	0.2250(3)	0.2850(2)	0.36306(16)	0.0216(8)
N(2)	0.2195(3)	0.3693(2)	0.23115(16)	0.0204(7)
N(3)	0.5784(3)	−0.2070(2)	0.16489(18)	0.0292(8)
N(4)	0.6636(3)	−0.0011(3)	0.18847(19)	0.0306(9)
C(1)	−0.0556(3)	0.1912(3)	0.2962(2)	0.0252(9)
C(2)	−0.0711(3)	0.2581(3)	0.2202(2)	0.0235(9)
C(3)	−0.0111(3)	0.1781(3)	0.15357(19)	0.0208(8)
C(4)	0.0441(3)	0.0613(3)	0.1884(2)	0.0219(8)
C(5)	0.0156(3)	0.0696(3)	0.2760(2)	0.0256(9)
C(6)	−0.1195(4)	0.2395(5)	0.3810(3)	0.0438(14)
C(7)	−0.1507(4)	0.3903(3)	0.2132(3)	0.0398(13)
C(8)	−0.0198(4)	0.2088(4)	0.0616(2)	0.0329(11)
C(9)	0.1164(4)	−0.0509(3)	0.1387(3)	0.0358(13)
C(10)	0.0426(5)	−0.0353(4)	0.3362(3)	0.0427(14)
C(11)	0.2435(3)	0.3693(3)	0.31198(19)	0.0188(8)
C(12)	0.2921(3)	0.4618(3)	0.34550(18)	0.0210(8)
C(13)	0.4325(4)	0.4392(3)	0.3489(2)	0.0282(10)
C(14)	0.4786(5)	0.5222(4)	0.3813(2)	0.0414(16)
C(15)	0.3854(6)	0.6292(4)	0.4108(2)	0.0478(16)
C(16)	0.2453(5)	0.6537(3)	0.4074(2)	0.0425(13)
C(17)	0.1981(4)	0.5702(3)	0.3753(2)	0.0321(10)
C(18)	0.2187(5)	0.3910(3)	0.5357(2)	0.0337(11)
C(19)	0.4566(4)	0.1718(3)	0.4732(2)	0.0323(11)
C(20)	0.1736(5)	0.1628(4)	0.5162(3)	0.0383(13)
C(21)	0.4336(5)	0.4267(6)	0.1228(3)	0.0511(18)
C(22)	0.1708(8)	0.6261(4)	0.1759(3)	0.065(2)
C(23)	0.1619(4)	0.4414(3)	0.0590(2)	0.0317(11)
C(24)	0.3553(3)	−0.0066(3)	0.3129(2)	0.0241(9)
C(25)	0.3422(3)	0.1164(3)	0.1097(2)	0.0237(9)
C(26)	0.5298(5)	−0.2511(4)	0.0937(3)	0.0395(12)
C(27)	0.5747(5)	−0.2830(3)	0.2389(3)	0.0455(13)
C(28)	0.7209(4)	−0.2097(4)	0.1451(3)	0.0387(11)
C(29)	0.7557(4)	−0.1271(4)	0.2009(3)	0.0404(11)
C(30)	0.7034(4)	0.0460(4)	0.1084(3)	0.0409(11)
C(31)	0.6722(4)	0.0741(4)	0.2567(3)	0.0435(16)
Li(1)	0.4711(6)	−0.0221(5)	0.1922(3)	0.0267(17)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

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Supporting Information Available: Tables of anisotropic thermal displacement parameters, hydrogen coordinates and thermal parameters, bond lengths, bond angles, and torsion angles (11 pages). Ordering information is given on any current masthead page.

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