# Strategies for the Synthesis of Lanthanum Dialkyl Complexes with Monoanionic Ancillary Ligands

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The synthesis of lanthanum dialkyl complexes with monoanionic ancillary ligands $[L]^-$ is pursued by three different strategies: (a) in situ peralkylation of $LaBr_3(THF)_4$ with 3 equiv of $LiCH_2SiMe_3$ followed by reaction with LH; (b) reaction of isolated $La(CH_2Ph)_3(THF)_3$ with LH; (c) stepwise salt metathesis on $LaBr_3(THF)_4$. Methods (a) and (b) generally work well for triazacyclononane-amide and amidinate ligands, but are unsuitable for the sterically demanding $\beta$-diketiminate $[HC(MeCNAr)_2]^-$ (Ar = 2,6-$i$$Pr_2C_6H_3$) due to its high affinity for the Li cation and the sluggish reactivity of the diketimine. Nevertheless, the $\beta$-diketiminate lanthanum dibenzyl complex $[HC(MeCNAr)_2]La(CH_2Ph)_2(THF)$ could be obtained by first reacting $LaBr_3(THF)_4$ with $K[HC(MeCNAr)_2]$ to form $[HC(MeCNAr)_2]LaBr_2(THF)_2$ and subsequent reaction of this dibromide complex with 2 equiv of $PhCH_2K$. When this reaction mixture is warmed, the product decomposes by H-abstraction from one of the diketiminate methyl groups and ligand redistribution, forming the coordination polymer $\{[\mu\text{-}\eta^2{:}\eta^1\text{-}ArNC(Me)CHC(CH_2)NAr]_2La[K(THF)_4]\}_\infty$.

## Introduction

Nonmetallocene organo-rare-earth metal (Ln) complexes are developing into an interesting class of catalysts for a variety of transformations such as hydroamination and olefin polymerization.[1] As the metal ionic radius is an important tunable parameter for these metals (for the $Ln^{3+}$ ions they vary from 0.74 Å for Sc to 1.03 Å for La, CN = 6),[2] versatile synthetic procedures that can access related compounds over the full metal size range are useful for finding the optimal ligand–metal ion combination for catalysis. The use of classic salt metathesis synthesis protocols for these metals can encounter several problems, such as metal halide occlusion, the formation of ate-complexes, and facile ligand redistribution.[3] These problems are especially severe for the larger metals in the series. One way to avoid these difficulties is the alkane elimination route, in which a homoleptic rare-earth metal alkyl $LnR_3(THF)_x$ is reacted with ligands that contain active protons (H**L**). Several types of homoleptic rare-earth metal alkyl species are known, such as $[LnMe_3]_n$ (Ln = Y, Lu)[4] and $Ln[CH(SiMe_3)_2]_3$,[5] $Ln(CH_2\text{-}C_6H_4\text{-}NMe_2\text{-}o)_3$,[6] and $Ln(CH_2SiMe_3)_3(THF)_2$.[7] Nevertheless, not all of these are suitable for this purpose, and only the tris(trimethylsilylmethyl) complexes have been extensively used for alkane elimination reactions.[8] These are only available for the small and intermediate size metals (Ln = Sc−Sm); attempts to isolate $Ln(CH_2SiMe_3)_3(THF)_x$ for the larger metals (Ln = Nd−La) have failed so far. Recently, we described an in situ alkylation procedure for the larger metals Nd and La,[9] as well as the synthesis of a well-defined tribenzyl complex for the largest of the rare-earth metals, lanthanum, $La(CH_2Ph)_3(THF)_3$.[10] In this contribution we provide a comparison of synthesis strategies for organometallics of lanthanum, showing advantages and disadvantages of the various methods, using the ligand systems H**L** shown in Chart 1.

## Results and Discussion

**In Situ Peralkylation.** In the in situ peralkylation procedure, $LaBr_3(THF)_4$ is reacted with 3 equiv of $LiCH_2SiMe_3$ in THF,

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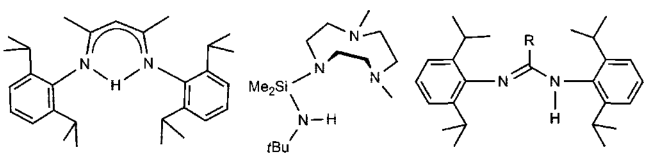
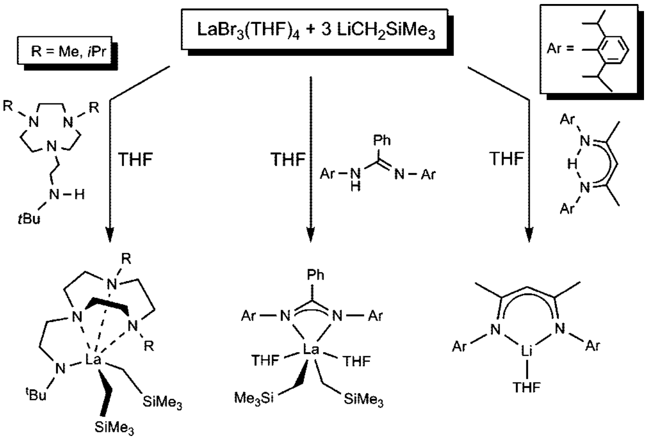
**Chart 1**



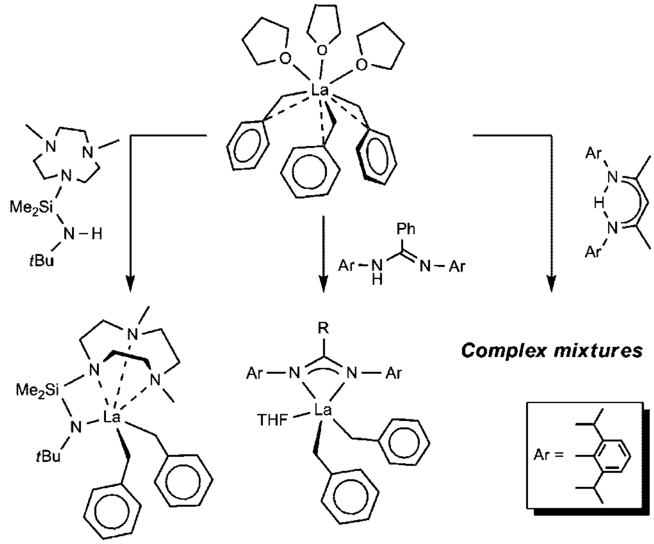
HL**1** HL**2** R = Ph (HL**3a**), *t*Bu (HL**3b**)

**Scheme 1**




followed by addition of a ligand with an active proton (H**L**) and extraction with an apolar solvent to give (**L**)La($CH_2SiMe_3$)$_2$(THF)$_n$ species (Scheme 1), albeit in rather moderate isolated yield (33–48%).[11] The relatively low isolated yields from this procedure might be related to the nature of the species actually formed in the in situ alkylation. To evaluate this, we monitored the reaction of $LaBr_3(THF)_4$ with 3, 4, and 5 equiv of $LiCH_2SiMe_3$ (LiR) in THF-$d_8$ by $^1$H NMR spectroscopy.[12] Upon addition of 3 equiv of LiR, the alkyl methylene protons show a rather broad resonance at $\delta$ −0.93 ppm, considerably downfield from the $\delta$ −2.3 ppm of LiR itself. Addition of a fourth equivalent of LiR leads to a slight upfield shift ($\delta$ −1.0 ppm) and a sharpening of the resonance, whereas addition of a fifth equivalent leads to renewed broadening and a further upfield shift to $\delta$ −1.3 ppm. This suggests that (a) the system is highly dynamic, with rapid interconversion of different alkyl species in solution and (b) that the thermodynamically most favorable species in the system probably has a La:R stoichiometry of 1:4. For smaller rare-earth metals, anionic $[Ln(CH_2SiMe_3)_4]^-$ species have been isolated.[13] Reaction of $LaBr_3(THF)_4$ with 4 equiv of LiR in THF, followed by addition of the benzamidine PhC(NAr)(NHAr) (Ar = 2,6-$i$Pr$_2$C$_6$H$_3$, H**L3a**, see Chart 1) and pentane extraction, afforded no pentane-soluble products, whereas the corresponding reaction using 3 equiv of LiR afforded the benzamidinate complex (**L3a**)La($CH_2SiMe_3$)$_2$(THF)$_2$[11c] in 33% isolated yield. A $^1$H NMR spectrum of the pentane-insoluble material in THF-$d_8$ suggested the presence of two (**L3a**)La(alkyl) species, the main product (80%) showing a ligand-to-alkyl ratio of 1:3, suggesting the formation of [(**L3a**)La($CH_2SiMe_3$)$_3$] anion. These results indicate that, although the in situ alkylation procedure has given us a first opportunity to obtain (**L**)Ln($CH_2SiMe_3$)$_2$ species for the largest rare-earth metals, the formation of ionic species in the alkylation step results in modest isolated yields of the desired neutral dialkyl complexes.

