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Synthesis and characterization of yttrium complexes bearing a bulky arylamido ancillary ligand

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Abstract

Reaction of anhydrous YCl_3 with 1 equiv. of arylamido lithium 2,6-^{i}$Pr_2C_6H_3NSi^iPr_3Li$ in THF gave an anionic mono-arylamido-ligated yttrium dichloride complex $\{[2,6\text{-}^iPr_2C_6H_3NSi^iPr_3]YCl_2(THF)\}_2[LiCl(THF)_2]$ (**1**). Alkylation of **1** with 4 equiv. of $LiCH_2SiMe_3$ afforded an anionic arylamido-ligated yttrium tris(alkyl) complex $[2,6\text{-}^iPr_2C_6H_3NSi^iPr_3]Y(CH_2SiMe_3)_3Li(THF)_2$ (**2**). Both complexes were characterized by NMR, elementary analysis, and X-ray structural determination.

Keywords: Arylamido yttrium complex; Synthesis; Crystal structure

1. Introduction

Organo rare earth metallocene complexes have been scrutinized intensively during the past two decades because these species can act as catalysts for organic transformation reactions and olefin polymerizations [1]. In an attempt to extend the possibility for modifying and controlling the reactivity of rare earth metal complexes, currently, alternative ligand setting other than cyclopentadienyl anions are also experiencing considerable attention to create different steric and electronic environments at the reactive site of rare earth metals [2]. Among those non-cyclopentadienyl spectator ligands, arylamide is one of the ideal candidates, for their steric and electronic environment can be tuned easily by the variation of substituents on both the phenyl ring and nitrogen atom. Although such ligands are able to create well-defined reaction metal centers in organometallic chemistry [3,4], we are aware the examples of mono-arylamido-ligated rare earth metal complexes remain quite limited [5]. Recently, we reported that arylamido anion $[2,6\text{-}^iPr_2C_6H_3NSiMe_3]^-$ can serve as monodentate ancillary ligand to stabilize not only rare earth metal bis(alkyl) complexes, but also active cationic rare earth mono(alkyl) complexes [5]. As part of this extensive study, we report here the synthesis, crystal structure of the yttrium complexes bearing a much bulkier arylamido ligand, $\{[2,6\text{-}^iPr_2C_6H_3NSi^iPr_3]YCl_2(THF)\}_2[LiCl(THF)_2]$ (**1**) and $[2,6\text{-}^iPr_2C_6H_3NSi^iPr_3]Y(CH_2SiMe_3)_3Li(THF)_2$ (**2**).

2. Results and discussion

2.1. Synthesis and characterization of $\{[2,6\text{-}^iPr_2C_6H_3NSi^iPr_3]YCl_2(THF)\}_2[LiCl(THF)_2]$ (1) and $[2,6\text{-}^iPr_2C_6H_3NSi^iPr_3]Y(CH_2SiMe_3)_2Li(CH_2SiMe_3)(THF)_2$ (2)

Previously, we reported that arylamido anion $[2,6\text{-}^iPr_2C_6H_3NSiMe_3]^-$ could serve as monodentate ligand to support rare earth metal bis(alkyl) complexes $[2,6\text{-}^iPr_2C_6H_3NSiMe_3]Ln(CH_2SiMe_3)_2(THF)$ (Ln = Sc, Y, Ho–Lu), which could be obtained from the alkane elimination reaction of the rare earth metal tris(alkyl) complexes $Ln(CH_2SiMe_3)_3(THF)_2$ with 1 equiv. amount of $2,6\text{-}^iPr_2C_6H_3NHSiMe_3$ in a straightforward manner [5]. Unexpectedly, when a sterically much bulkier arylamine

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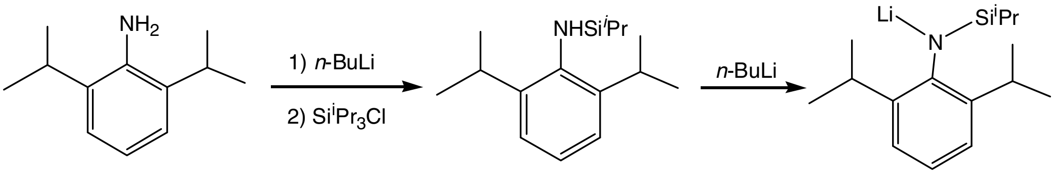


Scheme 1.

