# **ORGANOMETALLICS**

# Synthesis and Reactivity of Homoleptic α-Metalated *N*,*N*-Dimethylbenzylamine Rare-Earth-Metal Complexes

Andrew C. Behrle and Joseph A. R. Schmidt\*

Department of Chemistry, University of Toledo, 2801 W. Bancroft Street, MS 602, Toledo, Ohio 43606, United States

Supporting Information

**ABSTRACT:** A series of new homoleptic rare-earth-metal complexes was synthesized using salt metathesis reactions between LnCl<sub>3</sub> and  $\alpha$ -K(DMBA) (Ln = La (1), Ce (2), Pr (3), Nd (4), Sm (5), Gd (6), Y (7); DMBA = *N*,*N*-dimethylbenzylamine). All seven complexes were found to be free of coordinating solvent, and no formation of any "-ate" species was observed. The ligands in complexes 1–7 displayed  $\eta^4$  coordination to the metal center. Subsequently, the reactivity



of 1 and 7 was investigated via various protonolysis reactions using silylamines, anilines, and phenols to generate a diverse array of other homoleptic lanthanide complexes.

The effective use of f-element complexes as catalysts for reactions such as hydroamination,<sup>1-4</sup> ring-opening polymerization of lactide,<sup>5-8</sup> and hydrosilylation,<sup>9-12</sup> as well as precursors for the generation of thin films,<sup>13-16</sup> has been demonstrated in many recent reports. Unfortunately, the homoleptic starting materials underpinning this chemistry are generally derived from only a handful of ligands. That is, of the homoleptic lanthanide complexes that exist, the majority make use of alkylsilane  $(-CH_2SiMe_3)$ , silylamide  $(-N(SiMe_3)_2)$ , or benzyl  $(-CH_2C_6H_5)$  derivatives.<sup>17-25</sup> The preparation of these homoleptic starting materials via salt metathesis reactions between rare-earth-metal chlorides and lithium salts often leads to the generation of lanthanate ions  $([LnR_4]^-)$ .<sup>26</sup> Furthermore, alkylsilane complexes require careful sublimation to purify and have been shown to exhibit only moderate thermal stability.<sup>27</sup> In contrast, while the lanthanide tribenzyl complexes do not often form the lanthanate ion, they instead retain coordinated solvent, making them not truly homoleptic complexes and limiting their potential as starting materials in some cases.<sup>28</sup> Thus, the discovery of new homoleptic lanthanide complexes with easy isolation protocols and effective protonolysis reactivity would represent a significant advance in the field of lanthanide chemistry.

The paucity of trialkyl lanthanide complexes can be attributed to the required extended coordination sphere and high Lewis acidity or electrophilicity of these metals. The ionic radii of  $\text{Ln}^{3+}$ ions range from 1.00 to 1.17 Å.<sup>29</sup> While these properties make lanthanum alkyl complexes very reactive, in turn they also make their synthesis and manipulation quite challenging. Our efforts have focused on the development of unexplored homoleptic trialkyl rare-earth-metal complexes utilizing simple ligands that fulfill both the electronic and steric requirements of these metal centers. The *N*,*N*-dimethylbenzylamine ligand scaffold is not unknown in the literature; however, nearly all of its previous uses have been limited to ortho-metalated complexes.<sup>30,31</sup> There is only a single example of a crystallographically characterized  $\alpha$ -metalated transition-metal complex, a zirconium species by Norton and co-workers.<sup>32</sup> For the rare-earth metals, only orthometalated *N,N*-dimethylbenzylamine complexes exist and, of these, only the middle and late lanthanides proved to be stable enough for isolation.<sup>33,34</sup> Herein, we report our findings of a new class of homoleptic trialkyl rare-earth-metal complexes using  $\alpha$ -metalated *N,N*-dimethylbenzylamine ligands as stable benzyl ligand derivatives to form lanthanide complexes free of coordinating solvent.