**Scheme 2**




**2** R = Ph (**3a**), *t*Bu (**3b**)

Another limitation of the method was revealed in attempts to extend this synthesis protocol to the $\beta$-diketimine H[HC-(MeCNAr)$_2$] (H**L1**, Ar = 2,6-$i$Pr$_2$C$_6$H$_3$).[14] This led only to the isolation of the Li-diketiminate complex (**L1**)Li(THF)[15] in high yield (Scheme 1). Monitoring the reaction in THF-$d_8$ by NMR spectroscopy showed that this product is formed quantitatively. This shows that the in situ alkylation procedure is unsuccessful when the affinity of the ligand for lithium is particularly high. Thus, for the synthesis of (**L1**)La(alkyl)$_2$(THF)$_x$ species a different strategy is required.

**Use of La($CH_2Ph$)$_3$(THF)$_3$ as Precursor.** Reaction of La($CH_2Ph$)$_3$(THF)$_3$ (**1**) with the silylamino-substituted triazacyclononane Me$_2$TACN(SiMe$_2$)NH$t$Bu (H**L2**)[16] led to the clean formation of the monomeric, THF-free lanthanum dibenzyl complex (**L2**)La($CH_2Ph$)$_2$ (**2**, Scheme 2), which was isolated in 65% yield after crystallization. Earlier attempts to generate the analogous trimethylsilylmethyl complex (**L2**)La($CH_2SiMe_3$)$_2$ via the in situ alkylation approach mentioned above afforded the dinuclear complex {[($\mu$-CH$_2$)MeTACN(SiMe$_2$)N$t$Bu]La-($CH_2SiMe_3$)}$_2$,[16] which derives from intermolecular metalation of one of the TACN methyl substituents. The benzyl groups in **2** thus appear to stabilize the compound toward ligand deprotonation. The molecular structure of **2** was determined by X-ray diffraction (Figure 1, Table 1). When compared to typical La−CH$_2$−Si angles (126–142°) in (TACN-amide)La-CH$_2$SiMe$_3$ complexes,[16,17] the La−C(22)−C(23) angle of 94.8(2)° and

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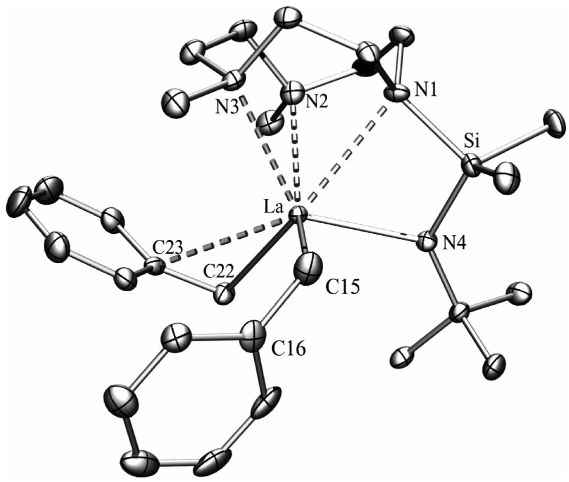


**Figure 1.** Molecular structure of **2** (ellipsoid probability level at 50%).

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 2**

| | |
|---|---|
| Bond Lengths | |
| La−C15 | 2.699(4) |
| La−C22 | 2.687(4) |
| La−C23 | 3.150(4) |
| La−N1 | 2.741(3) |
| La−N2 | 2.744(3) |
| La−N3 | 2.714(3) |
| La−N4 | 2.384(3) |
| Bond Angles | |
| La−C15−C16 | 98.6(3) |
| La−C22−C23 | 94.8(2) |
| N1−Si−N4 | 99.43(15) |
| N4−La−C15 | 88.06(13) |
| N4−La−C22 | 110.5(1) |

La−C(15)−C(16) angle of 98.6(3)° suggest additional $\eta^2$-like interaction of the benzyl group with the metal center in **2**. This may be the reason for the enhanced thermal stability of **2** over the trimethylsilylmethyl analogue. The structure of **2** shows a distorted octahedral geometry, with the three nitrogen atoms of the TACN moiety coordinated in a facial arrangement to lanthanum, with average La−N distances of 2.74 Å. The compound in the solid state is asymmetric, as seen in the difference between the two N(4)−La−$CH_2$ angles of 88.06(13)° for C15 and 110.5(1)° for C22. This asymmetry is similar to that of the related trimethylsilylmethyl derivatives of rare-earth metals. Nevertheless, the NMR (THF-$d_8$) spectra of **2** are consistent with an average $C_s$ symmetry, even down to −60 °C, with a broad $^1$H $LaCH_2$ resonance at $\delta$ 1.96 ppm and its $^{13}$C resonance at $\delta$ 66.8 ($^1J_{CH}$ = 133.6 Hz). Thus **2** appears to be more flexible in its geometry than related trimethylsilylmethyl derivatives.[11a]

We showed earlier that $La(CH_2Ph)_3(THF)_3$ (**1**) reacts smoothly with the sterically demanding benzamidine H[PhC(NAr)$_2$] (H**L3a**, Ar = 2,6-*i*Pr-$C_6H_3$) to afford (**L3a**)La$(CH_2Ph)_2$(THF) (**3a**).[10] The more sterically hindered amidine H[*t*BuC(NAr)$_2$] (H**L3b**), with a *tert*-butyl substituent on the backbone,[18] also leads to the corresponding amidinate dibenzyl complex (**L3b**)La$(CH_2Ph)_2$(THF) (**3b**) with concomitant elimination of 1 equiv of toluene. The isolated yield of **3b** from crystallization of 60% is somewhat lower than for **3a** (70%) due to the higher solubility of the former. Performing the reaction on an NMR tube scale in THF-$d_8$ showed that the reaction proceeds quantitatively. A crystal structure determination of **3b** (Figure 2, Table 2) reveals that both benzyl groups are $\eta^2$-bound to lanthanum, with the La−C130−C131 angle of 85.01(19)° noticeably smaller than the La−C137−C138 angle of 92.9(2)°. This contrasts with the presence of one $\eta^3$-benzyl and one $\eta^2$-benzyl group in **3a**. The difference is possibly caused by the steric demand of the *t*Bu group on the ligand backbone, which is reflected in the larger C−N−C(Ar) angles in **3b** of 129.4(3)° (C113−N11−C11) and 129.8(3)° (C113−N12−C118) versus the equivalent angles of 128.3(4)° and 124.3(3)° in **3a**.

The increased steric demand of **L3b** versus **L3a** is seen even more clearly in the structure of the cationic monobenzyl derivative [(**L3b**)La$(CH_2Ph)(THF)_3$][$BPh_4$] (**4**), which was obtained by reaction of **3b** with [$HNMe_2Ph$][$BPh_4$] in THF. Its structure (Figure 3, Table 3) shows the presence of three coordinated THF molecules and an $\eta^1$-bound benzyl group (La−$CH_2$−C = 132(3)°). It can be readily compared with the alkyl cation [(**L3a**)La$(CH_2SiMe_3)(THF)_4$]$^+$ (**5**) reported previously.[11c] The latter carries four, instead of three, coordinated THF molecules, revealing the increased steric demand of the ligand **L3b** relative to **L3a**. A comparison of the key bond angles within the [RC(NAr)$_2$]La core of the neutral (**3a**, **3b**) and cationic (**4**, **5**) complexes is shown in Figure 4.

Despite the success of the tribenzyl complex **1** in the synthesis of various derivatives, it still does not provide access to the lanthanum dibenzyl complex of the $\beta$-diketiminate ligand **L1**. The reaction of **1** with the diketimine H**L1** in THF-$d_8$ at ambient temperature is slow compared to the reactions described above, which are essentially instantaneous. After 6 h (with agitation of the mixture, as **1** is relatively poorly soluble) approximately 50% of H**L1** is consumed, as seen from the resonance of the acidic proton at $\delta$ 12.07 ppm. New resonances are observed, partly attributable to the expected (**L1**)La$(CH_2Ph)_2$(THF) species (vide infra), but also arising from gradual decomposition of this product. After full conversion of H**L1** (after 12 h), the $^1$H NMR spectrum is complex, showing that this is an inconvenient method for the synthesis of the $\beta$-diketiminate dibenzyl species.

