

Heteropolyagostic Interactions in Lanthanide(III) Diisopropylamido Complexes

William J. Evans,* Reiner Anwander, and Joseph W. Ziller

Department of Chemistry, University of California, Irvine, California 92717

Saeed I. Khan

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

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Introduction

Although lanthanide amide complexes are excellent synthetic precursors, particularly in reactions involving protic reagents,¹ relatively few types of amide complexes are available. In fact, lanthanide amide chemistry is dominated by a single ligand, the bulky bis(trimethylsilyl)amide. Hence, homoleptic lanthanide amide chemistry involves almost exclusively the Ln[N(SiMe₃)₂]₃ complexes,² although Ln(N^{*i*}Pr)₃ (Ln = Y, Yb, Nd) compounds were reported in 1976.³

Recently, we began to examine the utility of simple lanthanide amide complexes "Ln(NR₂)₃" with R = Me, Et, etc. as precursors to soluble heterobimetallic complexes⁴ which might be of interest as single-source precursors for semiconducting materials⁵ and as catalysts in olefin polymerization.⁶ For R = Me, the insoluble LnCl₃/LiNR₂ reaction product can be converted to soluble LnM₃ heterobimetallic complexes (M = Al, Ga) by reactions of the type shown in Scheme 1.

We were interested in determining how this scheme would be modified by using a soluble lanthanide amide precursor which is available in the R = ^{*i*}Pr case. We report here our results with N(^{*i*}Pr)₂ complexes which (a) definitively establish the existence of the *ate* complex (^{*i*}Pr₂N)₂Nd(μ-N^{*i*}Pr)₂Li(THF) as a hexane-soluble byproduct in this system, (b) show how LnAl₂ complexes can be accessed by this route, and (c) show that, by variation of the alkyl group in heterobimetallic complexes, diverse ligand combinations can be assembled and stabilized by *heteropolyagostic* interactions.

Results and Discussion

(^{*i*}Pr₂N)₂Nd(μ-N^{*i*}Pr)₂Li(THF), **2**. NdCl₃ is reported to react with LiN(^{*i*}Pr)₂ to form Nd(N^{*i*}Pr)₃(THF), **1**,³ a complex which

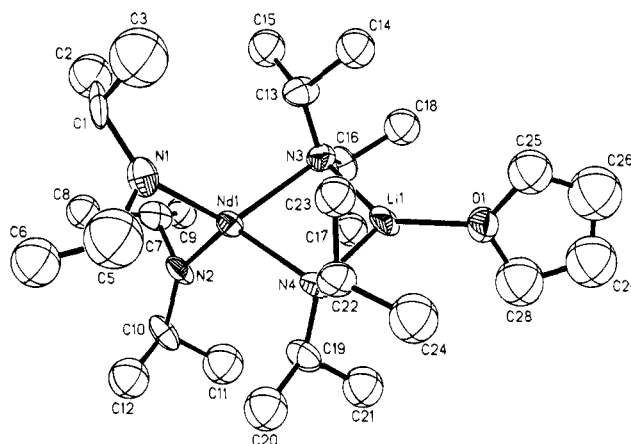
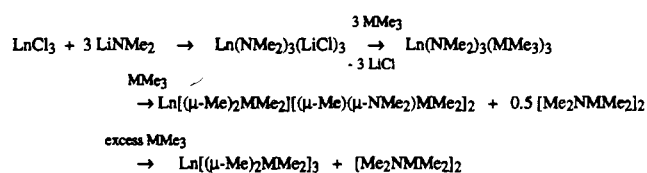


Figure 1. Molecular structure of (^{*i*}Pr₂N)₂Nd(μ-N^{*i*}Pr)₂Li(THF), **2**. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 1



appears to be sterically unsaturated compared to the recent X-ray crystal structure of the Ln[N(SiHMe₂)₃](THF)₂ (Ln = Y, Nd) complexes.⁷ In our hands, the NdCl₃/LiN(^{*i*}Pr)₂ reaction, even in the presence of a small excess of NdCl₃, gives complex **1** contaminated with the *ate* complex (^{*i*}Pr₂N)₂Nd(μ-N^{*i*}Pr)₂Li(THF), **2**, which has been fully defined by X-ray crystallography (Figure 1). Total elemental analysis established **1** as the main product of the NdCl₃/LiN(^{*i*}Pr)₂ reaction.

