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Sterically Demanding Chelating Diamide Complexes of Yttrium and Lutetium

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Deprotonation of the bridged diamine $ArHN(CH_2)_3NHAr$ ($Ar = 2,6\text{-}i Pr_2C_6H_3$) with *n*-butyllithium and potassium hydride, respectively, gives the corresponding alkali metal derivatives $M_2\{ArN(CH_2)_3NAr\}$ (M = Li (**1a**), K (**1b**)). **1a** reacts with yttrium trichloride to form the metalate complex $[Y\{ArN(CH_2)_3NAr\}(THF)_2(\mu\text{-}Cl)_2Li(THF)_2]$ (**2**). The coordination number of yttrium in **2** is six. The structure of **2** shows two bridging chloride ligands and an alkali metal bound by two solvate molecules. Further reaction of **2** with NaC_5H_5 in THF affords the complex $[Y\{ArN(CH_2)_3NAr\}(\eta^5\text{-}C_5H_5)(THF)]$ (**4**). The structure of **4** in solution and in the solid state is best described as a distorted tetrahedron. Reaction of **1b** with anhydrous lutetium trichloride leads to the unexpected ionic product $[LuCl_2(THF)_5][Lu\{ArN(CH_2)_3NAr\}_2]$ (**5**). **5** can be *formally* considered as a derivative of the ionic compound $[LuCl_2(THF)_5][LuCl_4(THF)_2]$, in which all four chlorine atoms of the anion are substituted by 2 equiv of the $\{ArN(CH_2)_3NAr\}^{2-}$ ligand. As seen from all three structures, the steric demand of the $\{ArN(CH_2)_3NAr\}^{2-}$ ligand is less than that of two $(C_5Me_5)^-$ moieties.

Introduction

Metallocenes of organolanthanides[1] have proven to be highly efficient catalysts[2] for a variety of olefin transformations including hydrogenation,[3,4] polymerization,[5] hydroamination,[4,6] hydrosilylation,[7] and hydroboration.[8] Organolanthanides combine facile ligand exchange and high electrophilicity, while the lanthanide series offers tunable reactivity not only via modification of the ligand sphere but also via variation of the metal ionic radius.[9] In an attempt to extend the possibility of modifying and controlling the reactivity, recent research efforts have been directed toward substitution of the cyclopentadienyl ligands in the metallocene setup by other anionic nitrogen-based bidentate ligand systems[10] such as diazadienes,[11] amidinates,[12] diamido ligands,[13] or other combinations of nitrogen and oxygen atoms[14] to increase the electrophilicity of the metal center and to create a different steric environment at the reactive site. Linking various anionic functionalities such as amides and aryloxides together by a covalent bridge has been a very useful concept in transition-metal chemistry to determine complex geometry and limiting ligand mobility.[13,15] Our attention is drawn to the sterically demanding

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bridged diamide ligand $\{ArN(CH_2)_3NAr\}^{2-}$ (Ar = 2,6-$i$$Pr_2C_6H_3$). We are particularly interested in the steric and electronic effects of this ancillary ligand. It is expected, that the linked diamide ligand system, together with the linked aminopyridinato[16] and aminotroponiminate ligands, will form an interesting set of ancillary ligands for a new kind of lanthanide chemistry.[17] The $\{ArN(CH_2)_3NAr\}^{2-}$ ligand was previously introduced by McConville et al. in group 4 chemistry by reaction of $ArHN(CH_2)_3NHAr$ with $[M(NMe_2)_4]$ (M = group 4 metal). The resulting products were further reacted to give new polymerization catalysts.[18]

In this article the synthesis of the alkali diamides $M_2\{ArN(CH_2)_3NAr\}$ (M = Li, K) is reported, along with details of further reactions of this reagent with yttrium and lutetium chlorides. These reactions lead to a series of lanthanide diamido complexes having the $\{ArN(CH_2)_3NAr\}^{2-}$ ligand in the coordination sphere.

Experimental Section

General Procedures. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual-manifold Schlenk line, interfaced to a high-vacuum (10^{-4} Torr) line, or in an argon-filled M. Braun glovebox. Ether solvents (tetrahydrofuran and diethyl ether) were predried over Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$. All solvents for vacuum line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Aldrich Inc. (all 99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on Bruker AC 250. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. $ArHN(CH_2)_3NHAr$ (Ar = 2,6-$i$$Pr_2C_6H_3$)[18c] was prepared according to literature procedures.