2,6-^{i}Pr$_2$C$_6$H$_3$NHSi^{i}Pr$_3$ was employed in the same synthetic strategy to prepare mono-arylamido-ligated rare earth metal bis(alkyl) complexes, no aimed product was observed from NMR monitoring experiments. Therefore, we turned our attention to prepare rare earth metal alkyl complexes by means of salt metathesis reaction.

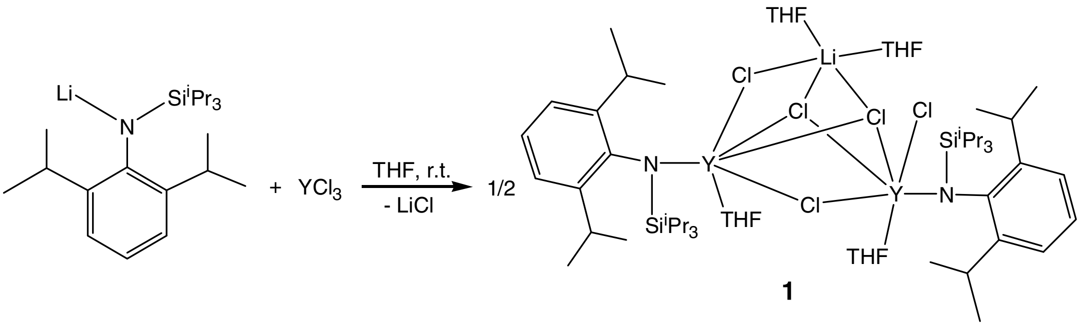
The bulky arylamine 2,6-^{i}Pr$_2$C$_6$H$_3$NHSi^{i}Pr$_3$ was synthesized by silylation of 2,6-^{i}Pr$_2$C$_6$H$_3$NH$_2$ with Si^{i}Pr$_3$Cl. Deprotonation of 2,6-^{i}Pr$_2$C$_6$H$_3$NH$_2$ with 1 equiv. of *n*-BuLi in THF at room temperature, followed by reaction of Si^{i}Pr$_3$Cl for three days gave 2,6-^{i}Pr$_2$C$_6$H$_3$NHSi^{i}Pr$_3$ as colorless oil in 59% isolated yield (Scheme 1). Lithiation of 2,6-^{i}Pr$_2$C$_6$H$_3$NHSi^{i}Pr$_3$ with *n*-BuLi at 1:1 molar ratio in THF produced the lithium salt 2,6-^{i}Pr$_2$C$_6$H$_3$NSi^{i}Pr$_3$Li in nearly quantitative yield, therefore, 2,6-^{i}Pr$_2$C$_6$H$_3$N-Si^{i}Pr$_3$Li could be used formed *in situ*.

When THF slurry of anhydrous YCl$_3$ reacted with one equiv. of 2,6-^{i}Pr$_2$C$_6$H$_3$NSi^{i}Pr$_3$Li at room temperature, after workup, an anionic mono-arylamido-ligated yttrium dichloride complex {[2,6-^{i}Pr$_2$C$_6$H$_3$NSi^{i}Pr$_3$]YCl$_2$ (THF)}$_2$-[LiCl(THF)$_2$] (**1**) was obtained in 90% isolated yield, as illustrated in Scheme 2. Alkylation of **1** with 4 equiv. of LiCH$_2$SiMe$_3$ in THF at room temperature could lead to a mono(arylamido) yttrium tris(alkyl) complex [2,6-^{i}Pr$_2$C$_6$H$_3$NSi^{i}Pr$_3$]Y(CH$_2$Si Me$_3$)$_3$Li(THF)$_2$ (**2**) in 56% isolated yield (Scheme 3).

