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Syntheses and Structures of Homoleptic Lanthanide Complexes with Chelating *o*-Dimethylaminobenzyl Ligands: Key Precursors in Lanthanide Chemistry

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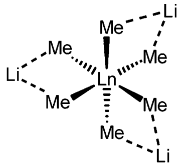
Reaction of *o*-Me_2N-$C_6H_4CH_2K$ with YCl_3 in THF yielded (*o*-Me_2N-$C_6H_4CH_2)_3Y$ (**5-Y**) in the form of light yellow crystalline plates (59% yield). The crystal structure shows three bidendate benzyl ligands bound to Y, which has a prismatic coordination sphere. The La analogue (**5-La**) was prepared similarly (41% crystalline yield) and is isostructural to **5-Y**, but shows more extensive multihapto bonding of the benzyl ligand to the larger metal (short aryl−La interactions). Attempted synthesis of (*o*-Me_3Si-$C_6H_4CH_2)_3La$ from *o*-Me_3Si-C_6H_4-CH_2K and $LaCl_3$ unexpectedly gave [(*o*-Me_3Si-$C_6H_4CH_2)_4La^-$][Li^+·$(THF)_4$] (32% crystalline yield), the source of the Li^+ ion being impure *o*-Me_3Si-$C_6H_4CH_2K$. Crystal structure determination revealed the (*o*-Me_3Si-$C_6H_4CH_2)_4La^-$ ion in which La has a distorted tetrahedral coordination sphere. The complexes (*o*-Me_2N-$C_6H_4CH_2)_3Y$ and (*o*-Me_2N-C_6H_4-$CH_2)_3La$ show extraordinary thermal stability, but also sufficient reactivity in deprotonation of 9-*t*-BuN(H)$SiMe_2$-fluorene. The product, (9-*t*-BuN$SiMe_2$-fluorenyl)(*o*-Me_2N-benzyl)Y·(THF) (**7**; 85% crystalline yield), shows a monomeric crystal structure with allylic coordination of the fluorenyl ring and bidentate coordination of the benzyl ligand. This complex was successfully hydrogenated with molecular H_2 (10 bar) to yield the dimer [(9-*t*-BuN$SiMe_2$-fluorenyl)YH·$(THF)_2]_2$ (**8**; 84% crystalline yield), in which the fluorenyl part of the ligand is bound to Y only in η^1-fashion.

Introduction

Highly reactive tris-alkyllanthanide compounds are extremely useful precursors in the syntheses of various lanthanide complexes and are the key to many lanthanide catalysts.[1] Their syntheses, however, are not straightforward and are limited to a few alkyl groups. These problems arise from the relatively high Lewis acidity of the +3-charged lanthanide cations (Ln^{3+}) combined with their respectable ionic sizes: the largest lanthanide ion, La^{3+} (1.03 Å), is comparable in size to Ca^{2+} (1.00 Å) and the smallest ion, Lu^{3+} (0.86 Å), is still much larger than Mg^{2+} (0.66 Å).[2] This combination of relatively high Lewis acidity and a large coordination sphere makes them on one hand very useful in catalysis, however, on the other hand creates problems in their syntheses.

Reaction of MeLi with several $LnCl_3$ salts led to the formation of a series of mixed-metal aggregates (**1**):[3−5] the small methyl anion is certainly not big enough to saturate the large coordination sphere of Ln^{3+}, and Me_3Ln therefore forms a stable adduct with the MeLi precursor.

Reaction of the bulkier *tert*-butyllithium with $LnCl_3$ resulted in formation of an “ate”-complex (**2**), which shows that even three *tert*-butyl anions cannot saturate the Ln coordination sphere.[6]



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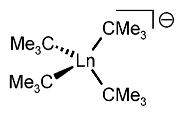

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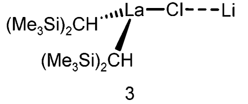

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Reaction of $LaCl_3$ with $LiCH(SiMe_3)_2$ resulted in the formation of the mixed-metal species tris(alkyl)La·(LiCl) (**3**).[7] Even a tris-alkyllanthanide with the bulky $CH(SiMe_3)_2$ group, so-called “big R”, tends to saturate the metal coordination sphere by retaining the side-product LiCl. True homoleptic tris-alkyllanthanide complexes

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were prepared by reaction of $LiCH(SiMe_3)_2$ with the sterically hindered lanthanide-phenoxide (2,6-*tert*-Bu_2-$C_6H_3O)_3Ln$.[8] The steric saturation of the lanthanide metal is partly achieved by the bulk of the ligand, but also via agostic $Si^{\delta-}-Me^{\delta+}\cdots Ln^{3+}$ interactions.

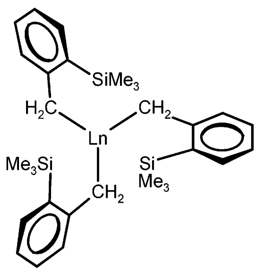
Although several $[(Me_3Si)_2CH]_3Ln$ complexes have been prepared, their reactivity is tempered by 2-fold substitution of the carbanion with stabilizing silyl groups. Syntheses and structural characterization of the tris-alkyllanthanide complexes with the smaller, less stabilized Me_3SiCH_2 group could be achieved for the smaller lanthanide metals (Lu, Yb, Er, Sm, and Y);[9–12] however, their THF-solvated complexes are not only air-sensitive but extremely thermally sensitive as well (a recent report showed that complexation with 12-crown-4 increases their stabilities significantly).[13] Although their syntheses from $LnCl_3$ and Me_3SiCH_2Li are straightforward, the preparation of the Li precursor from Me_3SiCH_2Cl and fresh Li suspension is tedious and requires sublimation.[14] Recently a surprisingly simple one-step procedure has been described[15] for tris(alkyl)Yb complexes: $8\ Yb + 12\ RI \rightarrow 2\ R_3Yb + 6\ YbI_2 + 3\ R-R$ (R = $-CH_2SiMe_3$ or $-CH_2CMe_3$). This method circumvents use of the Li precursor but is as yet only limited to Yb and not very economical on the lanthanide metal.