$Li_2\{ArN(CH_2)_3NAr\}$ (1a). A 1.6 M solution (16.3 mL, 26.0 mmol) of *n*BuLi in hexane was added slowly to a stirred solution of $ArHN(CH_2)_3NHAr$ (Ar = 2,6-$i$$Pr_2C_6H_3$) (4.67 g, 11.8 mmol) in 50 mL of *n*-pentane at 0 °C. A white precipitate was immediately formed. The mixture was then stirred for 16 h at room temperature and filtered, and the remaining white residue was dried in vacuo. Yield: 4.75 g (99%). ^{1}H NMR (THF-d_8, 250 MHz, 25 °C): δ 1.15 (d, 24H, CH*Me*$_2$, ^3J(H,H) = 6.8 Hz), 1.87 (br, 2H, NCH_2CH_2), 3.48 (sept, 4H, C*H*Me$_2$, ^3J(H,H) = 6.8 Hz), 3.54 (t, 4H, NCH_2CH_2, ^3J(H,H) = 5.9 Hz), 6.15 (d, 2H, Ph, ^3J(H,H) = 7.4 Hz), 6.68 (d, 4H, Ph, ^3J(H,H) = 7.3 Hz). ^{13}C NMR (THF-d_8, 62.5 MHz, 25 °C): δ 25.1 (CH*Me*$_2$), 28.8 (NCH_2CH_2), 40.4 (*C*HMe$_2$), 59.3 (NCH_2CH_2), 113.3 (Ph), 123.1 (Ph), 140.0 (Ph), 161.2 (Ph).

$K_2\{ArN(CH_2)_3NAr\}$ (1a). To a suspension of KH (1.6 g, 40.0 mmol) in THF was slowly added at 0 °C $ArHN(CH_2)_3NHAr$ (Ar = 2,6-$i$$Pr_2C_6H_3$) (5.2 g, 13.2 mmol) dissolved in 50 mL of THF. The mixture was warmed to room temperature and stirred for 6 h. The reaction mixture was refluxed for 8 h and then stirred again for 18 h at room temperature. The remaining KH was filtered off and the filtrate concentrated in vacuo. The remaining yellow residue was washed with *n*-pentane (3 × 50 mL) and dried in vacuo. Yield: 2.50 g (40%). ^{1}H NMR (THF-d_8, 250 MHz, 25 °C): δ 1.19 (d, 24H, CH*Me*$_2$, ^3J(H,H) = 6.4 Hz), 1.95 (quint, 2H, NCH_2CH_2, ^3J(H,H) = 6.9 Hz), 3.00 (t, 4H, NCH_2CH_2, ^3J(H,H) = 6.9 Hz), 3.37 (sept, 4H, C*H*Me$_2$, ^3J(H,H) = 6.9 Hz), 6.62 (d, 2H, Ph, ^3J(H,H) = 7.4 Hz), 7.01 (m, 4H, Ph, ^3J(H,H) = 7.3 Hz). ^{13}C NMR (THF-d_8, 62.5 MHz, 25 °C): δ 26.3 (CH*Me*$_2$), 28.3 (NCH_2CH_2), 33.0 (*C*HMe$_2$), 51.2 (NCH_2CH_2), 129.9 (Ph), 124.3 (Ph), 143.4 (Ph), 144.6 (Ph).

$[Y\{ArN(CH_2)_3NAr\}(THF)_2(\mu\text{-}Cl)_2Li(THF)_2]$ (2). THF (10 mL) was condensed at −196 °C onto a mixture of YCl_3 (234 mg, 1.2 mmol) and **1a** (406 mg, 1.0 mmol), and the mixture was stirred for 18 h at room temperature. The solvent was then evaporated in vacuo, and toluene (10 mL) was condensed onto the mixture. The solution was filtered, and the solvent was removed. The remaining solid was washed with *n*-pentane (10 mL) and dried in vacuo. Finally, the product was crystallized from THF/*n*-pentane (1:4). Yield: 520 mg (61%). ^{1}H NMR (THF-d_8, 250 MHz, 25 °C): δ 1.19 (d, 12H, CH*Me*$_2$, ^3J(H,H) = 6.9 Hz), 1.26 (d, 12H, CH*Me*$_2$, ^3J(H,H) = 6.8 Hz), 1.76 (m, THF), 2.48 (br, 2H, NCH_2CH_2), 3.34 (t, 4H, NCH_2CH_2, ^3J(H,H) = 5.3 Hz), 3.61 (m, THF), 4.18 (sept, 4H, C*H*Me$_2$, ^3J(H,H) = 6.8 Hz), 7.18 (m, 6H, Ph). ^{13}C NMR (THF-d_8, 62.5 MHz, 25 °C): δ 25.5 (CH*Me*$_2$), 25.9 (CH*Me*$_2$), 26.2 (NCH_2CH_2), 34.3 (*C*HMe$_2$), 59.1 (NCH_2CH_2), 119.8 (Ph), 121.2 (Ph), 145.5 (Ph), 154.9 (Ph). Anal. Calcd for $C_{43}H_{72}Cl_2LiN_2O_4Y$ (847.78): C 60.92; H 8.56; N 3.30. Found: C 60.22; H 8.23; N 3.19.