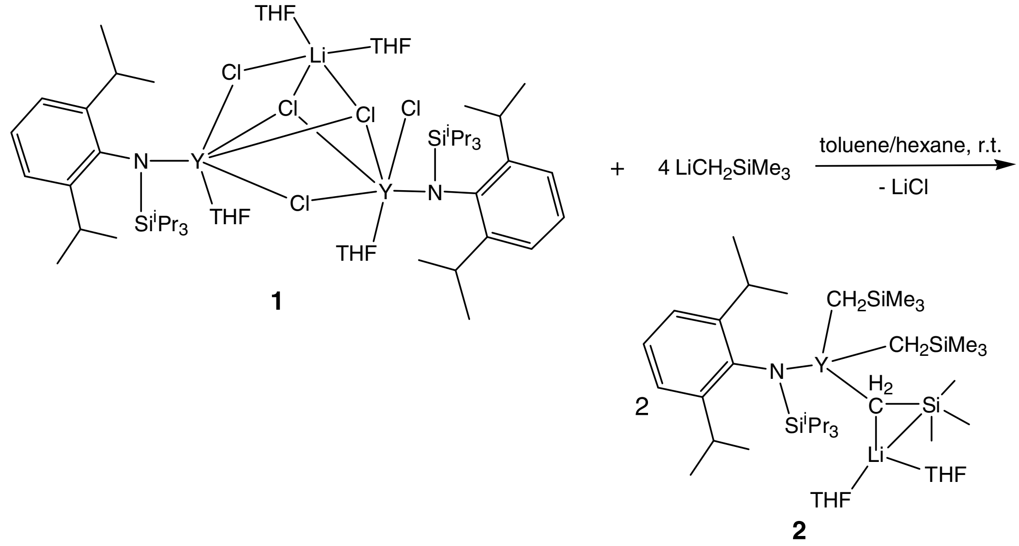
The formulae of **1** and **2** were confirmed by NMR, elementary analysis, and X-ray structural determination. Both complexes are colorless in the solid state, extremely sensitive to air and moisture, and thermally stable at room temperature. They have perfect solubility in THF, toluene, and even in hexane.

The diamagnetic yttrium complexes of **1** and **2** showed well-resolved NMR spectra. Ligand redistribution was not observed in solution as shown by NMR spectra. ^{1}H NMR and ^{13}C NMR spectra of **1** in THF-d_8 showed one set of signal for Si[(CH$_3$)$_2$CH]$_3$, two sets of signals for the isopropyl groups on the phenyl ring, suggesting that rotation of phenyl ring around the N–C$_{ipso}$ bond is highly restricted. Similarly, NMR spectra of **2** in C$_6$D$_6$ indicated the rotation of phenyl ring of the arylamido ligand is also strictly prohibited. In **2**, although there were two terminal trimethylsilylmethyl groups and one bridged trimethylsilylmethyl group, only one set of resonance for the methylene protons of trimethylsilylmethyl groups was observed at −0.67 in the ^{1}H NMR spectra. No Y–H coupling (J_{Y-H}) was observed as that in an analogous complex of [2,6-^{i}Pr$_2$C$_6$H$_3$NSiMe$_3$]Y(CH$_2$SiMe$_3$)$_2$(THF) [5]. In ^{13}C NMR spectrum of **2**, the methylene carbons bonded to yttrium were reported as a doublet with a coupling constant of $J_{Y-C} = 32$ Hz, which is much smaller than that observed in [2,6-^{i}Pr$_2$C$_6$H$_3$NSiMe$_3$]Y(CH$_2$SiMe$_3$)$_2$(THF) (43.5 Hz) [5].

Structures of **1** and **2** were determined by a single-crystal X-ray diffraction study. Crystals of **1** suitable for X-ray diffraction were grown from hexane at −30 °C. An OTEPT diagram depicting the molecular structure of **1** is shown in Fig. 1. Detailed crystal and structural refinement data are listed in Table 1, selected bond lengths and bond angles are given in Table 2. As shown in Fig. 1, the structure of **1** in the crystal is consistent with the above-mentioned spectroscopic data in solution. Complex **1** consists of two moieties, i.e., one is dinuclear part containing two yttrium centers bridged by three μ-chlorine atoms (Cl(1), Cl(2), and Cl(3)), the other is Li(THF)$_2$ cation, they are bonded together through three μ-chlorine atoms (Cl(1), Cl(2), and Cl(4)). In this case, Cl(1) and Cl(2) are μ$_3$-chlorine atoms, Cl(3) and Cl(4) are μ$_2$-chlorine atoms. Each yttrium



Scheme 2.



Scheme 3.

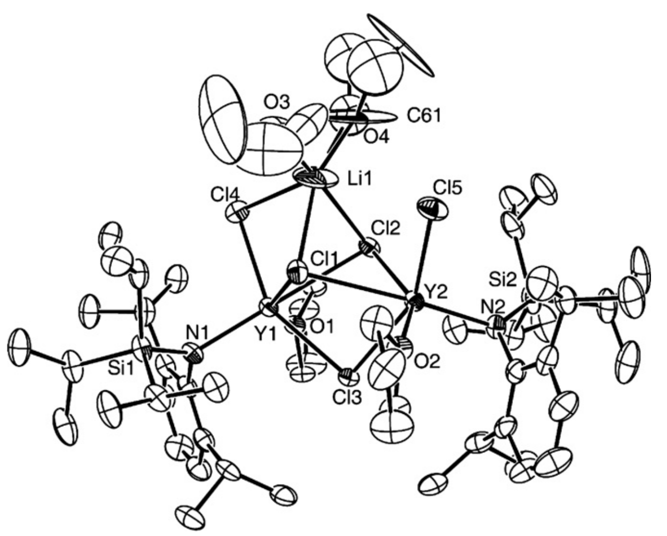


Fig. 1. ORTEP structure of **1** (thermal ellipsoids at the 30% level, hydrogen atoms are omitted for clarity).