All homoleptic tris-alkyllanthanide complexes R_3Ln known so far (R = $(Me_3Si)_2CH-$, Me_3SiCH_2-, *t*-$BuCH_2-$, and $(Ph_2P)_2CH-$)[8–12,15,16] have one thing in common: the lack of a β-H atom, which prevents decomposition via β-H elimination. In this light, it is odd that neutral homoleptic benzyllanthanide complexes received little attention. Only the preparation of a tris-benzyl complex of the lightest group 3b metal, the lanthanide-like Sc, has been described: (*o*-Me_2N-C_6H_4-$CH_2)_3Sc$.[17] Reactions of $PhCH_2Li$ with $LnCl_3$ (Ln = Y and Nd) resulted in mixtures of unusual complexes.[18] It is proposed that the products $(PhCH_2)_3Ln$ decompose by an α-elimination pathway producing Schrock-carbene-like products ($PhCH_2Ln{=}CHPh$), which can react further to carbyne-like species ($Ln{\equiv}CPh$).[18]

This work presents a simple route to the syntheses of homoleptic benzyl complexes of the lanthanides and shows their crystal structures and their usefulness as precursors in lanthanide chemistry.

Results and Discussion

To prepare benzyl complexes of even the largest lanthanide metal (La), steric or electronic saturation of the coordination sphere is the key to success. Therefore syntheses of the benzyl complexes **4** and **5** were pursued. Complex **4** would be stabilized not only by steric shielding of the lanthanides coordination sphere but also by possible agostic $Si^{\delta-}-Me^{\delta+}\cdots Ln^{3+}$ interactions. Complex **5** would be stabilized by intramolecular coordination via the *ortho*-NMe_2 substituent, similar to that described for heteroleptic benzyllanthanide[19] and aryllanthanide[17] complexes. The complexes **4** and **5** still feature an unstabilized and therefore highly basic (or nucleophilic) benzylic CH_2 functionality.



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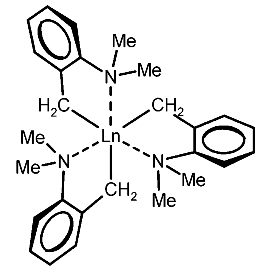

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A further necessity seemed the use of benzylpotassium instead of benzyllithium reagents in the reaction with the $LnCl_3$. This would produce the extremely insoluble KCl instead of the well-soluble LiCl, which has the advantage of bringing the reaction to completion as well as circumventing the formation of mixed-metal complexes such as $R_3Ln\cdot(KCl)$ or $[R_3LnCl^-][K^+]$.

The attempted preparation of **4-La** by reacting 3 equiv of *o*-Me_3Si-$C_6H_4CH_2K$ with $LaCl_3$ in THF unexpectedly yielded the ate-complex [(*o*-Me_3Si-$C_6H_4CH_2)_4$-$La^-][Li^+\cdot(THF)_4]$ (**6**) in the form of large red crystalline blocks (32%). The only explanation for the presence of the Li^+ ion is that the precursor *o*-Me_3Si-$C_6H_4CH_2K$, which was prepared by reacting *o*-Me_3Si-$C_6H_4CH_3$ with the superbase $BuLi/KOC(Et)_2Me$, still contains considerable quantities of *o*-Me_3Si-$C_6H_4CH_2Li$ (at least 10%). This could be due to either incomplete Li−K exchange or insufficient removal of the $LiOC(Et)_2Me$ from *o*-Me_3Si-$C_6H_4CH_2K$ (which seems reasonable considering the very sticky nature of the reaction product).

The crystal structure of [(*o*-Me_3Si-$C_6H_4CH_2)_4La^-$]-$[Li^+\cdot(THF)_4]$ (Figure 1, Table 1) shows a pseudo-S_4-symmetric $(Me_3Si$-$C_6H_4CH_2)_4La^-$ ion in which four benzyl ligands are bound to the La metal in a distorted tetrahedral fashion. Two of the C−La bonds (La−C11 2.668(5) Å, La−C31 2.650(5) Å) are distinctively shorter than the other two (La−C1 2.712(4) Å, La−C21 2.729(5) Å). The benzyl ligands with the longer C−La bonds, however, show a tendency toward η^2-bonding: short distances (2.887(5) and 2.891(4) Å) between C_{ipso} and the La metal are observed. The C_{ipso} atoms of the other benzyl ligands are nearly 3 Å away from La. Also distances between La and the *ortho*-carbon atoms are rather long (range 3.0−3.1 Å). The benzylic hydrogens could not be located and have been calculated; therefore no conclusions on the hybridization states of the benzylic carbons were drawn.

^1H NMR data show that the approximate S_4-symmetry of the $(Me_3Si$-$C_6H_4CH_2)_4La^-$ ion is likely retained

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Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 5-Y, 5-La, 6, 7, and 8