$[Y\{ArN(CH_2)_3NAr\}(\eta^5\text{-}C_5H_5)(THF)]$ (4). THF (10 mL) was condensed at −196 °C onto a mixture of **2** (350 mg, 0.41 mmol) and NaC_5H_5 (44 mg, 0.5 mmol), and the mixture was stirred for 18 h at room temperature. The solvent was then evaporated in vacuo, and toluene (10 mL) was condensed onto the mixture. The solution was filtered and the solvent was removed. The remaining solid was washed with *n*-pentane (10 mL) and dried in vacuo. Finally, the product was crystallized from toluene. Yield: 190 mg (75%). ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ 1.23 (d, 6H, CH*Me*$_2$, ^3J(H,H) = 7.0 Hz), 1.27 (m, THF), 1.29 (d, 6H, CH*Me*$_2$, ^3J(H,H) = 7.0 Hz), 1.64 (d, 6H, CH*Me*$_2$, ^3J(H,H) = 6.9 Hz), 1.71 (d, 6H, CH*Me*$_2$, ^3J(H,H) = 6.8 Hz), 3.24 (m, 1H, NCH_2CH_2), 3.28 (m, 1H, NCH_2CH_2), 3.34 (sept, 2H, C*H*Me$_2$, ^3J(H,H) = 6.8 Hz), 3.39 (m, 2H, NCH_2CH_2), 3.64 (m, THF), 3.85 (m, 2H, NCH_2CH_2), 4.16 (sept, 2H, C*H*Me$_2$, ^3J(H,H) = 6.8 Hz), 6.06 (s, 5H, C_5H_5), 7.16 (m, 6H, Ph). ^{13}C NMR (THF-d_8, 62.5 MHz, 25 °C): δ 25.3 (*C*HMe$_2$), 26.3 (CH*Me*$_2$), 26.4 (NCH_2CH_2), 28.2 (CH*Me*$_2$), 29.0 (CH*Me*$_2$), 29.2 (CH*Me*$_2$), 35.1 (*C*HMe$_2$), 59.8 (NCH_2CH_2), 113.1 (C_5H_5), 123.6 (Ph), 123.8 (Ph), 125.4 (Ph), 146.5 (Ph), 144.6 (Ph), 152.4 (Ph). Anal. Calcd for $C_{36}H_{53}N_2OY$ (618.71) C 69.88; H 8.63; N 4.53. Found: C 69.72; H 8.41; N 4.22.

$[LuCl_2(THF)_5][Lu\{ArN(CH_2)_3NAr\}_2]$ (5). THF (10 mL) was condensed at −196 °C onto a mixture of $LuCl_3$ (365 mg, 1.3 mmol) and **1b** (466 mg, 1.0 mmol), and the mixture was refluxed for 8 h. The solution was filtered, and the filtrate was concentrated in vacuo. Onto 5 mL of the solution 20 mL of *n*-pentane was layered. After 1 day colorless crystals were obtained. Yield: 216 mg (28%). ^{1}H NMR (THF-d_8, 250 MHz, 25 °C): δ 1.25 (br, 48H, CH*Me*$_2$), 1.76 (m, THF), 2.40 (m, 4H, NCH_2CH_2), 3.39 (m, 8H, NCH_2CH_2), 3.61 (m, THF), 4.15 (br, 8H, C*H*Me$_2$), 6.75−7.05 (m, 12H, Ph). ^{13}C NMR (THF-d_8, 62.5 MHz, 25 °C): δ 24.7 (CH*Me*$_2$), 25.9 (CH*Me*$_2$), 28.4 (NCH_2CH_2), 33.2 (*C*HMe$_2$), 51.3 (NCH_2CH_2), 123.3 (Ph), 124.0 (Ph), 145.7 (Ph), 146.8 (Ph). Anal. Calcd for $C_{74}H_{120}Cl_2Lu_2N_4O_5$ (1566.58): C 56.73; H 7.72; N 3.58. Found: C 56.21; H 7.62; N 3.14.

X-ray Crystallographic Studies of 2, 4, and 5. Crystals of **2** and **5** were grown from THF/*n*-pentane (1:4). Crystals of **4** were obtained from hot toluene. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber.