center is six-coordinated by one arylamido ligand, one THF molecule, four chlorine atoms, forming a distorted octahedral. Although both yttrium centers in **1** share Cl(1), Cl(2), and Cl(3) atoms, the significant coordination difference between Y(1) and Y(2) is that Y(1) contains a μ_2-chlorine atom (Cl(4)) connecting Li cation, while Y(2) possesses a terminal chlorine atom (Cl(5)). The bond lengths of Y(1)–N(1) and Y(2)–N(2) in **1** are nearly equal (2.229(7) and 2.228(7) Å, respectively). These two Y–N bond length values are identical to those in [2,2′-bis((*tert*-butyldimethylsily)amido)-6,6′-dimethylbiphenyl]YCl(THF)$_2$ (av. 2.25 Å) [6], $[2,6\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{NSiMe}_3]_2\mathrm{NdCl(THF)}$ (2.276 (2) and 2.264(2) Å) [4h], $[2,6\text{-}^i\mathrm{Me}_2\mathrm{C}_6\mathrm{H}_3\mathrm{NSiMe}_3]_2\mathrm{Nd}(\mu\text{-Cl})_2\mathrm{Li}$- $(\mathrm{THF})_2$ (2.318 (3) and 2.282(3) Å) [4h], $[\{\mu_2\text{-}p\text{-}(\mathrm{Me}_3\mathrm{SiN})_2\mathrm{C}_6\mathrm{H}_4\}\mathrm{YbCl(THF)}_2]_2$ (2.174(6) and 2.173(6) Å) [4b], and $[\mathrm{K(DME)}_2(\mathrm{THF})_3][\mathrm{Y}_2(\mu\text{-NHC}_6\mathrm{H}_3\mathrm{Me}_2\text{-}2,6)_2(\mu\text{-Cl})(\mathrm{NHC}_6\mathrm{H}_3\mathrm{Me}_2\text{-}2,6)_4$- $(\mathrm{THF})_2]$ (2.26(2)–2.30(2) Å) [4g], when the differences in radii and coordination number are considered [7]. The bond lengths of Y–Cl lie in the range 2.559–2.984 Å. Although the bond modes of Y(1)–Cl(4) and Y(2)–Cl(5) are bridged and terminal, respectively, the bond lengths are almost matched (2.575(3) for Y(1)–Cl(4) and 2.559(3) Å for Y(2)–Cl(5)).

Crystals of **2** suitable for X-ray diffraction were grown from toluene at −30 °C. An OTEPT diagram depicting the molecular structure of **2** is shown in Fig. 2. Detailed crystal and structural refinement data are listed in Table 1, selected bond lengths and bond angles are given in Table 3. As shown in Fig. 2, **2** is a mono-arylamido-ligated yttrium tris(alkyl) complex, which is incorporated by

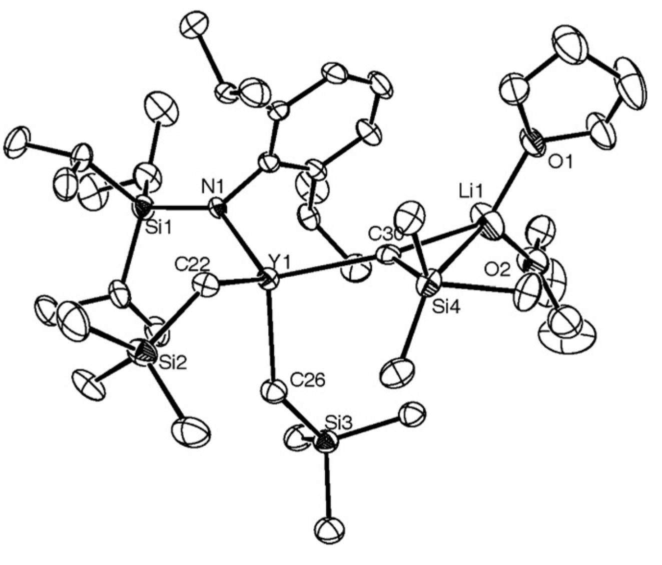


Fig. 2. ORTEP structure of **2** (thermal ellipsoids at the 30% level, hydrogen atoms are omitted for clarity).