Lanthanide *ate* complexes are often both favored coproducts and crystallization products.^{8–12} A lanthanum analog of **2** has been described in the literature,¹⁰ but it was not structurally characterized. The structurally characterized lanthanide amide complex most similar to **2** is that of LiHo[N(CH₃)CH₂CH₂N(CH₃)₂]₄.¹¹ Since this paper was originally submitted, a report on the synthesis of the La, Y, and Yb analogs of **2** using excess LiN(^{*i*}Pr)₂ has appeared.¹² This study also reported the formation of analogs of **2** in stoichiometric reactions to prepare analogs of **1** and that a 2.5:1 LiN(^{*i*}Pr)₂:LnCl₃ ratio was needed to obtain pure analogs of **1**. Crystallographic data for the Y and Yb analogs were collected, but disorder precluded the reporting of definitive structures for those compounds. The unit cell data for those compounds show them to be isostructural with **2**, which is described below.

The neodymium in **2** is surrounded in a distorted tetrahedral fashion by two terminal amide ligands with normal Nd–N distances of 2.283(17)–2.291(16) Å and two bridging amide ligands with Nd–N bonds about 0.1 Å longer, as expected (Table 1). To achieve steric saturation of the metal center, one

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Table 1. Selected Bond Distances (Å) and Angles (deg)

(a) $\text{LiNd}(\text{N}^i\text{Pr}_2)_4(\text{THF})_2$, 2 ^a			
Nd1–N1	2.291(16)	Nd1–N2	2.283(17)
Nd1–N3	2.393(15)	Nd1–N4	2.406(16)
Nd1–C4	2.950(22)	Nd1–C7	3.000(20)
Nd1–C13	2.996(22)	Nd1–C19	2.983(20)
Li1–N3	2.040(35)	Li1–N4	2.089(39)
Li1–O1	1.930(36)		
Nd1–N1–C1	139.5(14)	Nd1–N1–C4	101.8(13)
Nd1–N2–C7	104.5(12)	Nd1–N2–C10	140.9(13)
Nd1–N3–C13	98.9(12)	Nd1–N3–C16	123.7(13)
Nd1–N4–C19	97.1(12)	Nd1–N4–C22	127.5(13)
(b) $\text{Nd}[\text{N}^i\text{Pr}_2][(\mu\text{-N}^i\text{Pr}_2)(\mu\text{-Me})\text{AlMe}_2][(\mu\text{-Me})_2\text{AlMe}_2]$, 3			
Nd–N1	2.508(2)	Nd–N2	2.168(2)
Nd–C1	2.659(3)	Nd–C2	2.639(3)
Nd–C5	2.718(2)	Nd···C14	2.933(2)
Nd···H1a	2.621(33)	Nd···H1b	2.577(32)
Nd···H2a	2.589(35)	Nd···H2c	2.550(31)
Nd···H5c	2.559(27)	Nd···H14a	2.605(26)
Nd–Al1	3.216(1)	Nd–Al2	3.284(1)
C1–Nd–C2	79.1(1)	C5–Nd–N1	75.1(1)
Nd–N2–C14	106.1(1)	Nd–N2–C17	138.4(2)
Nd–N1–C8	117.4(1)	Nd–N1–C11	111.2(2)

^a Bond lengths and angles for the other molecule in the unit cell are very similar (see Supporting Information).