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Table 1. Crystallographic Details of [Y{ArN(CH$_2$)$_3$NAr}(THF)$_2$(μ-Cl)$_2$Li(THF)$_2$] (2), [Y{ArN(CH$_2$)$_3$NAr}(η^5-C$_5$H$_5$)(THF)] (4), and [LuCl$_2$(THF)$_5$][Lu{ArN(CH$_2$)$_3$NAr}$_2$] (5)[a]

	2	4	5
formula	$C_{43}H_{72}Cl_2LiN_2O_4Y$	$C_{36}H_{53}N_2OY$	$C_{74}H_{120}Cl_2Lu_2N_4O_5$
fw	847.78	618.71	1566.58
space group	*C*2/*c* (No. 15)	*Pnma* (No. 62)	*I*2/*a* (No. 15)
a, Å	34.75(2)	17.1924(12)	34.5244(2)
b, Å	13.164(10)	19.1941(13)	13.2780(7)
c, Å	20.355(10)	10.3713(7)	36.1322(2)
β, deg	100.83(6)		115.30(8)
V, Å^3	9145(9)	3422.5(4)	14975(15)
Z	8	4	8
density (g/cm^3)	1.232	1.201	1.390
radiation	Mo Kα ($\lambda = 0.71073$ Å)	Ag Kα ($\lambda = 0.56087$ Å)	Mo Kα ($\lambda = 0.71073$ Å)
μ, mm^{-1}	1.432	0.952	2.742
abs corr	none	none	none
no. of reflns collected	17 433	21 432	23 249
no. of unique reflns	5915 [$R_{int} = 0.0923$]	4506 [$R_{int} = 0.0935$]	10458 [$R_{int} = 0.0337$]
no. of obsd reflns	4926	3325	9135
no. of data; params	5722; 437	4506; 188	10 458, 693
*R*1;[b] w*R*2[c]	0.0697; 0.1947	0.0570; 0.1452	0.0347; 0.0948

[a] All data collected at 203 K. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

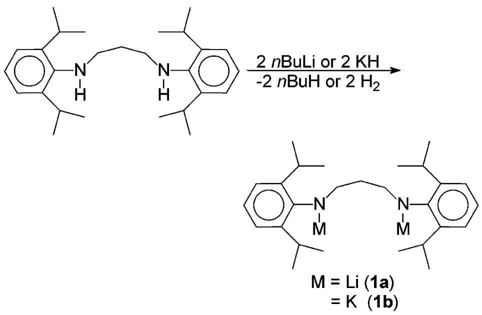
The crystal was transferred directly to the −73 °C cold N$_2$ stream of a Stoe IPDS diffractometer. Subsequent computations were carried out on an Intel Pentium III PC.

All structures were solved by the Patterson method (SHELXS-97[19]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97.[20] In the final cycles of each refinement, all non-hydrogen atoms except C28−C43 and O1 (**2**), C18−C21 (**4**), and C11−C12, C22−C24, C34−C36, C38−C39, C50−C51, C53−C54, C61, C71−C74 (**5**) were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-157635 (**2**), 186894 (**4**), and 157636 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Results and Discussion

The synthesis of the alkali diamides M$_2${ArN(CH$_2$)$_3$NAr} (M = Li, K; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) is reported first, followed by the synthesis and structural characterization of the yttrium and lutetium complexes [Y{ArN(CH$_2$)$_3$NAr}(THF)$_2$(μ-Cl)$_2$Li(THF)$_2$], [Y{ArN(CH$_2$)$_3$NAr}(η^5-C$_5$H$_5$)(THF)], and LuCl$_2$(THF)$_5$][Lu{ArN(CH$_2$)$_3$NAr}$_2$].

Alkali Metal Compounds. The lithium compound Li$_2${ArN(CH$_2$)$_3$NAr} (**1a**) was readily prepared by treatment of ArHN(CH$_2$)$_3$NHAr with 2 equiv of *n*-butyllithium in *n*-pentane (eq 1). It was obtained as a very air-sensitive white powder and was characterized by ^{1}H and ^{13}C NMR spectroscopy. **1a** was previously reported but not formally characterized.[21] In comparison to the neutral ligand, ArHN(CH$_2$)$_3$NHAr, the NMR signals of **1a** show only a slight shift. Most significant, the NC*H$_2$* group (δ 3.54) is shifted 0.53 ppm downfield upon metalation of the ligand. As has been observed previously for ArHN(CH$_2$)$_3$NHAr, the room-temperature NMR spectrum of **1a** is indicative of a symmetrical structure in solution.[18c]



(1)

The potassium salt K$_2${ArN(CH$_2$)$_3$NAr} (**1b**) was synthesized by treatment of the neutral ligand with an excess of KH in THF (eq 1) and was characterized by ^{1}H and ^{13}C spectroscopy. The observed chemical shift is in good agreement with the lithium salt **1a**.