**Salt Metathesis.** The problems observed above in the synthesis of $\beta$-diketiminate La dialkyl compounds are reminiscent of reported unsuccessful attempts to prepare (**L1**)yttrium dialkyl complexes via alkane and amine elimination as well as salt metathesis starting from $YCl_3$.[19] However, reaction of $YI_3(THF)_{3.5}$[20] with K**L1** afforded (**L1**)$YI_2$(THF),[19,21] which served to generate the dialkyl complex (**L1**)Y$(CH_2SiMe_3)_2$(THF).[19] Thus we pursued the synthesis of (**L1**)La$(CH_2Ph)_2$(THF) via sequential salt metathesis. Reaction of $LaBr_3(THF)_4$ with K**L1** in THF afforded (**L1**)La$Br_2(THF)_2$ (**6**) as yellow crystals in 76% isolated yield. A single-crystal X-ray structure determination of **6** (Figure 5 and Table 4) shows the complex to be monomeric with a distorted octahedral geometry around the metal center. The ligand nitrogen and the THF oxygen atoms N(1), N(1a), O(1), and O(1a) occupy the equatorial positions and Br(1) and Br(2) the axial sites. A crystallographic mirror plane is present through C(15), La, Br(1), and Br(2). The structure of **6** is related to that of [HC-

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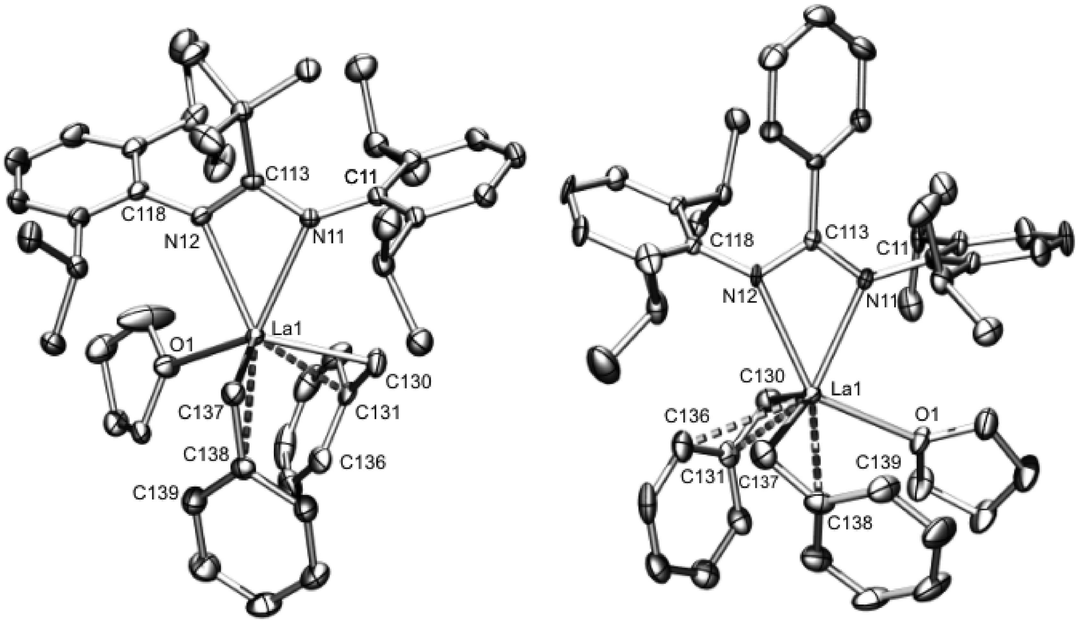


**Figure 2.** Molecular structure of **3b** (left) and **3a** (right) (ellipsoid probability level at 50%).

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 3b in Comparison to 3a**

| | 3b | 3a |
|---|---|---|
| Bond Lengths | | |
| La(1)−C(130) | 2.595(3) | 2.590(5) |
| La(1)−C(131) | 2.850(3) | 2.897(5) |
| La(1)−C(136) | 3.267(3) | 3.030(3) |
| La(1)−C(137) | 2.585(3) | 2.632(3) |
| La(1)−C(138) | 3.029(3) | 2.847(5) |
| La(1)−C(139) | 3.421(3) | 3.401(5) |
| La(1)−N(11) | 2.540(2) | 2.497(3) |
| La(1)−N(12) | 2.507(3) | 2.581(3) |
| La(1)−O(1) | 2.610(2) | 2.557(3) |
| Bond Angles | | |
| La(1)−C(130)−C(131) | 85.01(19) | 87.0(3) |
| La(1)−C(137)−C(138) | 92.9(2) | 83.3(2) |
| C(11)−N(11)−C(113) | 129.4(3) | 128.3(4) |
| C(118)−N(12)−C(113) | 129.8(3) | 124.3(3) |

$(MeCNPh)_2]GdBr_2(THF)_2$,[22] which has sterically less demanding substituents on the diketiminate nitrogen atoms. In the latter compound, the gadolinium is located in the plane defined by the NCCCN ligand backbone. In **6** the lanthanum center is located out of plane by 0.7347(3) Å. This puckered geometry is similar to that of scandium and yttrium complexes with $\beta$-diketiminates containing the 2,6-diisopropylphenyl substituents.[23] The steric demand of the ligand **L1** is illustrated by the comparison of six-coordinate **6** with lanthanum dibromide complexes of N,N-bidentate amidinate and aminopyrimidinato ligands,[24] which are seven-coordinate due to the presence of an additional THF ligand.

The lanthanum dibromide **6** was then used in subsequent alkylation reactions. Lithium alkyl reagents were avoided in view of the high affinity of **L1** anion to the lithium cation (as described above and elsewhere[19]). Nevertheless, reaction of **6** with methyl magnesium chloride in THF also led to quantitative ligand transfer from lanthanum to magnesium to generate the known compound (**L1**)MgMe(THF).[25] In contrast, reaction of the dibromide **6** with 2 equiv of $PhCH_2K$ in THF resulted in formation of the desired complex (**L1**)$La(CH_2Ph)_2(THF)$ (**7**, Scheme 3), which was isolated as analytically pure material by crystallization from a 3:1 hexane/THF mixture in 46% yield. Although crystals of sufficient quality for an X-ray structure determination could not be obtained, the NMR spectroscopic features of **7** are consistent with its formulation. The resonances of the ligand methyne group are found at $\delta$ 5.25 ppm ($^1$H) and $\delta$ 96.6 ppm ($^{13}$C; d, $J_{CH} = 154$ Hz) and those of the La-$CH_2$ groups at $\delta$ 1.35 ppm ($^1$H) and $\delta$ 70.3 ppm ($^{13}$C; t, $J_{CH} = 131$ Hz). The dibenzyl complex **7** reacts in THF-$d_8$ with the Brønsted acid $[HPhNMe_2][BPh_4]$ under liberation of toluene and the formation of the ionic monobenzyl species [(**L1**)$La(CH_2Ph)$(THF-$d_8)_x$]$[BPh_4]$, as seen by NMR spectroscopy. The La-$CH_2$

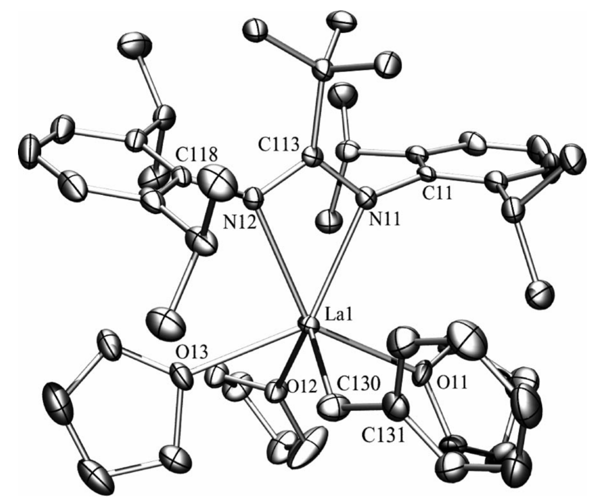


**Figure 3.** Molecular structure of **4** (ellipsoid probability level at 50%, anion is omitted).

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**Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 4**

| | |
|---|---|
| Bond Lengths | |
| La(1)−C(130) | 2.503(5) |
| La(1)−N(11) | 2.492(3) |
| La(1)−N(12) | 2.563(3) |
| La(1)−O(11) | 2.582(3) |
| La(1)−O(12) | 2.564(3) |
| La(1)−O(13) | 2.559(3) |
| Bond Angles | |
| La(1)−C(130)−C(131) | 132.0(3) |
| C(11)−N(11)−C(113) | 129.2(3) |
| C(118)−N(12)−C(113) | 130.0(3) |

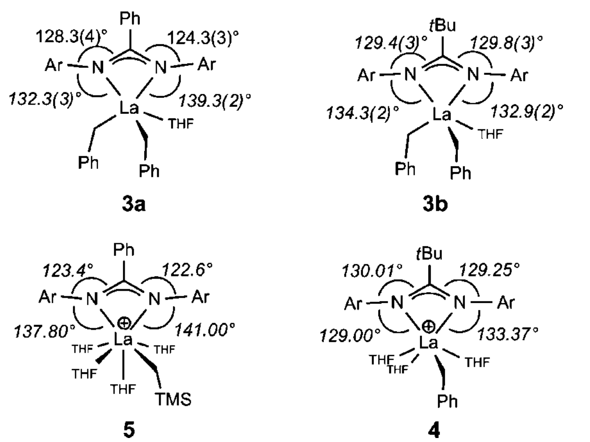



**Figure 4.** Schematic representation of the core structures of the neutral (**3a**, **3b**) and cationic (**4**, **5**) compounds.