α -carbon of each amide ligand is oriented toward Nd within 2.95–3.00 Å, distances which lie in the range observed for Ln···C distances in complexes containing agostic interactions.^{13–16} As a consequence of these agostic interactions,^{14–16} there is a large discrepancy in the Nd–N–C angles. The angles associated with the nearby carbon atoms are 97.1(12)–104.5(12)° whereas the others are 123.7(13)–140.9(13)°. Similar distortions are found in $(\text{Pr}_2\text{N})_2\text{La}[\mu\text{-}(\text{C}_6\text{H}_4\text{OMe-}o)_2\text{P}]\text{Li}(\text{THF})$ (La–N–C: 105.6(9), 141(1)°)¹⁰ and $[\text{ZrCl}(\mu\text{-Cl})\{\text{N}(\text{SiHMe}_2)_2\}_2]_2$ (Zr–N–C: 102.8(2), 129.6(2)°).¹⁵ Consistent with these structural features, an infrared absorption at 2668 cm^{-1} is observed.^{13e}

$\text{Nd}[\text{N}^i\text{Pr}_2][(\mu\text{-N}^i\text{Pr}_2)(\mu\text{-Me})\text{AlMe}_2][(\mu\text{-Me})_2\text{AlMe}_2]$, **3.** Stepwise addition of 3 equiv of AlMe_3 to **1** changed the color of the solution from blue to green and produced a white precipitate which had NMR and IR spectra consistent with $\text{LiAlMe}_3(\text{N}^i\text{Pr}_2)$. Precipitation ceased by addition of a fourth equivalent of AlMe_3 . Attempts to structurally characterize any paramagnetic products from this system were successful in the 4 equiv reaction, which produced some single crystals of **3** displaying a variety of ligand types, as shown in Figure 2.

Complex **3** contains a terminal N^iPr_2 ligand formally unchanged from the starting material, a $[(\mu\text{-N}^i\text{Pr}_2)(\mu\text{-Me})\text{AlMe}_2]$ group formed by addition of AlMe_3 to an amide ligand in the starting material, and a $[(\mu\text{-Me})_2\text{AlMe}_2]$ unit obtained by further reaction of AlMe_3 with a $[(\mu\text{-N}^i\text{Pr}_2)(\mu\text{-Me})\text{AlMe}_2]$ group. The existence of **3** suggests that a sequence of reactions much like

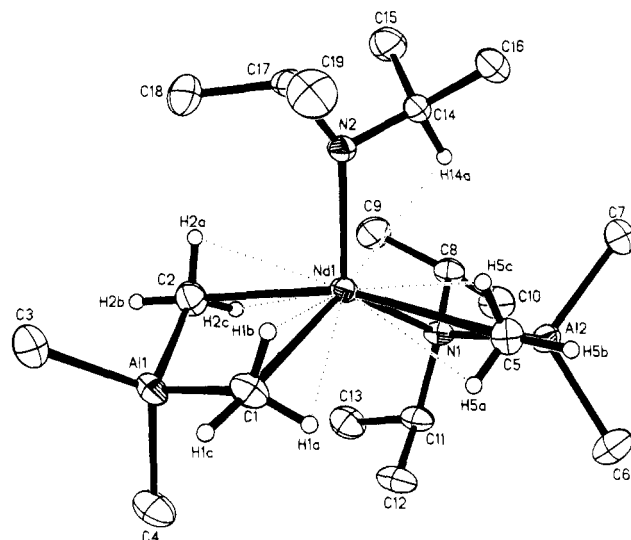


Figure 2. Thermal ellipsoid plot of the structure of $\text{Nd}[\text{N}^i\text{Pr}_2][(\mu\text{-N}^i\text{Pr}_2)(\mu\text{-Me})\text{AlMe}_2][(\mu\text{-Me})_2\text{AlMe}_2]$, **3**. Thermal ellipsoids are drawn at the 50% probability level.