Yttrium Complexes. Transmetalation of **1a** with anhydrous yttrium trichloride in THF at room temperature and crystallization from THF/*n*-pentane (1:4) leads to the reaction product [Y{ArN(CH$_2$)$_3$NAr}(THF)$_2$(μ-Cl)$_2$Li(THF)$_2$] (**2**) (eq 2). The new complex has been characterized by standard spectroscopic techniques, and the solid-state structure was established by single-crystal X-ray diffraction. As observed earlier for zirconium compounds such as [Zr{ArN(CH$_2$)$_3$NAr}Cl$_2$] and [Zr{ArN(CH$_2$)$_3$NAr}(NMe$_2$)$_2$], the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2** show a diastereotopic splitting of the isopropyl CH$_3$ signals, which is interpreted as a conse-

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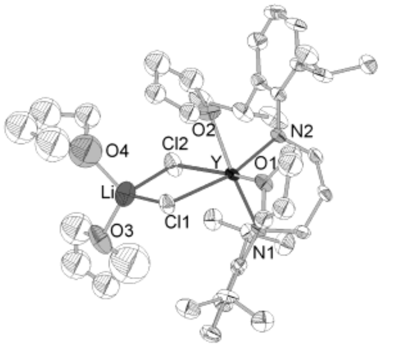
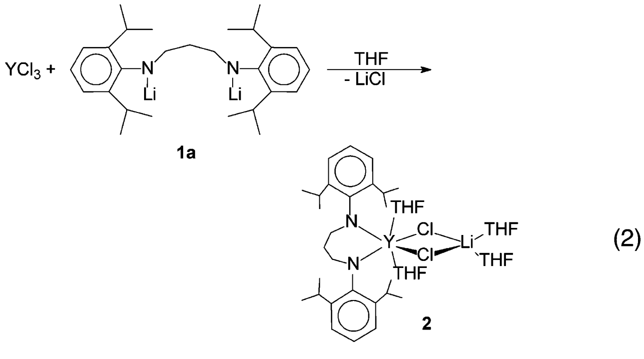


Figure 1. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of [Y{ArN(CH$_2$)$_3$NAr}(THF)$_2$(μ-Cl)$_2$Li(THF)$_2$] (2)

Bond Lengths (Å)	
Y−N1 2.218(4)	Y−N2 2.245(4)
Y−O1 2.449(4)	Y−O2 2.509(4)
Y−Cl1 2.788(2)	Y−Cl2 2.657(2)
Y−Li 3.650(12)	Li−O3 1.936(15)
Li−O4 1.96(2)	Li−Cl1 2.315(12)
Li−Cl2 2.311(13)	
Bond Angles (deg)	
N1−Y−N2 92.5(2)	N1−Y−O1 94.5(2)
N1−Y−O2 172.2(2)	N1−Y−Cl1 101.61(12)
N1−Y−Cl2 98.00(13)	N1−Y−Li 100.8(2)
N2−Y−O1 100.86(15)	N2−Y−O2 87.6(2)
N2−Y−Cl1 165.76(12)	N2−Y−Cl2 97.66(13)
O1−Y−O2 77.79(15)	O1−Y−Cl2 157.13(10)
O1−Y−Cl1 80.35(10)	O2−Y−Cl2 89.73(12)
O2−Y−Cl1 78.70(11)	Cl1−Y−Cl2 78.43(6)

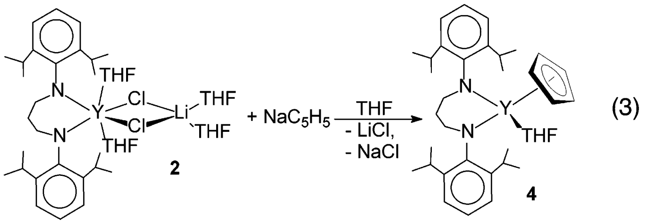
quence of restricted rotation about the N−C$_{ipso}$ bond.[18c]



(2)

The structure of **2** was confirmed by single-crystal X-ray diffraction in the solid state (Figure 1). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2. At first glance compound **2** looks like the numerous alkali metal adducts of the metallocenes and *ansa*-metallocenes of general formula [Ln(C$_5$Me$_5$)$_2$(μ-Cl)$_2$Li(ether)$_2$] and [Ln{Me$_2$Si(C$_5$Me$_4$)$_2$}(μ-Cl)$_2$Li(ether)$_2$].[1] These structures contain two bridging chloride ligands and an alkali metal bound by two solvate molecules. In contrast to these well-known structures in compound **2** two more molecules of THF are coordinated onto the metal center, which indicates that the steric demand of the {ArN(CH$_2$)$_3$NAr}$^{2-}$ ligand is lower than that of two (C$_5$Me$_5$)$^-$ ligands or one Me$_2$Si(C$_5$Me$_4$)$_2$$^-$ ligand. The coordination number of the metal center in **2** is thus increased. The yttrium atom is surrounded by six ligands in a distorted octahedral arrangement. Due to the 6-fold coordination sphere around the yttrium in **2**, the Cl1−Y−Cl2 angle of the constrained bridge to lithium (78.43(6)°) is smaller than in the metallocene [Y(C$_5$Me$_5$)$_2$(μ-Cl)$_2$Li(THF)$_2$] (**3**) (Cl1−Y−Cl2 84.8(1)°).[22] On the other hand, the Y−Cl and Li−Cl bond distances in **2** (Y−Cl1 2.788(2) Å, Y−Cl2 2.657(2) Å; Li−Cl1 2.315(12) Å, Li−Cl2 2.311(13) Å) and **3** (Y−Cl1 2.646(12) Å, Y−Cl2 2.655(4) Å; Li−Cl1 2.391(15) Å, Li−Cl2 2.357(3) Å) are as expected in a comparable range. In compound **2** the Y−N and Y−O bond lengths are in the expected range of Y−N1 2.218(4) pm, Y−N2 2.245(4) pm; Y−O1 2.449(4) Å, Y−O2 2.509(4) Å (Y−N 2.236(3) Å in [Y{(iPr)$_2$ATI}{N(SiMe$_3$)$_2$}$_2$] ({(iPr)$_2$ATI} = *N*-isopropyl-2-(isopropylamino)troponiminate)).[23] The N1−Y−N2 (92.5(2)°), N1−Y−O1 (94.5(2)°), and N2−Y−O2 bond angles (87.6(2)°) are in the range of 90°, whereas the N2−Y−O1 angle (100.86(15)°) is significantly larger.