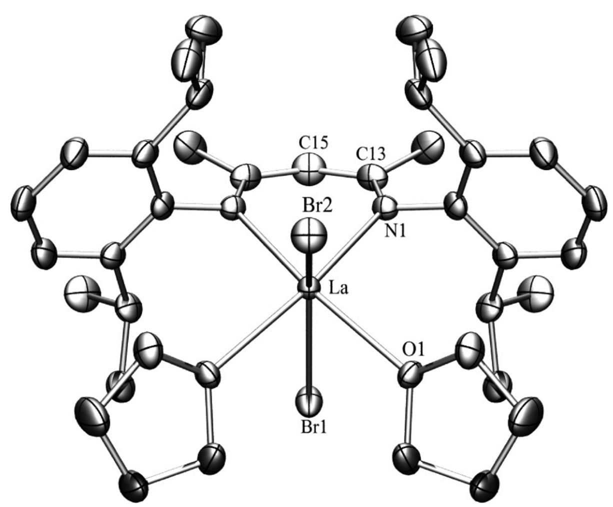



**Figure 5.** Molecular structure of **6** (ellipsoid probability level at 50%).

resonances in the cation at $\delta$ 1.61 ppm ($^1$H) and $\delta$ 77.2 ppm ($^{13}$C; t, $J_{CH}$ = 134 Hz) show typical downfield shifts, relative to the precursor **7**, associated with the formation of a cation.[10,11]

When monitoring the reaction of **6** with 2 equiv of $KCH_2Ph$ in THF-$d_8$ by NMR spectroscopy, it was observed that initial precipitation of KBr and formation of **7** is followed by a slow decomposition reaction in which toluene is released and a new compound is formed with a complex $^1$H NMR spectrum. Four inequivalent ligand *i*Pr groups appear to be present (four methyne septets and eight methyl doublets), but only a single ligand backbone methyne resonance ($\delta$ 5.19 ppm). The presence of three resonances in a 3:1:1 ratio, at $\delta$ 1.67 ppm (s), 2.78 and 2.07 ppm (both d, $J$ = 2.4 Hz)

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 6**

| | |
|---|---|
| Bond Lengths | |
| La−N(1) | 2.470(3) |
| La−Br(1) | 2.8592(9) |
| La−Br(2) | 2.9025(9) |
| La−O(1) | 2.592(3) |
| Bond Angles | |
| Br(1)−La−Br(2) | 149.89(2) |
| O(1)−La−O(1)′ | 91.25(10) |
| N(1)−La−Br(1) | 93.50(7) |
| N(1)−La−Br(2) | 110.39(7) |

respectively, suggests that one of the ligand backbone methyl groups has been deprotonated. From a 0.2 mmol scale reaction, performed at 80 °C, crystalline material was obtained that allowed X-ray diffraction. Although the crystal quality was poor, the composition and connectivity of the product was unequivocally established. It can be formulated as [(**L1**-H)$_2$La][K(THF)$_4$] (**8**, Figure 6), and its structure in the solid state is a coordination polymer of the type {[$\mu$-$\eta^2$:$\eta^1$-ArNC(Me)CHC(CH$_2$)NAr]$_2$La[K(THF)$_4$]}$_\infty$, in which [(**L1**-H)$_2$La] anions are bridged via the methylene groups of the deprotonated ligands to [K(THF)$_4$] cations in which the K ions are distorted octahedrons with the ligand methylene groups in the axial positions. The decomposition reaction thus involves deprotonation of the diketimine methyl group and a ligand redistribution. Very recently such a combination of ligand deprotonation and ligand redistribution was described for the reaction of (**L1**)YI$_2$(DME) with 2 equiv of $KCH_2SiMe_3$ to yield {[$\mu$-$\eta^5$:$\eta^1$-ArNC(Me)CHC(CH$_2$)NAr]$_2$-Y[K(DME)$_2$]}.[21] This product differs from **8** in its solid state structure in that it is monomeric, with the K ion interacting with the arene groups of the ligand rather than with the deprotonated methyl group.

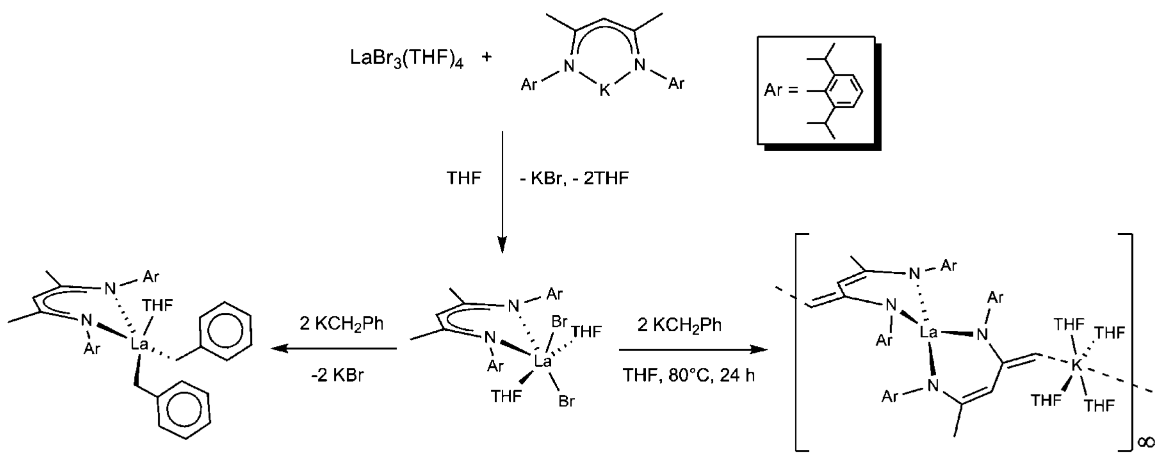
## Conclusions

We have applied three different synthesis routes to the preparation of lanthanum dialkyl complexes of three types of monoanionic ancillary ligand. The in situ alkylation procedure of LaBr$_3$(THF)$_4$ with 3 equiv of trimethylsilylmethyl lithium works well for triazacyclononane-amide and sterically demanding amidinate ligands, although isolated yields are moderate (at best up to 50%). This may be due to the predominant formation of [LaR$_4$]$^-$ species in the alkylation, although the alkyl groups appear to redistribute readily in this highly dynamic reaction mixture. The method fails when ligands with a very high affinity for Li$^+$ are used (in casu a sterically demanding $\beta$-diketiminate). An alternative could be the use of alkylpotassium reagents in the in situ alkylation process, this still needs to be investigated. The use of the preformed trialkyl La(CH$_2$Ph)$_3$(THF)$_3$ in combination with ligands with active protons H**L** affords very smooth and clean reactions, provided the H**L** species is sufficiently reactive. For the sterically demanding $\beta$-diketiminate ligand, the best option is stepwise salt metathesis (first introducing the ligand on the metal, then the alkyl groups), using potassium reagents exclusively. The observations made in this study can be useful for the identification of successful synthesis protocols for new organometallic compounds of the larger rare-earth metals.