that shown in Scheme 1 can occur, except in this case a product was obtained which contained all three ligand types in the same molecule. The isolation of **3** also suggests that the rates of the individual steps which convert a LnNR_2 unit to a $\text{Ln}(\text{Me}_2\text{MME}_2)$ group may differ just sufficiently that a complex with the three different ligands results. This suggests that, by control of the amido R group and reaction conditions and concentrations, a wide range of different combinations of ligands may be obtainable. For these heterobimetallic complexes, this provides a route to a variety of mixed-metal ratios with a variety of different coligands. Such variations should be useful in optimizing volatility or catalytic reactivity, depending on the practical use of the complex. It should be noted that this particular system has not provided synthetically useful amounts of **3** in pure form and further studies of compounds of this type should employ different metal/ligand combinations.

Complex **3** is unusual not only due to its diverse ligand composition but also due to its detailed structure. Superficially, the Nd appears to be in a square pyramidal environment generated by the three different ligand systems: the terminal isopropylamide in the axial position and the two chelating $[(\mu\text{-N}^i\text{Pr}_2)(\mu\text{-Me})\text{AlMe}_2]$ and $[(\mu\text{-Me})_2\text{AlMe}_2]$ groups in the basal sites. The 2.168(2) Å Nd–N2 distance involving the terminal amide is to our knowledge the shortest Ln–N distance ever observed (Table 1). It is much shorter than the Nd–N distances in four-coordinate **2** and is even comparable to Nd–O bond lengths e.g. in five-coordinate $\text{Nd}[\text{OC}(\text{CMe}_3)_3]_3(\text{CH}_3\text{CN})_2$ (2.149(5)–2.167(4) Å).¹⁷ Moreover, this terminal amide is not symmetrically oriented with respect to the metal: the 106.1(2) and 138.4(2)° Nd–N2–C angles differ significantly. The smaller angle orients C14 and one of its hydrogen atoms toward the metal. This β -H was located and refined, and the 2.605(26) Å Nd–H14a and 2.933(2) Å Nd–C14 contacts are in the agostic range.^{13,14}

The heteroleptic chelating $[(\mu\text{-N}^i\text{Pr}_2)(\mu\text{-Me})\text{AlMe}_2]$ ligand can be compared to the NMe_2 analogs in structurally characterized formally five-coordinate $\text{Nd}[(\mu\text{-NMe}_2)(\mu\text{-Me})\text{MMe}_2]_2(\mu\text{-NMe}_2)(\text{MMe}_3)$, **4** (M = Al, Ga).⁴ The major difference is that the

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2.508(2) Å Nd–N1 distance in **3** is about 0.1 Å longer. Additionally, in **3** the hydrogens of the bridging C5-methyl group could be located and refined. The 2.559(27) Å Nd–H5c distance is in the agostic range. The Nd–H5a distance is 2.73(3) Å.

The homoleptic chelating [(μ-Me)₂AlMe₂] ligand can be compared with the gallate ligands in Nd[(μ-Me)₂GaMe₂]₃.⁴ The 2.659(3) and 2.639(3) Å Nd–C distances in **3** are somewhat longer than those in Nd[(μ-Me)₂GaMe₂]₃ (average 2.599(11) Å). Both bridging methyl groups have hydrogen atoms oriented toward the neodymium metal with distances in the agostic range: Nd–H1a, 2.589; Nd–H1b, 2.622; Nd–H2a, 2.589; Nd–H2c, 2.541 Å. Hence **3** is a polyagostic complex with long-range interactions arising from three different ligand systems.

Conclusion

The bis(isopropyl)amide ligand provides soluble precursors from which 1:2 LnAl₂ complexes can be isolated. This ligand also allows the formation of a heterobimetallic complex with a diverse mixture of ligands which display polyagostic interactions. These results suggest that a variety of mixed-metal and mixed-ligand combinations may be accessed by reaction with heterometallic reagents.