By reaction of **2** with NaC$_5$H$_5$ in THF the chlorine atom, one molecule of THF, and the LiCl unit can be replaced by a η^5-coordinated cyclopentadienyl ligand to afford the complex [Y{ArN(CH$_2$)$_3$NAr}(η^5-C$_5$H$_5$)(THF)] (**4**) as crystalline solid (eq 3). Compound **4** can be considered to be isoelectronic to the zirconium complex [Zr{ArN(CH$_2$)$_3$NAr}(η^5-C$_5$H$_5$)Cl],[18c] in which the THF molecule of **4** is *formally* replaced by a chlorine atom. Due to the comparable ion radii of yttrium and zirconium, this analogy is not surprising. The new complex has been characterized by standard analytical/spectroscopic techniques. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **4** recorded in C$_6$D$_6$ as solvent are consistent with a pseudo tetrahedral geometry and C_s symmetry about yttrium. This gives rise to two isopropyl C*H* resonances and four isopropyl CH_3 resonances, which are consistent with restricted rotations about the N−C$_{ipso}$ bond. Similar patterns in the ^{1}H and ^{13}C{^{1}H} NMR were observed earlier for [Zr{ArN(CH$_2$)$_3$NAr}(η^5-C$_5$H$_5$)Cl],[18c] which indicate that the THF molecule in **4** is tightly coordinated to the yttrium atom. This is also supported by the ^{1}H and ^{13}C{^{1}H} NMR spectra of **4** recorded in THF-d_8 as solvent. Only broad NMR signals are observed for the isopropyl group in THF-d_8, pointing to a dynamic behavior of **4** in THF caused by a rapid exchange of the THF molecule. The resonance of the cyclopentadienyl ring is always observed as a sharp singlet (δ 6.06 in C$_6$D$_6$).



(3)

The solid-state structure of **4** was also established by single-crystal X-ray diffraction (Figure 2). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 3. Overall the structure of **4** is best described as a distorted tetrahedron. Due to the

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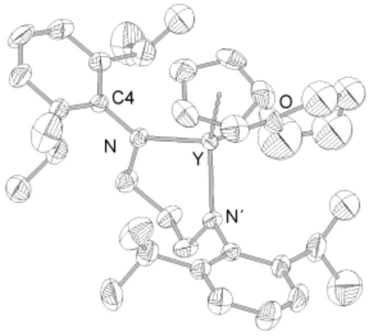


Figure 2. Perspective ORTEP view of the molecular structure of **4**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of [Y{ArN(CH_2)$_3$NAr}(η^5-C_5H_5)(THF)] (4)[a]

Bond Lengths (Å)	
N−Y 2.171(3)	O−Y 2.371(4)
C4−N 1.429(4)	Cg-Y 2.376(1)
Bond Angles (deg)	
N−Y−N′ 97.32(15)	N−Y−O 107.63(11)
C−N−Y 133.8(2)	N−Y−Cg 116.78(1)
O1−Y−Cg 109.69(1)	

[a] Cg ring centroid.

n-propyl bridge between the nitrogen atoms, the N−Y−N′ bond angle (97.32(15)°) is slightly constrained, whereas the N−Y−Cg angle (116.78(1)°) is enlarged (Cg ring centroid). The remaining two bond angles are in the expected range of a tetrahedral setup (O1−Y−Cg 109.69(1)°, N−Y−O 107.63(11)°). The N−Y (2.171(3) Å) and O−Y (2.371(4) Å) bond distances of **4** are slightly shorter than those observed in **2**. The ring centroid−Y bond distances of 2.376(1) Å fit well into the range of other cyclopentadienyl complexes (e.g., [Y(MeC_5H_4)$_2$(THF){OCN(iPr)$_2$NPh}]: Cg1−Y 2.421(1), 2.391(2) Å).[24] A comparison with metallocene complexes of the lanthanides such as [Ln(C_5Me_5)$_2$(η^5-C_5H_5)] (Ln = Sm, Nd),[25] which crystallize without any THF in the coordination sphere, shows again that the steric demand of the {ArN(CH_2)$_3$NAr}$^{2-}$ ligand is lower than that of two (C_5Me_5)$^-$ ligands.