## Experimental Section

**General Considerations.** All experiments were carried out under an inert atmosphere of purified N$_2$ using standard Schlenk and

**Scheme 3**




glovebox techniques, unless mentioned otherwise. Toluene, pentane, diethyl ether, and THF were distilled from Na or Na/K alloy before use or purified by percolation under a nitrogen atmosphere over columns of alumina, molecular sieves, and supported copper oxygen scavenger (BASF R3-11). Benzene-$d_6$ and THF-$d_8$ were dried over Na/K alloy and vacuum-transferred before use. Bromobenzene-$d_5$ was degassed and dried over $CaH_2$. H[HC(MeCNAr)$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, H**L1**),[14] Me$_2$TACNSiMe$_2$NH*t*Bu (H**L2**),[8e] Me$_3$SiCH$_2$Li,[26] LaBr$_3$(THF)$_4$,[27] KCH$_2$Ph,[28] H[RC(N-2,6-*i*Pr-C$_6$H$_3$)$_2$] (R = Ph,[8g] H**L3a**; *t*Bu,[29] H**L3b**), and La(CH$_2$Ph)$_3$(THF)$_3$[10] (**1**) were prepared according to published procedures. [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (Strem) was used as purchased. NMR spectra were recorded on Varian Unity 500, VXR 300, and Gemini 200 spectrometers. Elemental analyses were performed at the Microanalytical Department of H. Kolbe (Mülheim an der Ruhr).

**In Situ Alkylation of LaBr$_3$(THF)$_4$.** A mixture of LaBr$_3$(THF)$_4$ (66 mg, 0.1 mmol) and 3 equiv of LiCH$_2$SiMe$_3$ (28 mg, 300 $\mu$mol) was dissolved in THF-$d_8$ at ambient temperature. $^1$H NMR (500 MHz, THF-$d_8$, 20 °C): $\delta$ −0.21 (s, 27H, Si*Me*$_3$), −0.93 (s br, 6H, C*H*$_2$Si). $^{13}$C{$^1$H} NMR (125.8 MHz, THF-$d_8$, 20 °C): $\delta$ 49.0 (br, *C*H$_2$Si), 5.69 (Si*Me*$_3$). In similar fashion, samples with La:Li ratios 1:4 and 1:5 were made. Their $^1$H NMR spectra are shown in the Supporting Information.

**Reaction of LaBr$_3$(THF)$_4$/4 LiCH$_2$SiMe$_3$ with HL3a.** Solid LiCH$_2$SiMe$_3$ (188 mg, 2.00 mmol) was added to a suspension of LaBr$_3$(THF)$_4$ (335 mg, 0.50 mmol) in THF (20 mL) at ambient temperature. The colorless solution was stirred for 2 h, after which [PhC(N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$]H (H**L3a**, 220 mg, 0.50 mmol) was added. The resulting yellowish solution was stirred for 2 h, after which the volatiles were removed under vacuum. Residual THF was removed from the solids by stirring with pentane (10 mL), which was subsequently removed under vacuum. Attempts to extract the mixture with pentane (2 × 50 mL) did not afford any soluble product. Analysis of the residue by $^1$H NMR in THF-$d_8$ showed the presence of two compounds in a 4:1 ratio, as evidenced by two sets of signals attributable to the amidinate resonances. The major product appears to be an ionic species containing the {[PhC(N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$]La(CH$_2$SiMe$_3$)$_3$} anion. $^1$H NMR (300 MHz, THF-$d_8$) major product: $\delta$ 6.80 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, C$_6$H$_3$), 6.6 (m, 5 H, Ph), 6.55 (d, $^3J_{HH}$ = 7.2 Hz, 4 H, C$_6$H$_3$), 3.41 (sept, $^3J_{HH}$ = 6.5 Hz, 4 H, C*H*Me$_2$), 1.09 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, CH*Me*$_2$), 0.68 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, CH*Me*$_2$), −0.18 (s, 27 H, CH$_2$Si*Me*$_3$), −1.15 (s, 6 H, C*H*$_2$SiMe$_3$).

**Reaction of LaBr$_3$(THF)$_4$/3 LiCH$_2$SiMe$_3$ with HL1.** Solid LiCH$_2$SiMe$_3$ (280 mg, 3.00 mmol) was added to a suspension of LaBr$_3$(THF)$_4$ (0.66 g, 1.00 mmol) in THF (10 mL, ambient temperature). Within 5 min a colorless solution had formed. The solution was stirred for 30 min, after which H**L1** (0.42 g, 1.00 mmol) was added. The resulting yellowish solution was stirred for 18 h, after which the volatiles were removed under vacuum. The mixture was extracted with a pentane/toluene mixture (1:1, 50 mL). The obtained extract was evaporated to dryness, yielding (**L1**)Li(THF),[15] identified by NMR spectroscopy, as light yellowish crystals (350 mg, 0.7 mmol, 70.5%).

**Synthesis of [Me$_2$TACNSiMe$_2$NtBu]La(CH$_2$Ph)$_2$ (2).** Solid **1** (125.0 mg, 0.2 mmol) was reacted with a solution of H**L2** (57.0 mg, 200 $\mu$mol) in benzene (2 mL). The resulting red-brown solution was left to stand overnight, after which yellow crystals of **2** had deposited (70 mg, 0.11 mmol, 58%). $^1$H NMR (500 MHz, THF-$d_8$, 20 °C): $\delta$ 6.83 (t, $^3J_{HH}$ = 6.6 Hz, 2 H, *m*-Ph), 6.57 (d, $^3J_{HH}$ = 6.6 Hz, 4 H, *o*-Ph), 6.26 (t, $^3J_{HH}$ = 6.6 Hz, 2 H, *m*-Ph), 3.17 (m, 2 H, NCH$_2$), 2.70 (m, 6 H, NCH$_2$), 2.61 (m, 2 H, NCH$_2$), 2.46 (m, 2 H, NCH$_2$), 2.40 (s, 6H, NMe), 1.96 (br s, 4 H, LaCH$_2$), 1.31 (s, 9 H, *t*Bu), 0.24 (s, 6 H, SiMe$_2$). $^{13}$C NMR (125.7 MHz, THF-$d_8$, 20 °C): $\delta$ 155.3 (Ph C$_{ipso}$), 130.8 (d, $^1J_{CH}$ = 154.8 Hz, Ph CH), 123.3 (d, $^1J_{CH}$ = 151.9 Hz, Ph CH), 116.2 (d, $^1J_{CH}$ = 157.8 Hz, Ph CH), 66.8 (t, $^1J_{CH}$ = 133.6 Hz, LaCH$_2$), 58.5 (t, $^1J_{CH}$ = 134.0 Hz, NCH$_2$), 56.1 (t, $^1J_{CH}$ = 134.3 Hz, NCH$_2$), 55.0 (s, *t*Bu C), 48.4 (q, $^1J_{CH}$ = 134.8 Hz, NCH$_2$), 47.8 (t, $^1J_{CH}$ = 132.7 Hz, NCH$_2$), 36.4 (q, $^1J_{CH}$ = 123.9 Hz, NMe), 5.0 (q, $^1J_{CH}$ = 117.0 Hz, Me). Anal. Calcd for C$_{31}$H$_{50}$N$_4$SiLa(C$_6$H$_6$)$_{0.3}$: C 56.95; H 7.81; N 8.85. Found: C, 56.90; H, 7.74; N, 8.63.

**Synthesis of [*t*BuC(NAr)$_2$]La(CH$_2$Ph)$_2$(THF) (3b).** Solid La(CH$_2$Ph)$_3$(THF)$_3$ (**1**, 410 mg, 0.50 mmol) and [*t*BuC(N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$]H (H**L3b**, 0.21 g, 0.50 mmol) were mixed and dissolved in THF (10 mL). The solution was stirred at ambient temperature for 1 h, after which the volatiles were removed under vacuum. The residue was dissolved in hexanes (3 mL) with some added THF (ca. 1.0 mL). Cooling to −30 °C afforded crystalline **3b** (250 mg, 0.30 mmol, 60%). $^1$H NMR (500 MHz, C$_6$D$_6$, 20 °C): $\delta$ 7.07 (d, $^3J_{HH}$ = 7.3 Hz, 4 H, Ar H), 7.01 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, Ar H), 6.96 (t, $^3J_{HH}$ = 7.1 Hz, 4 H, Bz *m*-H), 6.61 (d, $^3J_{HH}$ = 7.1 Hz, 4 H, Bz *o*-H), 6.43 (t, $^3J_{HH}$ = 7.1 Hz, 2 H, Bz *p*-H), 3.71 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, C*H*Me$_2$), 2.52 (m, 4 H α-THF), 2.23 (s, 4 H, LaCH$_2$), 1.38 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, *i*Pr Me), 1.31 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, *i*Pr Me), 1.05 (s, 9 H, *t*Bu), 0.98 (m, 4 H $\beta$-THF). $^{13}$C NMR (75.4 MHz, C$_6$D$_6$, 20 °C): $\delta$ 178.8 (N*C*N), 150.0 (Bz C$_{ipso}$), 145.4 (Ar C$_{ipso}$), 141.8 (Ar C), 131.2 (d, $^1J_{CH}$ = 153.7 Hz, Bz CH), 128.5 (d, $^1J_{CH}$ = 157.5 Hz, Ar CH), 123.8 (d, $^1J_{CH}$ = 156.2 Hz, Ar CH), 122.0 (d, $^1J_{CH}$ = 155.1 Hz, Bz CH), 116.8 (d,