Experimental Section

General procedures have been previously described.¹⁹ NdCl₃ was obtained by dehydration²⁰ of the commercially available hydrate (Rhone-Poulenc). LiN(Pr)₂ was freshly prepared from the amine (dried over CaH₂) and ⁶BuLi in hexane and isolated as a white powder. AlMe₃ (Aldrich) was used as received.

Nd(NⁱPr)₂(THF), 1, and (Pr₂N)₂Nd(μ-NⁱPr)₂Li(THF), 2. In a glovebox, NdCl₃ (1.07 g, 4.28 mmol) was stirred in THF for 20 min. When LiNⁱPr₂ (1.35 g, 12.60 mmol) was added to this suspension, the mixture immediately turned blue purple and was stirred for 24 h. The solvent was removed under vacuum, and the residue was dried for 7 h. The resulting powder was extracted with hexane, and a blue green solution was separated from the white precipitate by centrifugation. Crystallization at –35 °C gave blue-violet crystals (1.94 g, 88% (based on **1**)) which contained some **2** by X-ray crystallographic analysis (see below) and primarily **1** by elemental analysis. Unit cell data for **2** were collected on crystals from at least five different syntheses. Crystals of **1** from the sample that contained **2** were also analyzed by X-ray diffraction but decomposed before data could be collected (preliminary unit cell: *a* = 17.763(16) Å, *b* = 10.534(9) Å, *c* = 10.625(10) Å, β = 121.575(15)°). Anal. Calcd for C₂₂H₅₀N₃NdO (MW = 516.9): C, 51.12; H, 9.75; N, 8.13; Nd, 27.90. Calcd for C₂₈H₆₄LiN₄NdO (*M_r* = 624.0): C, 53.90; H, 10.34; N, 8.98; Nd, 23.11; Li, 1.11. Found: C, 50.69; H, 9.75; N, 7.94; Nd, 26.30; Li, 0.21. IR (Nujol, cm⁻¹): 2668 m, 2587 m, 1350 s, 1320 m, 1305 m, 1165 vs, 1112 m, 1100 m, 1028 m, 1005 m, 936 w, 908 s, 875 m, 840 w, 818 m, 790 m, 541 w, 517 m, 407 m, 277 m. ¹H NMR (C₆D₆): δ 47.71 (s, CHMe₂), 3.23 (s, CHMe₂), –4.30 (s, THF), –8.36 (s, THF).

Nd[NⁱPr₂][(μ-NⁱPr)₂(μ-Me)AlMe₂][(μ-Me)₂AlMe₂], 3. AlMe₃ (0.38 mL, 3.96 mmol) was added to a solution of **2** (0.49 g, 0.78 mmol) in 25 mL of hexane via syringe over a 1 h period. A white precipitate was separated from the green solution by centrifugation. Upon crystallization at –35 °C, a few blue crystals formed at the top of the container and were analyzed as complex **3** by X-ray analysis. Formation of the precipitate and the solution was reproducible, but single crystals were only obtained once. Since single crystals are necessary to fully identify this paramagnetic, heteroligated complex and since single-crystal formation has not been reproducible, further studies of this class of compounds should involve different metal/ligand combinations; i.e. AlEt₃, a GaR₃ compound, or a different lanthanide should be used.

Table 2. Crystallographic Data for LiNd(NⁱPr)₂(THF), **2**, and Nd[NⁱPr₂][(μ-NⁱPr)₂(μ-Me)AlMe₂][(μ-Me)₂AlMe₂], **3**