(o-Me_2N-benzyl)$_3$Y (**5-Y**)							
Y−C11	2.471(3)	Y−C12	2.754(3)	C11−Y−N2	89.53(9)	C11−Y−N1	68.6(1)
Y−C21	2.487(3)	Y−C17	2.802(3)	C11−Y−C31	89.7(1)	C21−Y−N2	69.1(1)
Y−C31	2.458(3)	Y−C22	2.788(3)	N2−Y−C31	91.14(9)	C31−Y−N3	68.6(1)
Y−N1	2.555(3)	Y−C27	2.808(3)	N1−Y−C21	92.72(9)		
Y−N2	2.535(2)	Y−C32	2.861(3)	C21−Y−N3	88.32(9)		
Y−N3	2.609(3)	Y−C37	2.919(3)	N1−Y−N3	97.70(9)		
(o-Me_2N-benzyl)$_3$La (**5-La**)							
La−C11	2.635(3)	La−C12	2.853(2)	C11−La−N2	89.42(8)	C11−La−N1	64.64(8)
La−C21	2.661(3)	La−C17	2.881(3)	C11−La−C31	87.99(9)	C21−La−N2	64.58(7)
La−C31	2.638(3)	La−C22	2.886(2)	N2−La−C31	90.66(8)	C31−La−N3	64.87(8)
La−N1	2.695(2)	La−C27	2.899(2)	N1−La−C21	97.15(7)		
La−N2	2.697(2)	La−C32	2.913(2)	C21−La−N3	96.46(8)		
La−N3	2.705(2)	La−C37	2.928(2)	N1−La−N3	102.40(7)		
[(o-Me_3Si-benzyl)$_4La^-$][Li^+·(THF)$_4$] (**6**)							
La−C1	2.712(4)	La−C2	2.887(5)	C1−La−C11	118.9(2)	C11−La−C31	95.3(1)
La−C11	2.668(5)	La−C12	2.982(5)	C1−La−C21	78.4(1)	C21−La−C31	117.1(2)
La−C21	2.729(5)	La−C22	2.891(4)	C1−La−C31	124.0(2)		
La−C31	2.650(5)	La−C32	2.982(5)	C11−La−C21	126.2(2)		
(9-t-BuNSiMe$_2$-fluorenyl)(o-Me_2N-benzyl)Y·(THF) (**7**)							
Y−C1	2.409(3)	Y−O	2.357(2)	C1−Y−N1	67.58(9)	N1−Y−O1	83.22(6)
Y−C10	2.522(2)	Y−C11	2.733(2)	C1−Y−O1	115.80(8)	N1−Y−N2	163.19(7)
Y−N1	2.660(2)	Y−C22	2.763(3)	C1−Y−N2	100.9(1)	O1−Y−N2	91.53(7)
Y−N2	2.233(2)	Y···C2	2.957(3)	N2−Y−C10	69.52(7)		
		Y···C7	3.106(3)				
[(9-t-BuNSiMe$_2$-fluorenyl)YH(THF)2]$_2$ (**8**)							
Y−C1	2.541(9)	Y−H	2.333	C1−Y−N1	69.9(3)	O2−Y−C1	127.4(3)
Y−N1	2.196(8)	Y−H′	2.396	O1−Y−N1	157.1(2)	H−Y−H′	78.3
Y−O1	2.404(5)	Y···C13	3.019(8)	O1−Y−O2	83.1(2)	O1−Y−H	82.7
Y−O2	2.351(7)	Y···C22	3.415(9)	O1−Y−C1	89.3(3)	O1−Y−H′	92.8
		Y···Y′	3.663(3)	O2−Y−N1	101.7(3)		

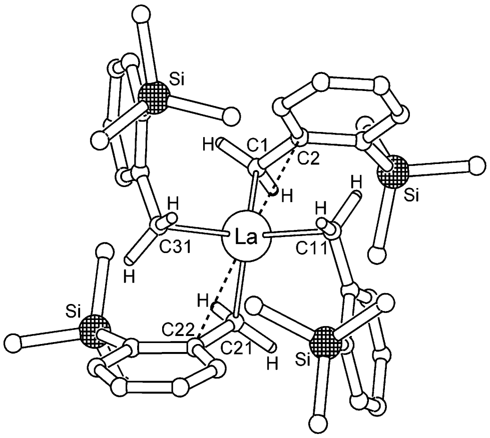

Figure 1. Crystal structure of [(o-Me_3Si-benzyl)$_4La^-$]-[Li^+·(THF)$_4$] (**6**). All hydrogens (except the benzylic H's) have been omitted for clarity.

in solution as well. An unusual high-field shift is observed for the aromatic proton in *ortho*-position of the benzylic CH_2 substituent (δ = 4.76 ppm). Partially negatively charged benzyl ligands normally show the largest high-field shift for the *para*-H.[20] The extraordinary high-field shift for the *ortho*-H in (Me_3Si-C_6H_4-CH_2)$_4La^-$ can be explained by the shielding ASIS effect[21] of the neighboring aromatic ring. In the S_4-symmetric structure of (Me_3Si-$C_6H_4CH_2$)$_4La^-$, all *ortho*-H's are positioned over an aromatic ring: the crystal structure shows H···Aryl$_{center}$ distances in the range 2.49−2.62 Å and C−H···Aryl$_{center}$ angles varying from 165° to 167°.

Reaction of 3 equiv of o-Me_2N-$C_6H_4CH_2K$ with YCl_3 in THF yielded (o-Me_2N-$C_6H_4CH_2$)$_3$Y (**5-Y**) in the form of light yellow crystalline plates (59% yield). The La analogue (**5-La**) could be prepared by a similar procedure and was obtained in the form of light orange crystals (41% yield).

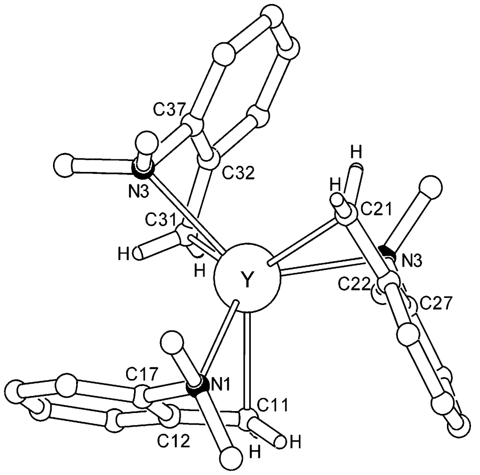

Figure 2. Crystal structure of (o-Me_2N-$C_6H_4CH_2$)$_3$Y (**5-Y**). All hydrogens (except the benzylic H's) have been omitted for clarity. The complex (o-Me_2N-$C_6H_4CH_2$)$_3$La (**5-La**) is isostructural but shows more extensive multihapto bonding to the metal (shorter aryl−metal interactions) than **5-Y**.