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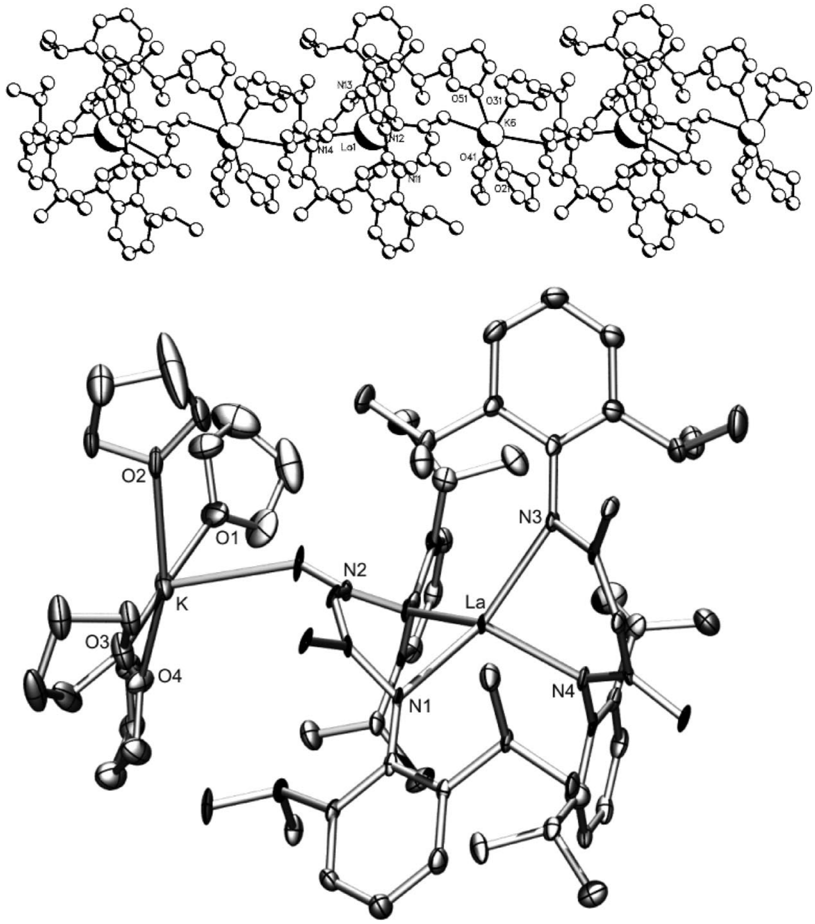


**Figure 6.** Solid state structure of **8**. Chain of the polymeric structure (top) and view of the repeating unit (bottom) (ellipsoid probability level at 50%).

**Table 5. Crystal Data and Collection Parameters of Complexes 2, 3b, 4, 6, and 8**

| | 2 | 3b | 4 | 6 | 8 |
|---|---|---|---|---|---|
| formula | $2[C_{28}H_{47}LaN_4Si]\cdot[C_6H_6]$ | $C_{47}H_{65}LaN_2O$ | $[C_{48}H_{74}LaN_2O_3]^+\cdot[C_{24}H_{20}B]^-\cdot[C_4H_8O]$ | $[C_{37}H_{57}Br_2LaN_2O_2]\cdot[C_4H_8O]$ | $[C_{58}H_{80}LaN_4]^-.[(C_4H_8O)_4K]^+\cdot 0.5(C_4H_8O)\cdot 0.5(C_6H_{14})$ |
| fw | 1291.51 | 812.95 | 1257.37 | 932.70 | 1378.87 |
| cryst color, habit | orange, needle | yellow, block | yellow, block | yellow, block | colorless, block |
| cryst size (mm) | 0.41 × 0.13 × 0.10 | 0.43 × 0.29 × 0.14 | 0.35 × 0.24 × 0.19 | 0.45 × 0.41 × 0.36 | 0.53 × 0.23 × 0.19 |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | *Pc*, 7 | $P2_1/c$, 14 | $P2_1/c$, 14 | $P2_1/m$, 11 | *C2/c*, 15 |
| *a* (Å) | 17.277(1) | 12.0223(9) | 21.148(1) | 10.045(2) | 21.519(3) |
| *b* (Å) | 9.7710(6) | 38.554(3) | 17.242(1) | 20.093(4) | 14.637(2) |
| *c* (Å) | 18.618(1) | 18.699(1) | 18.497(1) | 10.410(2) | 48.082(7) |
| α (deg) | | | | | |
| *β* (deg) | 94.561(1) | 102.521(1) | 92.309(1) | 91.951(3) | 96.458(2) |
| *γ* (deg) | | | | | |
| $V$ (Å$^3$) | 3133.0(3) | 8461.(1) | 6739.2(6) | 2099.9(7) | 15049(4) |
| *Z* | 2 | 8 | 4 | 2 | 8 |
| $\rho_{calcd}$, g cm$^3$ | 1.369 | 1.276 | 1.239 | 1.475 | 1.207 |
| $\mu$, cm$^{-1}$ | 14.27 | 10.45 | 6.83 | 29.57 | 6.73 |
| *F*(000), electrons | 1340 | 3408 | 2664 | 952 | 5808 |
| *θ* range (deg) | 2.57, 27.51 | 2.43, 28.28 | 2.26, 26.37 | 2.82, 26.73 | 2.32, 28.28 |
| R1 | 0.0283 | 0.0481 | 0.0575 | 0.0464 | 0.0911 |
| wR2(all data) | 0.0650 | 0.0991 | 0.1341 | 0.1271 | 0.1753 |
| index ranges (*h*,*k*,*l*) | ±22, −11→12, ± 24 | ±16, ± 51, −11→24 | ±26, ± 21, ± 23 | ±12, ± 25, −11→13 | ±28, ± 19, −63→64 |
| *T* (K) | 100 | 100 | 100 | 100 | 100 |
| GOF | 0.972 | 1.120 | 1.147 | 1.037 | 1.255 |

$^1J_{CH}$ = 157.4 Hz, Bz CH), 70.0 (t, $^1J_{CH}$ = 134.1 Hz, $LaCH_2$), 68.7 (t, $^1J_{CH}$ = 149.4 Hz, α-THF), 45.4 (s, tBu C), 31.0 (d, $^1J_{CH}$ = 127.8 Hz, *i*Pr CH), 28.8 (q, $^1J_{CH}$ = 125.2 Hz, *i*Pr Me), 25.2 (t, $^1J_{CH}$ = 133.9 Hz, *β*-THF), 25.2 (q, $^1J_{CH}$ = 125.2 Hz, *i*Pr Me), 23.6 (q, $^1J_{CH}$ = 129.4 Hz, *t*Bu C). Anal. Calcd for $C_{47}H_{65}LaN_2O$ [812.94]: C, 69.44; H, 8.06; N, 3.45. Found: C, 69.70; H, 8.26; N, 3.38.