formula	C ₂₈ H ₆₄ LiN ₄ NdO	C ₁₉ H ₄₉ N ₂ Al ₂ Nd
fw	624.0	503.8
space group	P2 ₁ /c	P1
<i>a</i> , Å	15.313(3)	9.269(3)
<i>b</i> , Å	21.564(4)	10.708(3)
<i>c</i> , Å	21.475(5)	13.702(4)
α, deg		93.67(2)
β, deg	94.21(2)	104.54(2)
γ, deg		95.42(2)
<i>V</i> , Å ³	7072(3)	1305.1(6)
<i>Z</i>	8	2
<i>T</i> , K	273	163
λ, Å	1.5418 (Cu Kα)	0.710 73 (Mo Kα)
ρ _{calcd} , g cm ⁻³	1.17	1.282
μ, mm ⁻¹	1.170	2.068
no. of obsd rflns	3518 (<i>F</i> > 6.0σ(<i>F</i>))	5793 (<i>F</i> > 2.0σ(<i>F</i>))
<i>R</i> (<i>F</i> _o) ^a	5.8	2.4
<i>R</i> _w (<i>F</i> _o) ^b	5.9	2.7

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

X-ray Data Collection and Structure Determination and Refinement for (Pr₂N)₂Nd(μ-NⁱPr)₂Li(THF), 2. A sample of **2** was mounted in a glass capillary under nitrogen. Intensity data were collected with Cu Kα radiation from a Rigaku AFC5R rotating-anode X-ray generator that operated at 9 kW. Crystal data are given in Table 2. Three check reflections showed only random (<3%) variation in intensity during data collection. The data were corrected for Lorentz and polarization effects. Further details are given in the Supporting Information.

Calculations were performed using the UCLA Crystallographic Computing Package and SHELX76.²¹ Scattering factors and corrections for anomalous dispersion were taken from a standard source.²² Absorption corrections for the weakly diffracting but strongly absorbing crystal were carried out by performing a Ψ-scan correction followed by an absorption correction using the DIFABS program.²³ Hydrogen atoms were calculated at their idealized positions and were fixed to appropriate carbon atoms through the use of a riding model with a fixed isotropic *U*. At least one hydrogen atom was located for each methyl carbon atom. The two disordered THF molecules were refined with constrained bond lengths. Most of the methyl carbon atoms showed evidence of disorder. In the final cycle of refinement all the carbon atoms and THF were kept isotropic and the remaining atoms were refined anisotropically to convergence. The largest features in the final difference map were 1.1 Å away from the Nd and are probably absorption artifacts.

X-ray Data Collection and Structure Determination and Refinement for Nd[NⁱPr₂][(μ-NⁱPr)₂(μ-Me)AlMe₂][(μ-Me)₂AlMe₂], 3. A pale blue crystal of approximate dimensions 0.33 × 0.33 × 0.47 mm was immersed in Paratone-D oil (Exxon). The oil-coated crystal was then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Siemens P3 diffractometer which is equipped with a locally modified LT-2 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described methods similar to those of Churchill.²⁴ Intensity data were collected at 163 K using a θ–2θ scan technique with Mo Kα radiation under the conditions listed in Table 1.

All 6397 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The crystal class is triclinic with the two possible space groups being the centrosymmetric *P1* and the noncentrosymmetric *P1*. Convergence of the model using the centrosymmetric space group proved to be correct.

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All crystallographic calculations were carried out using either the UCI modified version of the UCLA Crystallographic Computing Package²¹ or the SHELXTL PLUS program set.²⁵ The analytical scattering factors for neutral atoms were used throughout the analysis²²; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\sum w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F) + 0.0003F^2$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(C-H) = 0.96 \text{ \AA}$ and $U(\text{iso}) = 0.05 \text{ \AA}^2$. Refinement of positional and thermal parameters for all non-hydrogen

atoms led to convergence with $R_F = 2.6\%$, $R_{wF} = 3.3\%$, and GOF = 1.49 for 218 variables refined against those 5791 data with $F > 3.0\sigma(F)$. A final difference-Fourier synthesis yielded $\rho(\text{max}) = 0.93 \text{ e \AA}^{-3}$.

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Supporting Information Available: Tables of crystal data, positional parameters, thermal parameters, and bond distances and angles (19 pages). Ordering information is given on any current masthead page.

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