Table 1
Summary of crystallographic data of complex **1** and **2**

	1	**2**
Formula	$C_{29}H_{54}Cl_{2.5}Li_{0.5}NO_2SiY$	$C_{41}H_{87}LiNO_2Si_4Y$
Molecular weight	657.83	834.33
Crystal size (mm^3)	0.45 × 0.30 × 0.30	0.30 × 0.20 × 0.15
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
a (Å)	15.215(3)	19.129(5)
b (Å)	15.475(3)	14.501(4)
c (Å)	18.441(4)	18.821(5)
α (°)	103.082(3)	90
β (°)	95.757(4)	95.597(4)
γ (°)	112.670(3)	90
V (Å^3)	3816.5(14)	5196(2)
Z	4	4
ρ (g cm^{-3})	1.145	1.067
μ (Mo Kα) (mm^{-1})	1.756	1.243
T (K)	173(1)	173(1)
θ range (°)	1.48–25.09	1.77–25.09
Number of reflections collected	18523	24620
Number of reflections with $I(>2\sigma(I))$	13195 [$R_{int} = 0.0465$]	9168 [$R_{int} = 0.1039$]
Number of parameters	702	493
R_1 ($I > 2\sigma(I)$)	0.0682	0.0507
wR_2 ($I > 2\sigma(I)$)	0.2098	0.0485
Goodness-of-fit	1.011	0.742
Maximum/minimum residual density (e Å^{-3})	1.459/−0.722	0.614/−0.356

Table 2
Bond lengths (Å) and angles (°) for complex **1**

Y(1)–N(1)	2.229(7)	Y(2)–Cl(5)	2.559(3)
Y(1)–O(1)	2.343(6)	Y(2)–Cl(2)	2.649(3)
Y(1)–Cl(4)	2.575(3)	Y(2)–Cl(3)	2.698(2)
Y(1)–Cl(1)	2.650(3)	Y(2)–Cl(1)	2.984(3)
Y(1)–Cl(3)	2.708(3)	Cl(1)–Li(1)	2.67(4)
Y(1)–Cl(2)	2.963(3)	Cl(2)–Li(1)	2.62(3)
Y(1)–Y(2)	3.9521(14)	Cl(4)–Li(1)	2.70(5)
Y(2)–N(2)	2.228(7)	O(4)–Li(1)	2.03(5)
Y(2)–O(2)	2.317(6)	O(3)–Li(1)	2.05(4)
N(1)–Y(1)–O(1)	106.5(2)	N(2)–Y(2)–Cl(3)	102.4(2)
N(1)–Y(1)–Cl(4)	104.3(2)	O(2)–Y(2)–Cl(3)	85.06(18)
O(1)–Y(1)–Cl(4)	95.56(16)	Cl(5)–Y(2)–Cl(3)	152.92(10)
N(1)–Y(1)–Cl(1)	104.33(19)	Cl(2)–Y(2)–Cl(3)	79.27(8)
O(1)–Y(1)–Cl(1)	147.21(16)	N(2)–Y(2)–Cl(1)	175.4(2)
Cl(4)–Y(1)–Cl(1)	87.43(9)	O(2)–Y(2)–Cl(1)	74.75(16)
N(1)–Y(1)–Cl(3)	104.9(2)	Cl(5)–Y(2)–Cl(1)	79.87(9)
O(1)–Y(1)–Cl(3)	82.92(16)	Cl(2)–Y(2)–Cl(1)	72.05(7)
Cl(4)–Y(1)–Cl(3)	149.95(9)	Cl(3)–Y(2)–Cl(1)	73.15(7)
Cl(1)–Y(1)–Cl(3)	78.60(8)	Y(2)–Cl(3)–Y(1)	93.94(7)
N(1)–Y(1)–Cl(2)	176.60(19)	Y(1)–Cl(1)–Li(1)	85.0(11)
O(1)–Y(1)–Cl(2)	76.57(15)	Y(1)–Cl(1)–Y(2)	88.87(7)
Cl(4)–Y(1)–Cl(2)	76.65(8)	Li(1)–Cl(1)–Y(2)	86.4(8)
Cl(1)–Y(1)–Cl(2)	72.38(7)	Li(1)–Cl(2)–Y(2)	94.8(13)
Cl(3)–Y(1)–Cl(2)	73.80(7)	Li(1)–Cl(2)–Y(1)	79.9(8)
N(2)–Y(2)–O(2)	106.3(2)	Y(2)–Cl(2)–Y(1)	89.34(7)
N(2)–Y(2)–Cl(5)	104.6(2)	O(4)–Li(1)–O(3)	98.9(15)
O(2)–Y(2)–Cl(5)	90.10(18)	Cl(2)–Li(1)–Cl(1)	77.9(8)
N(2)–Y(2)–Cl(2)	106.28(19)	Cl(4)–Li(1)–Cl(1)	84.6(10)
O(2)–Y(2)–Cl(2)	146.15(17)	Cl(2)–Li(1)–Y(1)	54.3(5)
Cl(5)–Y(2)–Cl(2)	90.48(9)	Cl(4)–Li(1)–Y(1)	45.6(5)