The crystal structure of **5-Y** (Figure 2, Table 1) shows a paddle-wheel structure in which Y displays a prismatic coordination. The bidentate C,N ligand has a bite angle of 68.8(1)°. The 3-fold symmetry is broken by the "upside down" coordination of one of the benzyl ligands. This is probably due to steric hindrance between the Me_2N substituents as can be deduced from the bond angles between the ligands. The C−Y−C and C−Y−N bond angles within the triangular faces of the prism

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(N1−C21−N3 and C11−N2−C31) are close to 90°, whereas the N1−Y−N3 angle of 97.7(1)° is significantly larger. The bond distances between Y and the benzylic carbons vary between 2.458(3) and 2.487(3) Å and are significantly shorter than the distances between Y and C_{ipso} or C_{ortho} (range: 2.754(3)−2.919(3) Å).

The crystal structure of **5-La** (Figure 2, Table 1) is isostructural to that of the Y-analogue. The N−metal bonds in **5-La** are on average 0.133 Å longer than those in **5-Y**. This value corresponds well with the 0.132 Å difference in the ionic radii of both metals (the ionic radii for Y^{3+} and La^{3+} are respectively 0.90 and 1.032 Å).[2] The CH_2−metal bonds in **5-La**, however, are on average 0.173 Å longer than those in **5-Y** and thus longer than expected. On the other hand, the distances of La to the C_{ipso} and C_{ortho} atoms are on average only 0.078 Å longer than the corresponding distances in **5-Y**, therefore shorter than expected. This demonstrates a more pronounced multihapto bonding in **5-La**. The average bite angle of 64.7(1)° for the bidentate C,N ligand in **5-La** is smaller than in **5-Y**, which is due to the longer metal−ligand bond distances.

In both structures all hydrogen atoms could be located and refined. This allows a comparison of the hybridization at the benzylic carbons. The sums of the H−C−H and C−C−H angles for the three different benzylic carbons in **5-Y** are 344(2)°, 344(2)°, and 345(2)°. Summation of these angles in **5-La** gives 347(2)°, 347(2)°, and 348(2)°. Both benzyl ligands show a hybridization of the CH_2 group between sp^2 and sp^3, and the benzylic carbon in **5-La** seems slightly more planar (although standard deviations are high, the reproducibility of the values within the complexes is good).

The homoleptic benzyl complex **5-Y** is moderately soluble in aromatic solvents, whereas **5-La** is only slightly soluble in these solvents (a similar solubility was observed in THF). ^1H and ^{13}C NMR data show only one set of signals for the *o*-Me_2N-benzyl group, which means either that the asymmetry of the crystal structure is not retained in solution or that the ligand−metal coordination is dynamic on the NMR time scale. Cooling of the solutions resulted in broadening of the signals, but at −20 °C no splitting of the signals was observed (precipitation of **5-Y** from a diluted solutions in toluene started at −20 °C).

The $^1J_{C-H}$ coupling constants in the benzylic CH_2 groups are a sensitive probe for the hybridization of the benzylic carbon atom.[22] The coupling constant in **5-La** (142.8 Hz) is significantly higher than that in **5-Y** (133.2 Hz), thus confirming the less pyramidal structure of the benzylic carbon in **5-La** as observed in the solid state. This implies that the C−metal bond in **5-La** is more ionic than that in **5-Y**.

The thermal stabilities of the complexes **5-Y** and **5-La** are remarkable. Toluene solutions of these homoleptic compounds can be stored at room temperature for over four months with only negligible decomposition (ca. 3% *o*-Me_2N-toluene is observed). Solutions can also be heated to 75 °C with only minor decomposition (ca. 5% *o*-Me_2N-toluene was observed after heating overnight). Only overnight heating at 100 °C resulted in complete decomposition of the compounds. The remarkable stability of **5-Y** and **5-La** is likely due to the stabilizing intramolecular coordination of the Me_2N substituents.

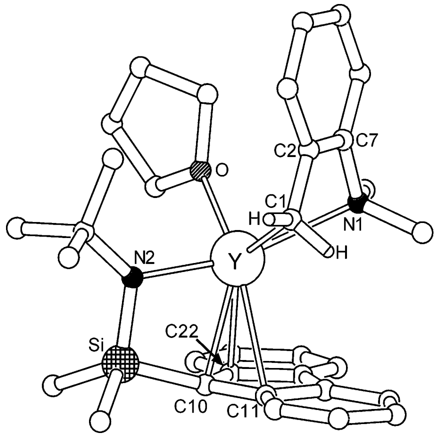
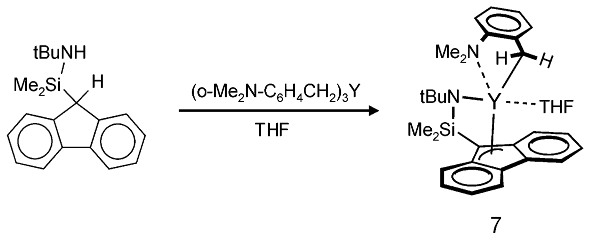
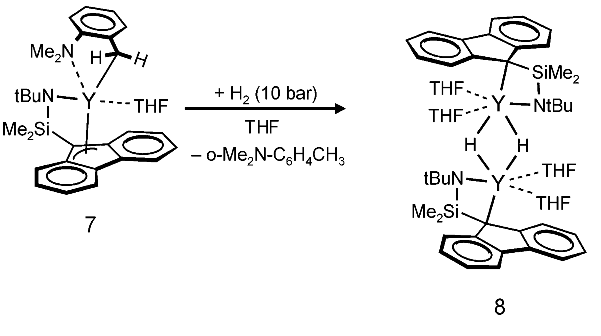


Figure 3. Crystal structure of (9-*t*-BuNSiMe$_2$-fluorenyl)-(*o*-Me_2N-$C_6H_4CH_2$)Y·(THF) (**7**). All hydrogens (except the benzylic H's) have been omitted for clarity.

