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The Use of Heterometallic Bridging Moieties To Generate Tractable Lanthanide Complexes of Small Ligands**

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

Dedicated to Professor M. Frederick Hawthorne on the occasion of his 65th birthday

Lanthanide chemistry is dominated by large, anionic ligands which meet the steric and electronic demands of these large electropositive metals. On the other hand, the chemistry of simple lanthanide complexes of general formula LnZ_3 in which Z is a small anionic ligand such as methanide, methanolate, ethanolate, or dimethylamido, is poorly developed since these complexes are either unstable or insoluble.^[1,2] The only homoleptic lanthanide complexes with small ligands which are tractable enough to be definitively characterized by X-ray crystallography are the hexamethyl "ate" complexes $[\text{LnMe}_6]^{3-}$ of the late lanthanides Ho, Er, and Lu.^[12]

We describe here a method for the synthesis of isolable, soluble lanthanide complexes of small ligands Z ($Z = \text{NMe}_2$, Me) which also provides a convenient route to heterometallic complexes which have component combinations of interest with respect to polymerization catalysis^[3] and the formation of materials from molecular precursors.^[4] We also report details of the first structurally characterized molecular complexes containing a lanthanide metal and gallium.^[5]

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For many years it has been known that trialkylaluminum complexes will add to lanthanide complexes containing bulky stabilizing co-ligands to form bridged heterometallic species such as those given in Scheme 1.

Scheme 1. Examples of lanthanide heterometallic complexes.

Recently, we have shown that AlMe_3 will also bridge and stabilize metal ligand combinations such as $\text{Y}(\text{OCMe}_3)_3$ in $[\text{Y}\{(\mu\text{-OCMe}_3)(\mu\text{-Me})\text{AlMe}_2\}_3]^{[9]}$ and $[(\text{C}_5\text{H}_4\text{SiMe}_3)\text{Y}(\text{OCMe}_3)_2]$ in $[(\text{C}_5\text{H}_4\text{SiMe}_3)\text{Y}\{(\mu\text{-OCMe}_3)(\mu\text{-Me})\text{AlMe}_2\}_2]^{[10]}$. We now report that AlMe_3 will not only react with soluble reagents containing bulky ligands, but that it will also react with and solubilize the insoluble materials formed from reactions of lanthanide halides with small anionic ligands.

The reaction of anhydrous NdCl_3 with three equivalents of LiNMe_2 ($Z = \text{NMe}_2$) in THF at room temperature formed a blue material which was identified as **1a** [Eq. (a)]. Reaction of AlMe_3 or GaMe_3 with a suspension of **1a** in hexane yielded the hexane-soluble products **2a** (violet-blue) and **2b** (blue), respectively.

The intensely colored solutions of **2** are stable at room temperature. Evaporation of the solvent results in oily residues which solidify at -35°C . These solids slowly decompose at room temperature to form large colorless crystals of $[\{\text{Me}_2\text{NNMe}_2\}_2]$ ($\text{M} = \text{Al}, \text{Ga}$ (**4**))^[11] which sublime to the top of the container. Compounds **2a** and **2b** can be isolated in 80% yield by crystallization of the initially isolated solids from hexane at -35°C ; the molecular structure of **2b** is shown in Figure 1.^[12]

Fig. 1. Molecular structure of **2b**; the numbering is identical to that of isostructural **2a**. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [Å] and angles [°] for **2b** are as follows (**2a** in brackets): Nd1-N1 2.395(5) [2.435(4)], Nd1-N2 2.362(10) [2.433(8)], Nd1-C1 2.749(7) [2.708(5)], Nd1-C6 3.28 [3.39], Nd1-C7 3.35 [3.21], Nd1-M1 3.276(1) [3.274(2)], Nd1-M2 3.242(1) [3.191(3)]; Nd1-N1-M1 94.7(2) [96.0(1)], Nd1-C1-M1 84.3(2) [85.7(1)], N1-Nd1-C1 77.3(2) [74.7(1)], N1-M1-C1 103.0(3) [102.5(2)], Nd1-N2-M2 94.5(4) [92.6(3)].