A series of homoleptic  $\alpha$ -metalated N,N-dimethylbenzylamine (DMBA) Ln complexes (Ln = La, Ce, Pr, Nd, Sm, Gd, Y) was synthesized by following a simple procedure<sup>35</sup> involving salt metathesis of rare-earth-metal chlorides with  $\alpha$ -potassiated dimethylbenzylamine at -50 °C in THF (Scheme 1).  $\alpha$ -La- $(DMBA)_3$  (1) was isolated by recrystallization from THF/ pentane at -25 °C, affording orange crystals in 77% yield.  $\alpha$ -Y(DMBA)<sub>3</sub> (7) was synthesized in a manner similar to that for 1, except the THF solvent was removed under reduced pressure at 0 °C in order to prevent product decomposition. Subsequently, 7 was recrystallized from a concentrated solution of pentane at room temperature to give yellow crystals in 79% yield. The La complex 1 showed no evidence of decomposition in THF at room temperature, while 7 decomposed readily in this solvent. Spectroscopically, 1 exhibited fluxional behavior at room temperature, but upon cooling to -78 °C, it displayed much sharper resolution with resonances indicative of a  $C_3$ -symmetric species. At low temperature, 1 adopted an ABCDX splitting pattern for the five protons of the phenyl rings, with a resonance shifted significantly upfield to 3.10 ppm in its <sup>1</sup>H NMR spectrum, assigned to the ortho proton closest to the metal center. This upfield chemical shift is indicative of a disruption of the aromatic system and can be attributed to  $\eta^2$  coordination of the phenyl

 Received:
 May 2, 2011

 Published:
 July 14, 2011

Scheme 1. Synthesis of  $\alpha$ -Ln(DMBA)<sub>3</sub> (Ln = La (1), Ce (2), Pr (3), Nd (4), Sm (5), Gd (6), Y (7; C<sub>3</sub> Isomer))



**Figure 1.** ORTEP diagram of **1**, showing the pseudo-3-fold rotation axis in these lanthanide complexes. Thermal ellipsoids are given at the 50% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for  $1-7^a$ 

	Ln-	Ln-	Ln-		$C_{ipso}-$	
	C <sub>benzyl</sub>	$C_{ipso}$	C <sub>ortho</sub>	Ln-N	$C_{benzyl} - Ln$	bite angle
La	2.648(3)	2.834(3)	2.856(2)	2.652(2)	82.65(15)	63.98(7)
Ce	2.617(3)	2.814(3)	2.840(3)	2.624(3)	82.99(19)	64.57(9)
Pr	2.597(4)	2.797(3)	2.830(3)	2.605(3)	82.93(19)	64.91(11)
Nd	2.588(3)	2.785(3)	2.818(3)	2.603(3)	82.73(18)	65.24(9)
Sm	2.555(4)	2.760(4)	2.803(4)	2.568(4)	83.0(2)	65.79(12)
Gd	2.545(3)	2.790(3)	2.743(3)	2.518(3)	84.49(17)	69.82(8)
Y	2.516(4)	2.758(4)	2.751(4)	2.471(3)	84.2(2)	69.53(12)
<sup>a</sup> All comp	values are plex.	averages	of those	observed	in the $\alpha$ -L	n(DMBA) <sub>3</sub>

ring to the lanthanum, giving rise to an overall  $\eta^4$  binding mode and resulting in a pseudoallylic arrangement for the three carbon atoms interacting with the metal center. In contrast, the yttrium complex 7 did not exhibit fluxional behavior at room temperature; however, unlike complex 1, its <sup>1</sup>H NMR displayed two independent isomers in a nearly 1:1 ratio, with one having  $C_3$ symmetry and the other  $C_s$  symmetry. The <sup>1</sup>H NMR spectrum of each isomer of 7 showed AA'BB'C coupling patterns for each inequivalent phenyl group. This indicates rapid rotation of these phenyl groups in solution, implying  $\eta^2$  coordination from the DMBA ligands to the yttrium metal center, unlike the  $\eta^4$ coordination observed in 1.



**Figure 2.** ORTEP diagram of 7, lacking the approximate  $C_3$  symmetry observed in 1–6. Thermal ellipsoids are given at the 50% probability level.