Although the complexes **5-Y** and **5-La** are stabilized by 3-fold intramolecular N−metal coordination, they are still well-accessible and reactive precursors for the syntheses of a variety of lanthanide complexes. For example, it can be shown that the less reactive yttrium complex **5-Y** is able to deprotonate fluorenes and alkylamines and could be an interesting precursor in the synthesis of constrained geometry catalysts based on lanthanides.[23] Reaction with the ligand 9-*t*-BuN(H)-SiMe$_2$-fluorene in THF produced the heteroleptic benzylyttrium complex **7** in the form of orange crystals in 85% yield (eq 1).



(1)



(2)

The crystal structure (Figure 3, Table 1) shows an allylic coordination mode for the fluorenyl ligand: the

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(22) Hoffmann, D.; Bauer, W.; Hampel; F.; van Eikema Hommes, N. J. R.; Schleyer, P. von R.; Otto, P.; Pieper, U.; Stalke, D.; Wright, D. S.; Snaith, R. *J. Am. Chem. Soc.* **1994**, *116*, 528.

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bond distance Y−C10 (2.522(2) Å) is significantly shorter than the distances to the neighboring C atoms (2.733(2) and 2.763(3) Å). The other two atoms in the five-membered ring are too remote (>3.05 Å) to be considered bonding even though the fluorenyl ring substantially bends toward the metal: the angle between the Si−C10 axis and the five-membered ring is 13.5(1)°. The bite angle of the benzylic C,N ligand (67.58(9)°) is similar to that in **5-Y**. The benzylic CH_2 group is pyramidal with a hybridization close to sp^3: the sum of the H−C−H and C−C−H angles is 337.6°.

The heteroleptic benzylyttrium complex **7** is slightly soluble in benzene at 20 °C. ^1H and ^{13}C NMR spectra show one sharp signal for the diastereotopic Me substituents in the Me_2Si bridge and one set of sharp signals for the diastereotopic sides of the fluorenyl group. Therefore the ligands bound to Y are in fast exchange at room temperature (lower temperatures could not be reached due to the insolubility of the complex).

The heteroleptic benzylyttrium complex **7** can easily be converted in an yttrium-hydrido complex: hydrogenation of **7** with molecular hydrogen (10 bar) gave crystals of the yttrium-hydrido complex **8** in 84% isolated yield (eq 2). The crystals contain several molecules of uncoordinated disordered THF molecules, resulting in poor crystal quality. Nevertheless a structure could be determined and even tentative H atoms were located in the difference Fourier map. The compound crystallizes as a C_2-symmetric dimer in which the hydrogen atoms bridge the Y atoms more or less symmetrically. The Y−H distances (2.33 and 2.39 Å) are significantly longer than reported earlier (cf. 2.18(2) Å for $[(MeCp)_2YH{\cdot}(THF)]_2$), however close to a Y−H bond distance of 2.30(4) Å in a comparable constrained geometry complex $[Me_4CpSi(Me)_2CH_2N(t\text{-}Bu)YH{\cdot}(THF)]_2$.[24] The Y⋯Y′ distance in **8** (3.663(3) Å) is comparable to those in other dimeric yttrium-hydrides with constrained geometry ligands ($[Me_4CpSi(Me)_2CH_2N(t\text{-}Bu)YH{\cdot}(THF)]_2$: Y⋯Y′ = 3.7085(8) Å; $[Me_4CpSi(Me)_2N(t\text{-}Bu)YH{\cdot}(THF)]_2$: Y⋯Y′ = 3.672(1) Å).[23d,24] The ring formed by Y and the hydride atoms is nearly planar, with a small Y−H−Y′−H′ torsion angle of 5.3(1)°. The fluorenyl ligand is coordinated to the Y in η^1-fashion: the neighboring carbon atoms are more than 3 Å away from the metal and do not contribute significantly to the bonding. However, the bite angle of the *ansa*-fluorenyl/amide ligand (C1−Y−N = 69.9(3)°) is similar to that in **7**. Complex **8** is only sparingly soluble at room temperature in THF-d_8. A sharp 1/2/1-triplet for the hydride protons in the ^1H NMR spectrum indicates that the solid state dimer, in which the Y atoms are bridged by two hydride protons, is also retained in solution. The coupling constant $^1J_{Y-H}$ of 29.3 Hz is in the 27.0−35.3 Hz range reported for other dimeric yttrium hydrido complexes.[23e] Broad signals for the diastereotopic sides of the fluorenyl group and two broadened singlets for the diastereotopic Me groups in the Me_2Si bridge are observed in the ^1H NMR spectrum of **8**. This means that at room temperature ligand exchange is slow. Heating the sample to +60 °C results in fast exchange of the diastereopic groups and coalescence of their signals: a set of two doublets and two triplets is observed for the fluorenyl ring, while the Me_2Si group is observed as a broad singlet. Coalescence for the Me_2Si signals is reached at +40 °C ($\Delta G^\ddagger = 14.9$ kcal mol^{-1}).