1 equiv. of $[Li(THF)_2]^+$. The yttrium center is four-coordinated by one arylamido ligand and three CH_2SiMe_3 groups, forming a distorted tetrahedral geometry. The yttrium moiety is connected with $Li(THF)_2$ cation by the methylene carbon of CH_2SiMe_3. The bond length of Y–N (2.259(3) Å) in **2** is identical to those in $\{[Me_2Si(NPh)_2]Yb(C_5H_5)_2\}\{Li(DME)_3\}$ (2.250(4) and 2.232(7) Å) [4a], $\{[Me_2Si(NPh)_2]Yb(MeC_5H_5)_2\}\{Li(DME)_3\}$ (2.242(4) and 2.254(4) Å) [4a], but is slightly longer than those in **1** (av. 2.228 Å), $[2,6\text{-}^iPr_2C_6H_3NSiMe_3]Y(CH_2SiMe_3)_2(THF)$ (2.190(2) Å) [5], $[2,6\text{-}^iPr_2C_6H_3NSiMe_3]_2YbCH_3(\mu\text{-}CH_3)Li(THF)_3$ (2.224 (6) and 2.227(6) Å) [4d]. The average bond length of $Y–CH_2SiMe_3$ (2.389 Å) (refers to Y(1)–C(22) and Y(1)–C(26)) is comparable to that in $[2,6\text{-}^iPr_2C_6H_3NSiMe_3]Y(CH_2SiMe_3)_2(THF)$ (2.367 Å) [5]. The bond length of Y(1)–C(30) is *ca.* 0.1 Å longer than those of Y(1)–C(22) and Y(1)–C(26), this contributes to that C(30) is a bridging carbon connecting the yttrium center and Li cation. The bond angle of Y(1)–C(30)–Li(1) is 149.4(3)°, which is approximately 30° smaller than that in $[2,6\text{-}^iPr_2C_6H_3NSiMe_3]_2YbCH_3(\mu\text{-}CH_3)Li(THF)_3$ (178.8(5)°) [4d].

Table 3
Selected bond lengths (Å) and angles (°) for complex **2**

Y(1)–N(1)	2.259(3)	Li(1)–O(1)	1.862(8)
Y(1)–C(26)	2.373(3)	Li(1)–O(2)	1.885(8)
Y(1)–C(22)	2.405(3)	Li(1)–C(30)	2.269(8)
Y(1)–C(30)	2.490(4)		
N(1)–Y(1)–C(26)	118.78(11)	C(22)–Y(1)–C(30)	107.39(14)
N(1)–Y(1)–C(22)	108.99(11)	O(1)–Li(1)–O(2)	106.9(4)
C(26)–Y(1)–C(22)	102.46(11)	O(1)–Li(1)–C(30)	125.9(4)
N(1)–Y(1)–C(30)	116.73(13)	O(2)–Li(1)–C(30)	126.9(4)
C(26)–Y(1)–C(30)	101.07(14)	Y(1)–C(30)–Li(1)	149.4(3)

3. Conclusion

In summary, we have synthesized an anionic yttrium dichloride bearing a bulky arylamido ligand, $\{[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NSi}^i\text{Pr}_3]\text{YCl}_2(\text{THF})\}_2[\text{LiCl}(\text{THF})_2]$ (**1**), which was obtained from the salt metathesis reaction of anhydrous YCl_3 with 1 equiv. amount of $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NSi}^i\text{Pr}_3\text{Li}$ in THF at room temperature. Further treatment of **1** with 4 equiv. of $\text{LiCH}_2\text{SiMe}_3$ at room temperature could lead to an anionic mono(arylamido) yttrium tris(alkyl) complex $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NSi}^i\text{Pr}_3]\text{Y}(\text{CH}_2\text{SiMe}_3)_3\text{Li}(\text{THF})_2$ (**2**).