X-ray-quality crystals were achieved for both 1 and 7, and their crystal structures were solved. Both 1 and 7 crystallized in monoclinic space groups. The structure of compound 1 confirmed its approximate  $C_3$  symmetry (Figure 1). The average La $-C_{\text{benzyl}}$  bond distance in 1 is 2.648(3) Å (Table 1), which is significantly shorter than the average La $-C_{\text{benzyl}}$  bond distance of 2.755(2) Å in La $(CH_2Ph)_3(THF)_3^{28}$  Similarly, the average  $La-C_{ipso}$  bond distance is 2.834(3) Å, somewhat shorter than the average La- $C_{ipso}$  bond distance of 2.873(6) Å for (*o*-Me<sub>2</sub>N- $C_6H_4$ - $CH_2$ )<sub>3</sub>La.<sup>35,36</sup> The shorter bond distances observed for the  $\alpha$ -DMBA ligands in 1 reflect the allylic nature of the three-carbon anionic fragment in these ligands, causing the entire unit to be closer to the metal center to properly bind in this allylic motif. The average bite angle for 1 is  $63.98(7)^{\circ}$  for N–La–C<sub>ortho</sub>. The tilt of the phenyl group can be measured as the Ln-C<sub>benzyl</sub>- $C_{ipso}$  angle, with an average phenyl tilt angle for 1 of 82.7(2)°. In contrast, we were fortunate to crystallize the low-symmetry isomer of complex 7, in which one of the three DMBA ligands is oriented in the opposite direction from the other two (Figure 2). The formation of this lower symmetry isomer is due to the smaller ionic radius of  $Y^{3+}$ , with reorientation necessary to relieve steric stress resulting from the decreased Y-C<sub>benzvl</sub> bond distances, which are more than 0.1 Å shorter than those observed in 1. Specifically, the Y-C<sub>benzyl</sub> bond distances fall in the range of 2.488(4) - 2.552(4) Å and are slightly elongated compared to the Y-C<sub>benzyl</sub> bond distances of Y(CH<sub>2</sub>Ph)<sub>3</sub>(THF)<sub>3</sub> (2.452(3)-2.463(3)Å).<sup>24</sup> The average  $Y-C_{ipso}$  bond distance is 2.758(4)Å and is somewhat shorter than the average  $Y-C_{ipso}$  bond distance of 2.801(3) Å for  $(o-Me_2N-C_6H_4-CH_2)_3Y$ .<sup>35</sup> The closer approach to the metal center also results in larger bite angles for 7  $(66.9(1)-72.4(1)^\circ)$ , while the phenyl tilt angles span a wide range (81.9(2)-87.5(2)°).

The remaining  $\alpha$ -Ln(DMBA)<sub>3</sub> complexes (Ln = Ce, Pr, Nd, Sm, Gd) were synthesized using procedures analogous to those used for 7, and each was recrystallized from toluene/pentane at  $-25 \,^{\circ}\text{C.}^{37}$  As expected, complexes 2-6 were paramagnetic, and their <sup>1</sup>H NMR spectra revealed only broad and uninterpretable signals. The magnetic moment of each complex was determined using the Evans NMR method<sup>38</sup> and showed no anomalous values (see the Supporting Information).<sup>39</sup> The solid-state structures of 2-6 were all very similar to that of  $\alpha$ -La(DMBA)<sub>3</sub> (1), containing

#### Scheme 2. Protonolysis Reactions of $\alpha$ -Ln(DMBA)<sub>3</sub><sup>*a*</sup>

$\alpha$ –La(DMBA) <sub>3</sub>	+	2 HOAr	THF	La(DMBA)(OAr) <sub>2</sub> (THF) (8)	+	2 HDMBA
$\alpha$ –Ln(DMBA) <sub>3</sub>	+	3 HOAr	THF	Ln(OAr) <sub>3</sub> ( <b>9-12</b> )	+	3 HDMBA
$\alpha$ –Ln(DMBA) <sub>3</sub>	+	3 H <sub>2</sub> NAr	THF	Ln(NHAr <sup>'</sup> ) <sub>3</sub> ( <b>13-15</b> )	+	3 HDMBA
$\alpha$ –Ln(DMBA) <sub>3</sub>	+	3 HN(SiMe <sub>3</sub> ) <sub>2</sub>	THF	Ln[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> ( <b>16-17</b> )	+	3 HDMBA