Lutetium Complex. In contrast to the formation of **2**, no clean product could be obtained by the reaction of **1a** with $LuCl_3$. Due to the slightly smaller ion radius of lutetium (Lu: 0.861 Å; Y: 0.900 Å),[26] the formation of a lutetium complex, which is analogous to **2**, might be prevented. On the other hand, transmetalation of **1b** with anhydrous lutetium trichloride in refluxing THF followed by crystallization from THF/*n*-pentane (1:4) leads to the unexpected ionic product [$LuCl_2$(THF)$_5$][Lu{ArN(CH_2)$_3$NAr}$_2$] (**5**) (eq 4). The solid-state structure of the new complex was established by single-crystal X-ray diffraction (Figure 3), and characterization by standard NMR techniques has been performed. Data collection parameters and selected bond lengths and angles are given in Tables 1 and 4, respectively. In the ^{1}H and ^{13}C{^{1}H} NMR spectra of **5** only broad NMR signals are observed for the isopropyl groups, pointing to a dynamic behavior of **5**. Even, at lower temperatures, no sharp signals were observed.

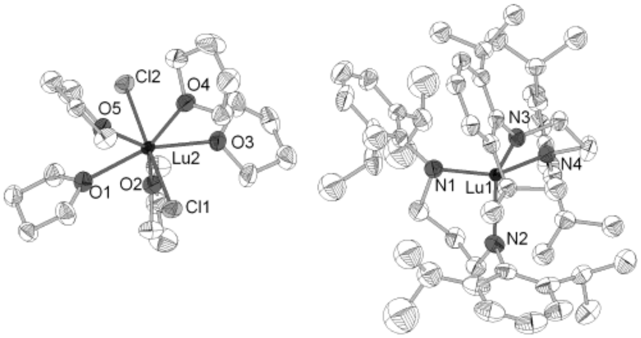
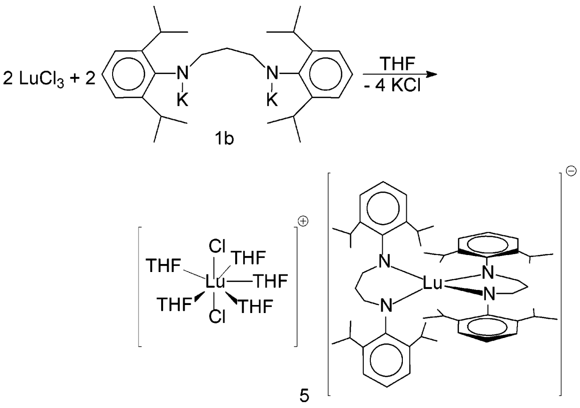


Figure 3. Perspective ORTEP view of the molecular structure of **5**. Thermal ellipsoids are drawn to encompass 30% probability. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of [$LuCl_2$(THF)$_5$][Lu{ArN(CH_2)$_3$NAr}$_2$] (5)

Bond Lengths (Å)	
Lu1−N1 2.180(5)	Lu1−N2 2.198(5)
Lu1−N3 2.194(5)	Lu1−N4 2.197(5)
Lu2−O1 2.339(5)	Lu2−O2 2.349(4)
Lu2−O3 2.352(4)	Lu2−O4 2.366(5)
Lu2−O5 2.347(4)	Lu2−Cl1 2.502(2)
Lu2−Cl2 2.506(2)	
Bond Angles (deg)	
N1−Lu1−N2 97.0(2)	N1−Lu1−N3 123.4(2)
N1−Lu1−N4 114.0(2)	N2−Lu1−N3 116.3(2)
N2−Lu1−N4 112.7(2)	N3−Lu1−N4 94.4(2)
O1−Lu2−Cl1 89.34(10)	O2−Lu2−Cl1 93.24(9)
O3−Lu2−Cl1 88.26(10)	O4−Lu2−Cl1 88.98(10)
O5−Lu2−Cl1 89.82(9)	O1−Lu2−Cl2 91.79(10)
O2−Lu2−Cl2 88.58(9)	O3−Lu2−Cl2 91.74(10)
O4−Lu2−Cl2 89.21(10)	O5−Lu2−Cl2 89.05(9)
Cl1−Lu2−Cl2 178.09(5)	