4. Experimental

4.1. Materials and procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and a Mikrouna glovebox. Solvents (toluene, tetrahydrofuran, and hexane) were distilled from sodium/benzophenone ketyl, degassed by the freeze–pump-thaw method, and dried over fresh Na chips in the glovebox. $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NHSi}^i\text{Pr}_3$ was prepared by the reaction of $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NHLi}$ with $^i\text{Pr}_3\text{SiCl}$ in THF at room temperature. $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NHLi}$ was synthesized by the reaction of $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}_2$ with *n*-BuLi in THF according to the literature [4d,4h]. *n*-BuLi (1.6 M solution in hexane), $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}_2$ and $^i\text{Pr}_3\text{SiCl}$ were obtained from Acros, and used without purification. Anhydrous YCl_3 was purchased from STREM. $\text{LiCH}_2\text{SiMe}_3$ (1 M solution in pentane) was obtained from Aldrich, and used as powder after drying up the solvent under vacuum. C_6D_6 and THF-d_8 were obtained from ISOTEC, and were dried by Na chips in the glovebox.

Samples of yttrium complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova-400 spectrometer at 25 °C. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument, quoted data are the average of at least two independent determinations.

4.2. Synthesis of $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_4\text{NHSi}^i\text{Pr}_3$

To a 50 mL of THF solution of $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_4\text{NHLi}$ (68 mmol), which was prepared from the reaction of $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_4\text{NH}_2$ with 1 equiv. of *n*-BuLi in a mixture solution of THF and hexane, added a THF solution of $^i\text{Pr}_3\text{SiCl}$ (13.23 g, 68 mmol) at room temperature. The reaction mixture was stirred at room temperature for 3 days, and it changed from clear orange solution to cloudy slurry solution. After drying up the solvents in vacuum, the residue oil product was distilled under 190 °C/5 mmHg to give $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_4\text{NHSi}^i\text{Pr}_3$ as colorless oil (13.5 g, 59%). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.10 (d, 18 H, $\text{CH}(\text{C}H_3)_2$), 1.26 (d, 12 H, $\text{CH}(\text{C}H_3)_2$), 2.42 (b s, 1 H, N-*H*), 3.55 (m, 2 H, $\text{C}H(\text{CH}_3)_2$), 7.06–7.11 (3 H, C_6H_3). ^{13}C NMR (C_6D_6, 100 MHz): δ 13.97, 18.82, 23.74, 28.42, 123.30, 123.81, 140.82, 143.79. *Anal.* Calc. for $\text{C}_{21}\text{H}_{39}\text{NSi}$: C, 75.60; H, 11.78; N, 4.20. Found: C, 75.49; H, 11.71; N, 4.09%.

4.3. Synthesis of $\{[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NSi}^i\text{Pr}_3]\text{YCl}_2(\text{THF})\}_2\text{-}[\text{LiCl}(\text{THF})_2]$

To a 30 mL of THF slurry of YCl_3 (1.05 g, 5.38 mmol) was added $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NSi}^i\text{Pr}_3\text{Li}$ (5.38 mmol), which was prepared *in situ* from the reaction of $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NHSi}^i\text{Pr}_3$ (1.80 g, 5.38 mmol) with *n*-BuLi (5.38 mmol, 3.4 mL) in THF at room temperature. The mixture was stirred for 24 h at room temperature. The resulting reaction mixture was dried in vacuo, and the residue was extracted with 30 mL of hexane. After filtration, the pale yellow solution was concentrated, and cooled at −30 °C overnight to give $\{[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NSi}^i\text{Pr}_3]\text{YCl}_2(\text{THF})\}_2[\text{LiCl}(\text{THF})_2]$ as colorless cubic-shaped crystals (3.2 g, 4.86 mmol, 90% yield). ^{1}H NMR (THF-d_8, 400 MHz): δ 0.97 (d, 36H, $J_{\text{H–H}} = 8.0$ Hz, $\text{NSi}[(\text{C}H_3)_2\text{CH}]_3$), 0.99 (m, 6 H, d, $\text{C}H(\text{CH}_3)_2$), 1.06 (d, 12H, $J_{\text{H–H}} = 6.4$ Hz, $\text{CH}(\text{C}H_3)_2$), 1.09 (d, 12H, $J_{\text{H–H}} = 6.4$ Hz, $\text{CH}(\text{C}H_3)_2$), 1.69 (m, 16H, THF), 3.53 (m, 16H, THF), 3.94 (m, 4H, $\text{C}H(\text{CH}_3)_2$), 6.64 (d, 4 H, *m*-Ph*H*), 6.84 (t, 2H, *p*-Ph*H*). ^{13}C NMR (THF-d_8, 100 MHz): δ 15.84 ($\text{NSi}[(\text{CH}_3)_2C\text{H}]_3$), 19.58 ($\text{NSi}[(C\text{H}_3)_2\text{CH}]_3$), 22.51 ($C\text{H}(\text{CH}_3)_2$), 25.38 (THF-β-*C*), 26.09 ($\text{CH}(C\text{H}_3)_2$), 67.29 (THF-α-*C*), 121.66, 123.86, 141.52, 155.79 ($C_6\text{H}_3$). *Anal.* Calc. for $\text{C}_{29}\text{H}_{54}\text{Cl}_{2.\,5}\text{Li}_{0.5}\text{NO}_2\text{SiY}$: C, 52.95; H, 8.29; N, 2.13. Found: C, 52.54; H, 8.77; N, 1.96%.