<sup>*a*</sup> Legend: Ln = La, Y; Ar = 2,6-di-*tert*-butylphenyl, 4-*tert*-butylphenyl; Ar = 2,6-diisopropylphenyl, 4-*tert*-butylphenyl.



Figure 3. ORTEP diagram of 8 with *tert*-butyl methyl groups removed for clarity. Thermal ellipsoids are given at the 50% probability level.

a 3-fold axis of rotation and  $\eta^4$  coordination to the metal centers (see the Supporting Information). As anticipated, the Ln-C<sub>benzyl</sub> bond distance decreased as the metal's ionic radius became smaller, due to the lanthanide contraction (Table 1). One noticeable feature of complexes **2**–**6** is the increase in the phenyl tilt angle as the Ln-C<sub>benzyl</sub> bond length decreased. This phenyl tilt angle implies that, as the ionic radius of the metal shrinks, the phenyl group becomes more orthogonal to the metal. Also, as the metal's radius decreases, the ligands move closer to the metal, resulting in larger ligand bite angles. On the basis of a comparison of the Ln-C<sub>benzyl</sub> bond distances and the phenyl tilt angles of **6** and 7,  $\alpha$ -Gd(DMBA)<sub>3</sub> (**6**) may represent the absolute minimum radius necessary to fully preserve the 3-fold symmetry.

In order to demonstrate the utility of  $\alpha$ -Ln(DMBA)<sub>3</sub> complexes as effective precursors in lanthanide chemistry, the reactivity of 1 and 7 was investigated through a series of protonolysis reactions. Initial attempts consisted of treatment of these complexes with 1 equiv of 2,6-di-tert-butylphenol. The expected monoaryloxide product was not formed; rather, a disubstituted product, La(DMBA)(OAr)<sub>2</sub>(THF) (8), was generated in low yield. As a means to increase the yield of 8, the reaction was repeated with nearly 2 equiv of 2,6-di-tert-butylphenol to more appropriately reflect the product stoichiometry (Scheme 2). 8 was recrystallized from a THF/pentane solution at room temperature. Its <sup>1</sup>H NMR spectrum and X-ray crystal structure (Figure 3) revealed a decrease in hapticity of the N,Ndimethylbenzylamine ligand from  $\eta^4$  to  $\eta^2$ . The <sup>1</sup>H NMR spectrum of 8 displayed a classical AA'BB'C splitting pattern for the phenyl group of the N,N-dimethylbenzylamine ligand.

This decrease in hapticity is likely a result of minimization of the steric interactions caused by the very bulky aryloxides. The La–C<sub>benzyl</sub> and La–N bond distances are 2.602(2) and 2.664(2) Å, respectively, which are quite similar to those in the homoleptic  $\alpha$ -La(DMBA)<sub>3</sub> precursor. While the generation of **8** was initially unanticipated, it provided insight into the donor capabilities and Lewis basicity of *N*,*N*-dimethylbenzylamine. The lanthanum clearly preferred the more basic aryloxide and neutral tetrahydrofuran ligands over neutral *N*,*N*-dimethylbenzylamine, which is present in solution as a reaction byproduct. This result stems from the fact that the aryloxide and tetrahydrofuran are both harder bases than the tertiary amine, and THF has less steric bulk than the neutral *N*,*N*-dimethylbenzylamine.