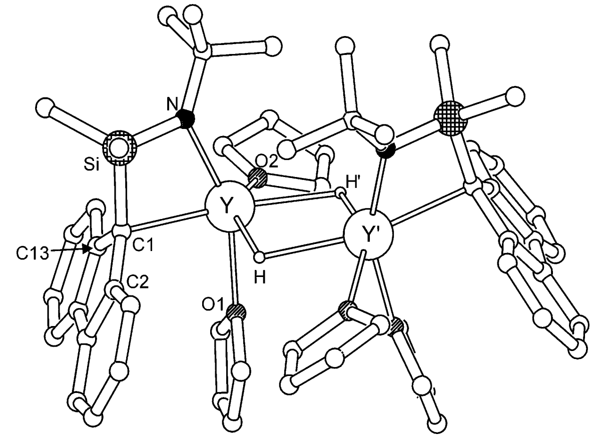

Figure 4. Crystal structure of $[(9\text{-}t\text{-}BuNSiMe_2\text{-fluorenyl})YH{\cdot}(THF)_2]_2$ (**8**). All hydrogens (except the hydrido H) have been omitted for clarity.

The benzyl- and hydrido-lanthanide complexes (**7** and **8**) might be attractive species for numerous catalytic processes. Their broader scope in catalysis is currently under investigation.

Conclusion

Neutral homoleptic tris(o-Me_2N-benzyl)lanthanide complexes can be prepared from the corresponding benzylpotassium and $LnCl_3$ and can be obtained in crystalline purity in reasonable yields. Although these compounds are stabilized by intramolecular $Me_2N{\cdots}Ln$ coordination, the high deprotonating power of the benzyl anion is useful in organolanthanide syntheses. Reaction with C−H and N−H acidic ligands generates a heteroleptic benzyllanthanide compound, which can be converted to a hydride.

Experimental Section

General Comments. All experiments were carried out under argon using predried solvents and Schlenk techniques. o-Me_2N-benzylpotassium was prepared according to our earlier reported procedure.[25] The ligand 9-t-$BuN(H)SiMe_2$-fluorene was prepared according to literature[26] with the exception that the intermediate 9-$ClSiMe_2$-fluorene was isolated and crystallized before reaction with t-$BuNH_2$. o-Me_3Si-toluene was prepared according to the literature.[27] The metal salts $YCl_3{\cdot}(THF)_{3.5}$ and $LaCl_3{\cdot}(THF)_{3.5}$ were also prepared according to literature procedures, and the THF content was determined by C,H analysis.[28,29]

Synthesis of o-Me_3Si-benzylpotassium. n-Butyllithium (2.1 M, 10.0 mL, 21.0 mmol) was added dropwise to a solution of o-Me_3Si-toluene (4.28 g; 26.1 mmol) in THF (25 mL) and potassium 3-methyl-3-pentanolate (3.13 g, 22.4 mmol) precooled at −70 °C (the BuLi was added such that drops float

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Table 2. Crystal Data for the Compounds 5-Y, 5-La, 6, 7, and 8

	5-Y	**5-La**	**6**	**7**	**8**
formula	$C_{27}H_{36}N_3Y_1$	$C_{27}H_{36}N_3La_1$	$[C_{40}H_{60}La_1Si_4]$-$[C_{16}H_{32}Li_1O_4]$	$C_{32}H_{43}N_2O_1Si_1Y_1C_6H_6$	$C_{54}H_{80}N_2O_4Si_2Y_2$-$[C_4H_8O]_4$
MW	491.50	541.50	1087.51	666.79	1343.65
size (mm^3)	0.6 × 0.6 × 0.1	0.5 × 0.4 × 0.3	0.5 × 0.5 × 0.4	0.5 × 0.5 × 0.4	0.5 × 0.4 × 0.2
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a (Å)	16.810(3)	17.102(3)	12.162(1)	11.739(1)	13.341(2)
b (Å)	9.4486(9)	9.4466(9)	12.485(1)	15.907(1)	21.961(5)
c (Å)	16.615(3)	16.649(2)	20.850(2)	18.4633(2)	12.815(3)
α (deg)	90	90	97.414(9)	90	90
β (deg)	111.163(13)	110.079(9)	105.217(8)	98.877(9)	90
γ (deg)	90	90	92.930(9)	90	90
V (Å^3)	2461.0(7)	2526.3(6)	3017.4(6)	3406.5(6)	3755(1)
Z	4	4	2	4	2
ρ (g.cm^{-3})	1.327	1.424	1.197	1.300	1.188
μ(Mo Kα) (mm^{-1})	2.388	1.709	0.827	1.779	1.601
T (°C)	−120	−120	−90	−120	−120
θ(max)	26.1	26.5	25.4	27.0	25.0
no. of unique reflns, R_{int}	4867, 0.033	5244, 0.015	11 167, 0.044	7470, 0.031	4304, 0.068
no. of obsvd reflns ($I > 2\sigma(I)$)	3582	4488	8505	5057	2823
no. of params	424	424	609	584	295
R_1	0.034	0.022	0.049	0.036	0.068
wR_2	0.086	0.053	0.143	0.085	0.193
GOF	1.04	1.06	0.99	1.01	0.97
max./min. resd (e Å^{-3})	−0.62/0.62	−0.64/0.63	−1.40/1.37	−0.40/0.39	−0.74/0.74

along the cooled walls of the Schlenk tube). The solution, which immediately turned dark red, was stirred at −70 °C for ca. 1 h. Subsequently, the solution was slowly warmed to 0 °C and the solvents were removed under vacuum, allowing the temperature to rise to 20 °C in the later stages. The sticky dark red paste was washed five times with 40 mL portions of hexane. The resulting extremely air-sensitive dark red powder was dried under vacuum (40 °C, 1 Torr, 30 min). Yield: 5.10 g (96%). ^{1}H NMR (C_6D_6/THF-d_8, 250 MHz, 20 °C): 0.40 (s, 9H, Me_3Si); 2.97 (s, 1H, CH_2); 3.10 (s, 1H, CH_2); 5.21 (t, 6.3 Hz, 1H, aryl); 5.80 (d, 7.5 Hz, 1H, aryl); 6.35 (t, 7.0 Hz, 1H, aryl); 6.70 (d, 7.0 Hz, 1H, aryl). ^{13}C NMR (C_6D_6/THF-d_8, 62.86 MHz, 20 °C): −1.7 (Me_3Si); 62.9 (CH_2); 96.7; 108.4; 110.2; 112.3; 138.6; 152.9 (aromatics).