4.4. Synthesis of $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\ \text{NSi}^i\text{Pr}_3]\text{Y}(\text{CH}_2\text{Si}\ \text{Me}_3)_3\text{Li}(\text{THF})_2$

To a 20 mL of hexane/toluene solution of $\{[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NSi}^i\text{Pr}_3]\text{YCl}_2\ (\text{THF})\}_2[\text{LiCl}(\text{THF})_2]$ (1.32 g, 2.0 mmol) was added slowly $\text{LiCH}_2\text{SiMe}_3$ (0.76 g, 8.0 mmol) in hexane at room temperature. The mixture was stirred for 1 h at room temperature. The resulting solution was dried up, and the residue was extracted with toluene. After concentration, the toluene solution was cooled at −30 °C overnight to give$[2,6\text{-}^i\text{Pr}_2\text{C}_6\ \text{H}_3\text{NSi}^i\text{Pr}_3]\text{Y}(\text{CH}_2\text{Si}\ \text{Me}_3)_2\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{THF})_2$ as colorless cubic-shaped crystals (1.4 g, 1.2 mmol, 56% yield). ^{1}H NMR (C_6D_6, 400 MHz): δ −0.67 (s, 6 H, $\text{C}H_2\text{SiMe}_3$), 0.34 (s, 9H, $\text{CH}_2\text{Si}Me_3$), 0.36 (s, 18H, $\text{CH}_2\text{Si}Me_3$), 1.33 (d, 18H, $J_{\text{H–H}} = 5.2$ Hz, $\text{SiCH}(\text{C}H_3)_2$), 1.35 (d, 6H, $J_{\text{H–H}} = 6.3$ Hz, $\text{CH}(\text{C}H_3)_2$), 1.38 (m, 8H, THF), 1.42 (d, 6H, $J_{\text{H–H}} =$ 6.3 Hz, $\text{CH}(\text{C}H_3)_2$), 1.51 (m, 3H, $\text{SiC}H(\text{CH}_3)_2$), 3.25 (m, 8H, THF), 4.16 (m, 2 H, $\text{C}H(\text{CH}_3)_2$), 6.88 (t, 1 H, *p*-Ph*H*), 7.04 (d, 2H, *m*-PhH). ^{13}C NMR (C_6D_6, 100 MHz): δ 5.02 ($\text{CH}_2\text{Si}\ Me_3$), 5.11 ($\text{CH}_2\text{Si}Me_3$), 16.12 ($\text{NSi}[(\text{CH}_3)_2C\text{H}]_3$), 20.91 ($\text{NSi}[(C\text{H}_3)_2\text{CH}]_3$), 25.80 ($(C\text{H}_3)_2\text{CH}$), 27.08 (THF-β-*C*), 28.16 ($C\text{H}(\text{CH}_3)_2$), 35.04 ($J_{\text{Y–C}} = 32$ Hz, $C\text{H}_2\text{SiMe}_3$), 69.30 (THF-α-*C*), 121.71, 125.04, 146.01, 148.75 (C_6H_3). *Anal.* Calc. for $C_{41}H_{87}LiNO_2Si_4Y$: C, 59.02; H, 10.53; N, 1.68. Found: C, 58.70; H, 10.29; N, 1.99%.

4.5. X-ray structural determination

A suitable pale yellow crystal was sealed in a thin-walled capillary under a microscope in the glovebox. Data collection was performed on a Bruker SMART APEX diffractometer with a CCD area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The determination of crystal class and unit cell was carried out by SMART program package [8]. The raw frame data were processed using SAINT [9] and SADABS [10] to yield the reflection data file. The structure was solved using SHELXTL program [11]. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

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Appendix A. Supplementary material

CCDC 640090 and 640091 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.08.010.

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