As a means to more readily demonstrate the breadth of ligands amenable to protonolysis reactions with  $\alpha$ -Ln(DMBA)<sub>3</sub>, we turned our attention to full protonolysis of 1 and 7, in which all three DMBA ligands were displaced by other anionic ligands, such as bulky aryloxides, anilides, and silylamides. Overall, 1 and 7 showed excellent reactivity in full protonolysis reactions to very simply generate numerous other homoleptic lanthanide complexes (Scheme 2). As expected for the less sterically encumbered aryloxides,  $La(OAr)_3$  (9) and  $Y(OAr)_3$  (11) exhibited dimeric behavior in solution for the less bulky 4-tert-butylphenyl derivatives. In each case, to achieve full protonolysis, 1 was treated with 3 equiv of protonating agent in THF at room temperature, while the analogous reactions of 7 were conducted at -78 °C in order to prevent decomposition of 7 in THF. Product isolation consisted of either simply washing the solid with pentane or extracting the product into pentane after the THF had been removed under reduced pressure, followed by crystallization at -25 °C. No traces of liberated neutral N,N-dimethylbenzylamine could be found in any of the products after isolation, confirming that full protonolysis had occurred and that no tertiary amine remained coordinated to the metal. Thus, protonolysis of  $\alpha$ -Ln(DMBA)<sub>3</sub> proved to be a very effective and simple means of generating homoleptic aryloxide and amide complexes.

In conclusion, we have disclosed the synthesis of a new series of solvent-free homoleptic rare-earth-metal complexes [ $\alpha$ -Ln- $(DMBA)_3$ ]. These complexes were readily produced via salt metathesis with no formation of the corresponding "-ate" species. The size of the metal's ionic radius determined whether a 3-fold axis of symmetry was produced at the metal center, while the  $\alpha$ -DMBA ligand showed  $\eta^4$  coordination in virtually every case. The reactivity of 1 and 7 was probed via protonolysis reactions. A heteroleptic lanthanide complex (8) was isolated, revealing that lanthanum preferred coordination of a THF molecule to the neutral N,N-dimethylbenzylamine ligand. Full protonolysis reactions with several phenols and amines resulted in easily isolated homoleptic complexes, demonstrating the utility and versatility of the  $\alpha$ -Ln(DMBA)<sub>3</sub> compounds as precursors to other Ln complexes. Further investigation of the organometallic reactivity of  $\alpha$ -Ln(DMBA)<sub>3</sub> complexes and their use in catalysis is underway.

# ASSOCIATED CONTENT

**Supporting Information.** Text, figures, tables, and CIF files giving full experimental procedures and characterization data for  $\alpha$ -K(DMBA) and 1–17, crystallographic procedures and crystal data for 1–8, ORTEP diagrams of 2–6, and additional crystallographic data, including bond lengths and angles, of compounds 1–8. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: Joseph.Schmidt@utoledo.edu. Tel: 419-530-1512.

## ACKNOWLEDGMENT

We gratefully acknowledge The University of Toledo for generous start-up funding, as well as the staff of the Ohio Crystallography Consortium housed at The University of Toledo for assistance with X-ray crystallography.

#### REFERENCES

(1) Yuen, H. F.; Marks, T. J. Organometallics 2009, 28, 2423-2440.

(2) Mueller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. Chem. Rev. 2008, 108, 3795–3892.

(3) Stanlake, L. J. E.; Schafer, L. L. Organometallics 2009, 28, 3990–3998.

(4) Bambirra, S.; Tsurugi, H.; van Leusen, D.; Hessen, B. Dalton Trans. 2006, 1157–1161.

(5) Stanford, M. J.; Dove, A. P. Chem. Soc. Rev. 2010, 39, 486–494.

(6) Miao, W.; Li, S. H.; Cui, D. M.; Huang, B. T. J. Organomet. Chem. 2007, 692, 3823–3834.

(7) Platel, R. H.; Hodgson, L. M.; Williams, C. K. Polym. Rev. 2008, 48, 11–63.

(8) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. Chem. Rev. 2004, 104, 6147–6176.

(9) Molander, G. A.; Romero, J. A. C. Chem. Rev. 2002, 102, 2161–2186.

(10) Molander, G. A.; Dowdy, E. D.; Noll, B. C. Organometallics 1998, 17, 3754–3758.