Attempted Synthesis of (*o*-Me$_3$Si-benzyl)$_3$La (4-La). A precooled (−50 °C) solution of *o*-Me_3Si-benzylpotassium (1.08 g, 5.34 mmol) in THF (10 mL) was added at once to a suspension of $LaCl_3$·(THF)$_{3.5}$ (0.89 g, 1.78 mmol) in 10 mL of THF of the same temperature. After slowly warming to 20 °C and stirring for 2 h a dark red solution with a little precipitate resulted. All THF was removed under vacuum, and 15 mL of hexane was added. The resulting suspension was centrifuged and the clear red mother liquor was slowly cooled to −30 °C, resulting in the precipitation of a crop of large dark red crystalline blocks. Concentration of the mother liquor resulted in a second crop (combined yields: 0.46 g). X-ray diffraction shows the composition: [(*o*-Me_3Si-benzyl)$_4La^-$][Li^+·(THF)$_4$] (**6**; yield based on *o*-Me_3Si-$C_6H_4CH_2K$: 24%). ^{1}H NMR (THF-d_8, 250 MHz, 20 °C): 0.29 (s, 9H, Me_3Si); 1.65 (sb, 2H, CH_2); 1.76 (m, 16 H, THF); 3.64 (m, 16H, THF); 4.76 (d, 7.5 Hz, 1H, aryl); 6.15 (t, 7.2 Hz, 1H, aryl); 6.80 (t, 7.5 Hz, 1H, aryl); 7.02 (d, 7.0 Hz, 1H, aryl). ^{13}C NMR (C_6D_6/THF-d_8, 62.86 MHz, 20 °C): 0.3 (Me_3Si); 26.3 (THF); 68.1 (THF); 65.9 (CH_2); 112.3; 115.9; 127.5; 134.2; 137.9; 155.4 (aromatics). Anal. Calcd for $C_{56}H_{92}LaLiO_4Si_4$: C 61.85; H 8.53. Found: C 61.31; H 8.21.

Synthesis of (*o*-Me$_2$N-benzyl)$_3$Y (5-Y). A precooled (−50 °C) solution of *o*-Me_2N-benzylpotassium (4.05 g, 30.0 mmol) in THF (20 mL) was added at once to a suspension of YCl_3·(THF)$_{3.5}$ (4.48 g, 10.0 mmol) in THF (20 mL) of the same temperature. The red color of the potassium precursor disappeared immediately, and a yellow-brown suspension resulted. After warming to 20 °C and stirring for 1 h, the suspension was concentrated to about one-third of its original volume and 25 mL of hexane was added. After centrifugation, the mother liquor was isolated and the precipitate was extracted three times with 15 mL portions of a THF/hexane mixture (ratio 1:2). The combined THF/hexane layers were concentrated to ca. 25 mL and slowly cooled to −30 °C. The product crystallized in the form of light yellow plates. Concentration of the mother liquor resulted in a second crop (combined yields: 2.88 g; 59%). ^{1}H NMR (C_6D_6, 250 MHz, 20 °C): 1.63 (s, 2H, CH_2); 2.09 (s, 6H, Me_2N); 6.66 (t, 7.0 Hz, 1H, aryl); 6.82 (d, 7.5 Hz, 1H, aryl); 6.98 (t, 6.8 Hz, 1H, aryl); 7.06 (d, 6.5 Hz, 1H, aryl). ^{13}C NMR (C_6D_6, 62.86 MHz, 20 °C): 44.0 (Me_2N); 45.5 (d, $^1J(^{13}C{-}^{89}Y)$ = 21.0 Hz, CH_2); 117.5; 120.3; 127.6; 129.0; 135.4; 142.1 (aromatics). Anal. Calcd for $C_{27}H_{36}N_3Y$: C 65.98; H 7.38. Found: C 65.68; H 7.28.

Synthesis of (*o*-Me$_2$N-benzyl)$_3$La (5-La). A precooled (−50 °C) solution of *o*-Me_2N-benzylpotassium (4.05 g, 30.0 mmol) in THF (30 mL) was added at once to a suspension of $LaCl_3$·(THF)$_{3.5}$ (4.98 g, 10.0 mmol) in THF (30 mL) of the same temperature. The red color of the potassium precursor disappeared immediately and a yellow-green suspension resulted. After warming to 20 °C and stirring for 1 h, the suspension was centrifugated and the mother liquor was isolated. The precipitate was extracted two times with 10 mL THF portions, and the combined THF fractions were concentrated to ca. 20 mL. Hexane (ca. 5 mL) was added, and the solution was slowly cooled to −30 °C: The product crystallized in the form of light orange plates. Concentration of the mother liquor resulted in a second crop (combined yields: 2.22 g; 41%). ^{1}H NMR (toluene-d_8, 250 MHz, 45 °C): 1.76 (sb, 2H, CH_2); 2.10 (s, 6H, Me_2N); 6.43 (t, 7.0 Hz, 1H, aryl); 6.75−6.87 (m, 3H, aryl). ^{13}C NMR (toluene-d_8, 62.86 MHz, 45 °C): 41.6 (Me_2N); 57.8 (CH_2); 115.0; 121.9; 127.5; 127.7; 132.0; 142.4 (aromatics). Anal. Calcd for $C_{27}H_{36}N_3La$: C 59.89; H 6.70. Found: C 59.72; H 6.48.