**Synthesis of {[*t*BuC(NAr)$_2$]La(CH$_2$Ph)(THF)$_3$}[BPh$_4$]·THF (4).** THF (1 mL) was added to a mixture of **3b** (81.0 mg, 100.0 $\mu$mol) and $[HNMe_2Ph][B(C_6H_5)_4]$ (44.0 mg, 0.1 mmol). The resulting yellowish solution was layered with 2 mL of hexanes. Upon standing overnight at ambient temperature, yellow crystals formed (80 mg, 64%). $^1$H NMR (500 MHz, THF-$d_8$, 20 °C): $\delta$ 7.15–7.08 (m, 6 H, Ar H), 7.00 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, Bz *m*-H), 6.67 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, Bz *o*-H), 6.57 (t, $^3J_{HH}$ = 7.3 Hz, 1 H, Bz *p*-H), 3.30 (sept, ${}^3J_{HH}$ = 6.7 Hz, 4 H, C*H*Me$_2$), 1.70 (s, 4 H, LaCH$_2$), 1.35 (d, ${}^3J_{HH}$ = 6.7 Hz, 12 H, *i*Pr Me), 1.18 (d, ${}^3J_{HH}$ = 6.7 Hz, 12 H, *i*Pr Me), 0.95 (s, 9 H, *t*Bu). ${}^{13}$C NMR (75.4 MHz, THF-$d_8$, 20 °C): $\delta$ 182.7 (N*C*N), 166.1 (q, ${}^1J_{CB}$ = 49.6 Hz, BPh$_4$ C$_{ipso}$), 151.6 (Bz C$_{ipso}$), 145.0 (Ar C$_{ipso}$), 143.5 (Ar C), 137.9 (dt, ${}^1J_{CH}$ = 153.6, 7.3 Hz, BPh$_4$ *o*-H), 131.9 (d, ${}^1J_{CH}$ = 156.2 Hz, Bz CH), 131.6 (d, ${}^1J_{CH}$ = 160.3 Hz, Ar CH), 126.7 (d, ${}^1J_{CH}$ = 152.5 Hz, BPh$_4$-m), 123.3 (d, ${}^1J_{CH}$ = 156.2 Hz, Ar CH), 120.7 (d, ${}^1J_{CH}$ = 152.1 Hz, Bz CH), 118.2 (d, ${}^1J_{CH}$ = 160.3 Hz, Bz CH), 81.2 (b, LaCH$_2$), 47.0 (s, *t*Bu C), 32.0 (d, ${}^1J_{CH}$ = 125.5 Hz, *i*Pr CH), 30.5 (q, ${}^1J_{CH}$ = 125.4 Hz, *i*Pr Me), 28.0 (q, ${}^1J_{CH}$ = 125.2 Hz, *i*Pr Me). 245. (q, ${}^1J_{CH}$ = 126.2 Hz, *t*Bu Me). Anal. Calcd for $C_{76}H_{102}LaBN_2O_4$ [1257.3]: C, 72.60; H, 8.18; N, 2.23. Found: C, 71.60; H, 8.23; N, 2.51. For this material we consistently obtained analyses with a relatively low carbon content, but could not detect specific impurities.

**Synthesis of KL1.** To a stirred solution of H**L1** (2.0 g, 5 mmol) in toluene (20 mL) was added solid KCH$_2$Ph (0.65 g, 5 mmol). The initially orange suspension formed a yellow solution within 5 min. The solvent was removed and the residue was rinsed with cold (0 °C) pentane, yielding the title compound (2.2 g, 4.8 mmol, 96%). ${}^1$H NMR (300 MHz, THF-$d_8$, 20 °C): $\delta$ 5.89 (d, 4H, *J* = 7.6 Hz, C$_6$H$_3$), 6.68 (t, 2H, *J* = 7.6 Hz, C$_6$H$_3$), 4.19 (s, 1H, $\gamma$-CH), 3.28 (sept, 4H, *J* = 6.8 Hz, C*H*Me$_2$), 1.48 (s, 6H, Me), 1.11 (d, 12H, *J* = 6.8 Hz, CH*Me*$_2$), 1.03 (d, 12H, *J* = 6.8 Hz, CH*Me*$_2$). ${}^{13}$C NMR (300 MHz, THF-$d_8$, 20 °C): $\delta$ 161.5 (C-N), 154.0 (ipso, Ar, C-N), 144.1 (ipso, Ar, *C-i*Pr), 124.0 (d, *J* = 151.6 Hz, Ar), 121.9 (d, *J* = 158.6 Hz, Ar), 91.7 (d, *J* = 150.8 Hz, $\gamma$-C), 29.0 (d, *J* = 131.2 Hz, *C*HMe$_2$), 25.8 (q, *J* = 126.0 Hz, Me), 25.4 (q, *J* = 125.3 Hz,CH*Me*$_2$), 25.2 (q, *J* = 122.6 Hz, CH*Me*$_2$). Anal. Calcd for $C_{29}H_{41}N_2K$ [456.7]: C, 76.26; H, 9.05; N, 6.13. Found: C, 76.55; H, 9.38; N, 6.13.

**Synthesis of (L1)LaBr$_2$(THF)$_2$ (6).** To a suspension of LaBr$_3$(THF)$_4$ (1330 mg, 2.00 mmol) in THF (30 mL) was added a THF (5 mL) solution of K**L1** (0.91 g, 2 mmol). The yellowish reaction mixture was stirred for 2 h and centrifuged to separate formed KBr. The clear yellow solution was evaporated to dryness to afford a sticky solid, which was subsequently rinsed with hexanes (10 mL) to yield **6** as a yellowish microcrystalline solid (1300 mg, 1.5 mmol, 76%). ${}^1$H NMR (500 MHz, THF-$d_8$, 20 °C): $\delta$ 7.20–7.14 (m, 6H, C$_6$H$_3$), 5.01 (s, 1H, $\gamma$-CH), 3.48 (sept, 4H, *J* = 6.6 Hz, C*H*Me$_2$), 1.68 (s, 6H, Me), 1.32 (d, 12H, *J* = 6.6 Hz, CH*Me*$_2$), 1.07 (d, 12H, *J* = 6.6 Hz, CH*Me*$_2$). ${}^{13}$C NMR (125.8 MHz, THF-$d_8$, 20 °C): $\delta$ 166.7 (C-N), 146.7 (ipso, Ar, *C-i*Pr), 144.1 (ipso, Ar, C-N), 127.8 (d, *J* = 160.0 Hz, Ar), 126.1 (d, *J* = 156.7 Hz, Ar), 100.6 (d, *J* = 149.5 Hz, $\gamma$-C), 30.3 (d, *J* = 129.3 Hz, *C*HMe$_2$), 26.5 (q, *J* = 127.0 Hz, Me), 26.4 (q, *J* = 126.1 Hz,CH*Me*$_2$), 26.3 (q, *J* = 126.1 Hz, CH*Me*$_2$). Anal. Calcd for $C_{37}H_{57}Br_2N_2LaO_2$ [860.75]: C, 51.64; H, 6.68; N, 3.26. Found: C, 51.58; H, 6.63; N, 3.25.

**Reaction of 6 with MeMgCl.** To a solution of (**L1**)LaBr$_2$(THF)$_2$ (**6**, 860 mg, 1.00 mmol) in THF (10 mL) was added a THF solution (3 M) of MeMgCl (0.70 mL, 2 mmol). The yellow solution was stirred for 2 h, after which the solvent was removed under reduced pressure. The residue was extracted with a hexane/THF mixture (9:1, 10 mL) and filtrated. The filtrate cooled to −30 °C yielded (**L1**)MgMe(THF),[25] identified by NMR spectroscopy, as white crystals (370 mg, 70%).

**Synthesis of (L1)La(CH$_2$Ph)$_2$THF (7).** To a solution of **6** (172 mg, 0.2 mmol) in THF (2 mL) was added a THF (4 mL) solution of KCH$_2$Ph (52 mg, 400 $\mu$mol). The orange solution was stirred for 1 h, filtered, and evaporated to dryness. The residue was dissolved in a mixture of hexane/THF (3:1, 4 mL total volume) and cooled to −30 °C, yielding **7** as yellow crystals (75 mg, 0.09 mmol, 46%). ${}^1$H NMR (500 MHz, THF-$d_8$, 20 °C): $\delta$ 7.16–7.08 (m, 6H, C$_6$H$_3$), 6.66 (t, ${}^3J_{HH}$ = 7.5 Hz, 4H, Ph-m), 6.25 (t, ${}^3J_{HH}$ = 7.5 Hz, 2H, Ph-p), 6.15 (d, ${}^3J_{HH}$ = 7.5 Hz, 4H, Ph-o), 5.25 (s, 1H, $\gamma$-CH), 3.03 (sept, ${}^3J_{HH}$ = 6.8 Hz, 4H, C*H*Me$_2$), 1.80 (s, 6H, Me), 1.35 (s, 4H, LaCH$_2$), 1.12 (d, ${}^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$), 1.10 (d, ${}^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$). ${}^{13}$C NMR (500 MHz, THF-$d_8$, 20 °C): $\delta$ 166.5 (C-N), 152.3 (ipso, Ph), 147.3 (ipso, Ar, C-N), 144.4 (ipso, Ar, *C-i*Pr), 131.4 (d, ${}^1J_{CH}$ = 152.9 Hz, Ph-m), 127.2 (d, ${}^1J_{CH}$ = 160.9 Hz, Ar), 125.8 (d, ${}^1J_{CH}$ = 155.6 Hz, Ar), 122.8 (d, ${}^1J_{CH}$ = 150.2 Hz, Ph-o), 117.7 (d, ${}^1J_{CH}$ = 158.2 Hz, Ph-p), 96.6 (d, ${}^1J_{CH}$ = 154.2 Hz, $\gamma$-C), 70.3 (t, ${}^1J_{CH}$ = 130.6 Hz, LaCH$_2$), 30.3 (d, ${}^1J_{CH}$ = 126.8 Hz, *C*HMe$_2$), 26.4 (q, ${}^1J_{CH}$ = 127.5 Hz, Me), 26.3 (q, ${}^1J_{CH}$ = 127.1 Hz, CH*Me*$_2$). Anal. Calcd for $C_{47}H_{63}LaN_2O$ [810.92]: C, 69.61; H, 7.83; N, 3.45. Found: C, 70.10; H, 8.13; N, 3.43.