(4)

5 can be *formally* considered as a derivative of the ionic compound [$LuCl_2$(THF)$_5$][$LuCl_4$(THF)$_2$], in which all four chlorine atoms of the anion are substituted by 2 equiv of the {ArN(CH_2)$_3$NAr}$^{2-}$ ligand. Although the ionic compound [$LuCl_2$(THF)$_5$][$LuCl_4$(THF)$_2$] is so far not characterized by single-crystal X-ray diffraction, structures of [$LnCl_2$(THF)$_5$][$LnCl_4$(THF)$_2$] (Ln = Gd, Dy, Er, Tb) are known.[27] Due to the already mentioned lesser steric demand of the {ArN(CH_2)$_3$NAr}$^{2-}$ ligand compared to (C_5Me_5)$^-$, the formation of an ate-complex is possible. The Lu1−N distances are in the expected

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range of 2.180(5)−2.197(5) Å.[1b] The N−Lu1−N angles are fixed by the chelating ligand. Thus, the N−Lu1−N angles of the metallacycles are 97.0(2)° (N1−Lu1−N2) and 94.4(2)° (N3−Lu1−N4), whereas the other N−Lu1−N angles range from 112.7(2)° to 123.2(2)°. Surprisingly, the counterion is not potassium, but a $[LuCl_2(THF)_5]^+$, which is pentagonal bipyramidal. The two chlorine atoms are located in the axial positions (Cl1−Lu2−Cl2: 178.09(5)°) having Lu−Cl bond lengths of Cl1−Lu2 2.502(2) Å and Cl2−Lu2 2.502(2) Å. The five THF molecules are arranged in the equatorial positions of the pentagonal bipyramid with almost rectangular O−Lu2−Cl angles (O−Lu2−Cl: 89.34(10)−93.24(9)°) The Lu2−O distances are in the range 2.339(5)−2.366(5) Å. The $[LuCl_2(THF)_5]^+$ cation has been described previously. It was isolated as $[LnCl_2(THF)_5][Co(CO)_4]$ (Ln = Yb, Lu) from the reaction of $LnCl_3$ with $Na[Co(CO)_4]$ in THF.[28] In $[LuCl_2(THF)_5][Co(CO)_4]$ the Lu−O distances are in the range 2.353(1)−2.364(11) Å, whereas the Lu−Cl distance is 2.520(5) Å.

The mechanistic pathway that leads to the formation of **5** remains unclear. Compound **5** may be formed via a disproportionation of an $[Lu\{ArN(CH_2)_3NAr\}Cl]$ intermediate or by a reaction of **1b** with $[LuCl_2(THF)_5][LuCl_4(THF)_2]$. Using the same reaction conditions that led to **5** in yttrium chemistry does not give clean products.

Summary

In summary, it can be emphasized that the deprotonation of $ArHN(CH_2)_3NHAr$ with 2 equiv of *n*-butyllithium and potassium hydride, respectively, gives the corresponding alkali metal derivatives $M_2\{ArN(CH_2)_3NAr\}$ (M = Li (**1a**), K (**1b**)). **1a** reacts with yttrium trichloride to form the metalate complex $[Y\{ArN(CH_2)_3NAr\}(THF)_2(\mu\text{-}Cl)_2Li(THF)_2]$ (**2**), which can be further reacted with NaC_5H_5 in THF to afford the complex $[Y\{ArN(CH_2)_3NAr\}(\eta^5\text{-}C_5H_5)(THF)]$ (**4**). In contrast to the corresponding metallocenes complexes, $[Y(C_5Me_5)_2(\mu\text{-}Cl)_2Li(THF)_2]$ (**3**) and $[Ln(C_5Me_5)_2(\eta^5\text{-}C_5H_5)]$, in **2** and **4** THF is coordinated onto the center metals. Thus, the steric demand of the $\{ArN(CH_2)_3NAr\}^{2-}$ ligand is lesser than that of two $(C_5Me_5)^-$ moieties. This is also supported by the formation of $[LuCl_2(THF)_5][Lu\{ArN(CH_2)_3NAr\}_2]$ (**5**). In the ionic compound **5** the anion consists of two $\{ArN(CH_2)_3NAr\}^{2-}$ ligands, which coordinate onto one lutetium atom. **5** can be *formally* considered as a derivative of the ionic compound $[LuCl_2(THF)_5][LuCl_4(THF)_2]$, in which all four chlorine atoms of the anion are substituted by 2 equiv of the $\{ArN(CH_2)_3NAr\}^{2-}$ ligand. The mechanistic pathway for the formation of **5** is not completely understood.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2**, **4**, and **5** are available free of charge via the Internet at http://pubs.acs.org.

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