Synthesis of (9-*t*-BuNSiMe$_2$-fluorenyl)(*o*-Me$_2$N-benzyl)-Y·(THF) (7). A solution of (*o*-Me_2N-benzyl)$_3$Y (2.34 g, 4.76 mmol) and 9-*t*-BuN(H)$SiMe_2$-fluorene (1.42 g, 4.76 mmol) in THF (20 mL) was stirred for 2 h at 68 °C. Subsequent removal of all solvent under vacuum gave an orange oil, which solidified after adding hexane. The solid was washed twice with 10 mL portions of hexane and then dried under vacuum (0.01 Torr, 70 °C, 5 min). The orange powder was then dissolved in 20 mL of hot benzene. Slowly cooling to +5 °C gave large orange crystals of the product, which crystallized with one C_6H_6 molecule (yield: 2.70 g, 85%). ^{1}H NMR (C_6D_6, 250 MHz, 50 °C): 0.86 (s, 6H, Me_2Si); 0.90 (m, 4H, THF); 1.32 (s, 6H, NMe_2); 1.45 (s, 9H, *t*Bu); 1.68 (d, $^2J(^1H{-}^{89}Y)$ = 1.2 Hz, 2H, CH_2); 2.87 (m, 4H, THF); 6.21 (d, 7.5 Hz, 1H, aryl); 6.31 (t, 7.5 Hz, 1H, aryl); 6.71 (t, 7.2 Hz, 1H, aryl); 6.89 (d, 7.0 Hz, 1H, aryl); 7.22 (t, 7.8 Hz, 2H, fluorenyl); 7.44 (t, 7.9 Hz, 2H, fluorenyl); 8.16 (d, 7.5 Hz, 2H, fluorenyl); 8.25 (d, 7.5 Hz, 2H, fluorenyl). ^{13}C NMR (C_6D_6, 62.86 MHz, 50 °C): 6.1 (Me_2Si); 25.0 (THF); 36.2 (*t*Bu); 42.5 (Me_2N); 46.8 (d, $^1J(^{13}C-^{89}Y) = 31.5$ Hz, CH_2); 54.4 (*t*Bu); 71.5 (THF); 89.9; 117.8; 118.9; 119.5; 199.7; 121.2; 125.1; 127.3; 129.3; 130.9; 139.7; 140.9; 144.7 (aromatics). Anal. Calcd for $C_{32}H_{43}N_2OSiY$: C 65.29; H 7.36. Found: C 65.23; H 7.12.

Synthesis of [(9-*t*-BuNSiMe$_2$-fluorenyl)YH·(THF)$_2$]$_2$ (8). A solution of (9-*t*-BuNSiMe$_2$-fluorenyl)(*o*-Me$_2$N-benzyl)Y·(THF) (**7**) (1.24 g, 2.08 mmol) in 25 mL of benzene was stirred for 7 h in an autoclave under H_2-pressure (10 bar) at 70 °C. After the hydrogenolysis, all solvent was removed and the yellow-orange solid residue was washed with 15 mL of hexane and subsequently dried under vacuum (0.01 Torr, 50 °C, 10 min). The yellow-orange powder was dissolved in 8 mL of hot THF, and the solution was slowly cooled to −30 °C. The product crystallized in the form of large yellow plates, which were crushed and subjected to vacuum (0.01 Torr, 10 min) to remove THF enclosed in the crystal lattice (yield: 0.92 g, 84%). ^{1}H NMR (THF-d_8, 250 MHz, 60 °C): 0.35 (sb, 6H, Me_2Si); 1.57 (s, 9H, *t*Bu); 1.75 (m, 8H, THF); 3.64 (m, 8H, THF); 6.36 (t, $^1J(^1H-^{89}Y) = 29.3$ Hz, Y-H); 6.85 (t, 7.2 Hz, 2H, fluorenyl); 7.13 (t, 7.2 Hz, 2H, fluorenyl); 7.83 (d, 7.5 Hz, 2H, fluorenyl); 7.95 (d, 7.5 Hz, 2H, fluorenyl). ^{13}C NMR data could not be recorded due to the low solubility of the complex and broad signals as a consequence of dynamic processes. Anal. Calcd for $C_{54}H_{80}N_2O_4Si_2Y_2$: C 61.47; H 7.64. Found: C 61.82; H 7.83.

Crystal Structures. Crystal diffraction data were measured on an Enraf-Nonius CAD4 diffractometer (crystal data are given in Table 2). All crystal structures were solved with DIRDIF[30] and refined with SHELXL-97.[31] In all cases absorption correction was applied using the psi-scans method incorporated in PLATON,[32] which was also used for geometry calculations and graphics. For the structures **5-Y**, **5-La**, and **7**, all hydrogen atoms have been observed and were refined isotropically. All hydrogens in **6** and those in **8** (except for the hydride hydrogen) have been calculated and were refined in a riding mode.

The crystal structure of **6** contains a $Li^+ \cdot (THF)_4$ ion in which one of the THF ligands shows severe ring-puckering disorder, which could not be resolved and was refined with large anisotropical displacement parameters. The maximum and minimum residual electron densities are in the area of the disordered THF molecule.

Crystals of **8** are extremely brittle and contain large voids, which are filled with disordered noncoordinating THF molecules (as confirmed by NMR analysis). The disorder of these THF molecules could not be solved and was therefore treated with the bypass method using the SQUEEZE procedure[33] incorporated in PLATON. The asymmetric unit contained ca. 3.5 molecules of disordered THF (electron count = 109).

Acknowledgment. The author is grateful to the DFG for supporting this research within the AM^2-network (a German-Canadese cooperation on polymerization chemistry).

Supporting Information Available: All crystallographic information for **5-Y**, **5-La**, **6**, **7**, and **8** (bond distances and angles, crystal data, refinement details, ORTEP plots) is available free of charge via the Internet at http://pubs.acs.org.

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