(11) Ge, S.; Meetsma, A.; Hessen, B. Organometallics 2008, 27, 3131–3135.

(12) Trambitas, A. G.; Panda, T. K.; Jenter, J.; Roesky, P. W.; Daniliuc, C.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2010**, *49*, 2435–2446.

(13) Edelmann, F. T. Chem. Soc. Rev. 2009, 38, 2253-2268.

(14) Lim, B. S.; Rahtu, A.; Park, J.-S.; Gordon, R. G. Inorg. Chem. 2003, 42, 7951–7958.

(15) Paivasaari, J.; Dezelah, C. L.; Back, D.; El-Kaderi, H. M.; Heeg, M.; Putkonen, M.; Niinisto, L.; Winter, C. H. *J. Mater. Chem.* **2005**, 15, 4224–4233.

(16) Daly, S. R.; Kim, D. Y.; Yang, Y.; Abelson, J. R.; Girolami, G. S. J. Am. Chem. Soc. 2010, 132, 2106–2107.

(17) Zimmermann, M.; Anwander, R. Chem. Rev. 2010, 110, 6194–6259.

(18) Lappert, M. F.; Pearce, R. J. Chem. Soc., Chem. Commun. 1973, 126.

(19) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. J. Chem. Soc., Dalton Trans. 1973, 1021–1027.

(20) Carver, C. T.; Diaconescu, P. L. J. Am. Chem. Soc. 2008, 130, 7558–7559.

(21) Carver, C. T.; Monreal, M. J.; Diaconescu, P. L. Organometallics 2008, 27, 363–370.

(22) Meyer, N.; Roesky, P. W.; Bambirra, S.; Meetsma, A.; Hessen, B.; Saliu, K.; Takats, J. *Organometallics* **2008**, *27*, 1501–1505.

(23) Ge, S.; Meetsma, A.; Hessen, B. Organometallics 2009, 28, 719–726.

(24) Mills, D. P.; Cooper, O. J.; McMaster, J.; Lewis, W.; Liddle, S. T. Dalton Trans. 2009, 4547–4555.

(25) Wooles, A. J.; Mills, D. P.; Lewis, W.; Blake, A. J.; Liddle, S. T. Dalton Trans. 2010, 39, 500-510.

(26) Schumann, H.; Freckmann, D. M. M.; Dechert, S. Z. Anorg. Allg. Chem. 2002, 628, 2422–2426.

(27) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. J. Chem. Soc., Chem. Commun. 1978, 140–142. (28) Bambirra, S.; Meetsma, A.; Hessen, B. Organometallics 2006, 25, 3454–3462.

(29) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M.

Advanced Inorganic Chemistry, 6th ed.; Wiley: New York, 1999; p 1109.
(30) Abicht, H. P.; Issleib, K. J. Organomet. Chem. 1980, 185, 265–275.

(31) Wayda, A. L.; Atwood, J. L.; Hunter, W. E. Organometallics 1984, 3, 939-941.

(32) Lubben, T. V.; Plossl, K.; Norton, J. R.; Miller, M. M.; Anderson, O. P. Organometallics **1992**, 11, 122–127.

(33) Petrov, A. R.; Rufanov, K. A.; Harms, K.; Sundermeyer, J. J. Organomet. Chem. 2009, 694, 1212–1218.

(34) Petrov, A. R.; Thomas, O.; Harms, K.; Rufanov, K. A.; Sundermeyer, J. J. Organomet. Chem. 2010, 695, 2738–2746.

(35) Harder, S. Organometallics 2005, 24, 373-379.

(36) Harder, S.; Ruspic, C.; Bhriain, N. N.; Berkermann, F.; Schuermann, M. Z. Naturforsch., B: Chem. Sci. 2008, 63, 267–274.

(37) Gentle heating of these compounds showed no evidence of isomerization to the ortho-metalated derivatives, while higher temperatures merely resulted in thermal decomposition.

(38) Evans, D. F. J. Chem. Soc. 1959, 2003-2005.

(39) Jones, C. J. *d-and f-Block Chemistry*; Wiley-Interscience: New York, 2002.