**Synthesis of {[$\mu$-$\eta^2$:$\eta^1$-ArNC(Me)CHC(CH$_2$)NAr]$_2$La[K-(THF)$_4$]}$_\infty$ (8).** To a solution of **6** (172 mg, 0.2 mmol) in THF (2 mL) was added a THF (5 mL) solution of KCH$_2$Ph (52 mg, 0.4 mmol). The dark orange solution was stirred at 80 °C for 24 h, allowed to cool to ambient temperature, and filtered. The filtrate was layered with hexanes (5 mL) and left to stand overnight, whereupon the title compound crystallized as colorless needles (92 mg, crude yield 70%). Its structure was corroborated by X-ray diffraction analysis. Elemental analysis of the bulk solid revealed significantly lower C and H values than expected for pure **8**, indicating the presence of coprecipitated metal salt. ${}^1$H NMR (500 MHz, THF-$d_8$, 20 °C): $\delta$ 6.97 (d, ${}^3J_{HH}$ = 7.5 Hz, 2H, C$_6$H$_3$), 6.94 (d, ${}^3J_{HH}$ = 7.5 Hz, 2H, C$_6$H$_3$), 6.84 (t, ${}^3J_{HH}$ = 7.5 Hz, 2H, C$_6$H$_3$), 6.73 (t, ${}^3J_{HH}$ = 7.5 Hz, 2H, C$_6$H$_3$), 6.70 (d, ${}^3J_{HH}$ = 7.5 Hz, 2H, C$_6$H$_3$), 6.69 (d, ${}^3J_{HH}$ = 7.5 Hz, 2H, C$_6$H$_3$), 5.18 (s, 2H, $\gamma$-CH), 3.61 (sept, ${}^3J_{HH}$ = 7.0 Hz, 2H, C*H*Me$_2$), 3.48 (sept, ${}^3J_{HH}$ = 7.0 Hz, 2H, C*H*Me$_2$), 3.14 (sept, ${}^3J_{HH}$ = 7.0 Hz, 2H, C*H*Me$_2$), 2.95 (sept, ${}^3J_{HH}$ = 7.0 Hz, 2H, C*H*Me$_2$), 2.78 (d, ${}^3J_{HH}$ = 2.4 Hz, 2H, NCC*H*$_2$), 2.07 (d, ${}^3J_{HH}$ = 2.4 Hz, 2H, NCC*H*$_2$), 1.67 (s, 6H, Me), 1.45 (d, ${}^3J_{HH}$ = 7.0 Hz, 12H, CH*Me*$_2$), 1.22 (d, ${}^3J_{HH}$ = 7.0 Hz, 12H, CH*Me*$_2$), 1.08 (d, ${}^3J_{HH}$ = 7.0 Hz, 12H, CH*Me*$_2$), 0.97 (d, ${}^3J_{HH}$ = 7.0 Hz, 12H, CH*Me*$_2$), 0.91 (d, ${}^3J_{HH}$ = 7.0 Hz, 12H, CH*Me*$_2$), 0.88 (d, ${}^3J_{HH}$ = 7.0 Hz, 12H, CH*Me*$_2$), 0.41 (d, ${}^3J_{HH}$ = 7.0 Hz, 12H, CH*Me*$_2$), 0.11 (d, ${}^3J_{HH}$ = 7.0 Hz, 12H, CH*Me*$_2$). ${}^{13}$C NMR (125.7 MHz, THF-$d_8$, 20 °C): $\delta$ 164.5 (C-N), 154.0 (ipso, C$_6$H$_3$), 149.4 (ipso, C$_6$H$_3$), 146.9 (ipso, C$_6$H$_3$), 145.9 (ipso, C$_6$H$_3$), 143.3 (ipso, C$_6$H$_3$) 142.4 (ipso, C$_6$H$_3$), 127.0 (d, ${}^1J_{CH}$ = 160.2 Hz, C$_6$H$_3$), 124.8 (d, ${}^1J_{CH}$ = 160.9 Hz, C$_6$H$_3$), 124.5 (d, ${}^1J_{CH}$ = 156.0 Hz, C$_6$H$_3$), 124.0 (d, ${}^1J_{CH}$ = 155.6 Hz, C$_6$H$_3$), 123.6 (d, ${}^1J_{CH}$ = 158.2 Hz, C$_6$H$_3$), 122.4 (d, ${}^1J_{CH}$ = 158.6 Hz, C$_6$H$_3$), 100.6 (d, ${}^1J_{CH}$ = 152.2 Hz, $\gamma$-C), 77.0 (t, ${}^1J_{CH}$ = 153.4 Hz, NC*C*H$_2$), 33.3 (d, ${}^1J_{CH}$ = 126.8 Hz, *C*HMe$_2$), 29.3, 29.2, 29.1 (d, ${}^1J_{CH}$ = 127.8 Hz, *C*HMe$_2$), 28.7, 27.9, 26.8, 26.7, 26.5, 25.5, 24.8, 22.4 (Me, CH*Me*$_2$).

**Generation of [(L1)La(CH$_2$Ph)(THF)$_x$][BPh$_4$] (9).** A solution of **7** (26 mg, 0,032 mmol) in THF-$d_8$ (0.6 mL) was added to [HNMe$_2$Ph][B(C$_6$H$_5$)$_4$] (14 mg, 32.0 $\mu$mol). The obtained solution was transferred into a NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the ionic monoalkyl species **9**, toluene, and free PhNMe$_2$. ${}^1$H NMR (500 MHz, 20 °C, THF-$d_8$): $\delta$ 7.23 (br, 8H, o-H BPh$_4$), 6.81 (t, ${}^3J_{HH}$ = 7.8 Hz, 8H, m-H BPh$_4$), 6.68 (t, ${}^3J_{HH}$ = 7.8 Hz, 4H, p-H BPh$_4$), 6.56 (t, ${}^3J_{HH}$ = 6.60 Hz, 2H, Ph-m), 6.47 (t, ${}^3J_{HH}$ = 6.60 Hz, 1H, Ph-p), 6.05 (t, ${}^3J_{HH}$ = 6.60 Hz, 2H, Ph-o), 5.3 (s, 1H, $\gamma$-CH), 2.80 (sept, ${}^3J_{HH}$ = 6.8 Hz, 4H, C*H*Me$_2$), 1.83 (s, 6H, Me), 1.61 (s, 2H, LaCH$_2$), 1.23 (d, ${}^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$), 1.17 (d, ${}^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$). ${}^{13}$C NMR (500 MHz, THF-$d_8$, 20 °C): $\delta$ 167.7 (C-N), 166.0 (q, 49.0 Hz, ipso-BPh$_4$), 150.7 (ipso, Ph), 145.0 (ipso, Ar, C-N), 143.9 (ipso, Ar, *C-i*Pr), 137.9 (d, *J* = 152.0 Hz, o-BPh$_4$), 133.4 (d, ${}^1J_{CH}$ = 162.9 Hz, Ph-m), 128.7 (d, ${}^1J_{CH}$ = 158.7 Hz, Ar), 126.7 (d, *J* = 150.9 Hz, m-BPh$_4$), 125.8 (d, ${}^1J_{CH}$ = 155.6 Hz, Ar), 123.5 (d, ${}^1J_{CH}$ = 152.7 Hz, Ph-o), 123.0 (d, *J* = 155.4 Hz, p-BPh$_4$), 121.0 (d, ${}^1J_{CH}$ = 164.7 Hz, Ph-p), 96.8 (d, ${}^1J_{CH}$ = 155.2 Hz, $\gamma$-C), 77.2 (t, ${}^1J_{CH}$ = 133.8 Hz, LaCH$_2$), 31.2 (d, ${}^1J_{CH}$ = 126.8 Hz, *C*HMe$_2$), 26.1 (q, ${}^1J_{CH}$ = 127.0 Hz, Me), 25.0 (q, ${}^1J_{CH}$ = 127.0 Hz,CH*Me*$_2$).

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**Supporting Information Available:** Experimental details of the reaction of $LaBr_3(THF)_4$ with varying amounts of $LiCH_2SiMe_3$. Crystallographic data for **2**, **3b**, **4**, **6**, and **8** including atomic coordinates, full bond distances, and bond angles as well as anisotropic thermal parameters (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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