X-ray crystallography revealed that compounds **2a** and **2b** are isostructural, which is somewhat surprising considering the structural differences of the aluminum and gallium starting reagents and their different bonding patterns towards transition metal centers.^[13] The overall structure shown in Figure 1 lacks the three-fold symmetry found in $[Y\{\mu\text{-OCMe}_3\}(\mu\text{-Me})\text{AlMe}_2]_3$.^[9] Instead, there are only two symmetrically identical $[(\mu\text{-NMe}_2)(\mu\text{-Me})\text{MMe}_2]$ chelating units (involving N1 and N1a) which have planar four-membered Nd-C-M-N metallacyclic rings. The third NMe_2MMe_3 unit involving N2 is disordered about the twofold symmetry axis and the methyl groups attached to aluminum or gallium in this unit are not as close to the Nd center as those in the other two units. A planar four-membered ring is not formed because neither of the two closest carbon atoms, C6 and C7, lie in a plane with Nd1, N2, and M.

The five ligands directly bound to Nd in **2** describe a distorted square pyramid in which N2 is slightly disordered. The Nd1–N1 distances of the bridges (**2a**, 2.435(4); **2b**, 2.395(5) Å) are longer than the terminal Nd–N(silylamido) distances in five-coordinate $[\text{Nd}\{\text{N}(\text{SiHMe}_2)_2\}_3(\text{thf})_2]$ (2.343(5) Å)^[14] and lie in the range found for terminal Nd–N(pyrazolato) bond lengths in the eight-coordinate complex $[\text{Nd}\{3,5\text{-di}(\text{tert-butyl})\text{pyrazolato}\}_3(\text{thf})_2]$ (2.443(9) Å).^[15] The Nd1–N2 distances are similar to the Nd1–N1 lengths (**2a**, 2.433(8); **2b**, 2.362(10) Å). The Nd1–C1 distances (**2a**, 2.708(5); **2b**, 2.749(7) Å) are similar to the Sm–C($\mu\text{-Me}$) distances in $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Me})\text{AlMe}_2(\mu\text{-Me})]_2$ (2.743(16) and 2.750(16) Å).^[18b] In contrast, the Nd1–C6 and Nd1–C7 distances are more in the range of agostic interactions.^[16] The bridging M1–C(methyl) distances (**2a**, 2.056(4); **2b**, 2.073(6), Å) the M–N bond lengths (**2a**, 1.950(5) and 1.955(8) Å; **2b**, 2.048(6) and 2.043(11) Å), and the terminal M1–C(methyl) distances (average: **2a**, 1.958(9); **2b**, 1.984(11) Å) are not unusual.^[17, 8, 13b]

Although solvent-free heterometallic peralkyl compounds like NaBMe_4 and LiAlMe_4 ($Z = \text{Me}$) have been very common reagents for a long time,^[17] compounds of the type $\text{M}_x\text{M}'_y\text{R}_z$ containing a transition metal and a main group metal are very rare.^[18] Furthermore, the above-mentioned “-ate” derivatives like $[\text{Ln}\{(\mu\text{-Me})_2\text{Li}(\text{tmeda})\}_3]$ ^[12] are known only in the presence of coordinating donor solvents and are more stable for the late lanthanide elements.

The reaction of **1a** with six equivalents or an excess of GaMe_3 under mild conditions (room temperature, hexane) afforded the heterometallic peralkyl complex **3** in 84% yield [Eq. (b)].

The formation of **3** is likely to occur through an intermediate **2b**, which can be seen clearly by the disappearance of M–NMe₂ vibrational modes in the IR spectra. The formation of the very stable **4**^[11] undoubtedly helps drive the reaction to completion. Complex **3** is not sublimable and decomposes above 50 °C under high vacuum. Both **3** and **4** are very soluble in hexane and can be separated by fractional crystallization at –35 °C. Complex **3** crystallizes first as large blue pyramids (edge lengths ca. 5 mm), after which **4** crystallizes as colorless cubes. Complex **3** was characterized by IR spectroscopy, elemental analysis, and X-ray structural analysis (Fig. 2).^[19]

The methyl groups in **3** are arranged in an octahedral geometry around Nd and a tetrahedral geometry around Ga. Each Nd–C–Ga–C ring is planar to within <0.07 Å. The fact that octa-

Fig. 2. Molecular structure of **3** with probability ellipsoids drawn at the 50% level. Selected distances [Å] and angles [°]: Nd1–C1 2.605(10), Nd1–C2 2.591(11), Nd1–C5 2.619(10), Nd1–C6 2.597(11), Nd1–C9 2.581(10), Nd1–C10 2.599(10), Ga–($\mu\text{-C}$) 2.115(11), Ga–C(1) 1.989(13), Nd1–Ga1 3.129(1), Nd1–Ga2 3.136(1), Nd1–Ga3 3.117(1); Ga1–Nd1–Ga2 116.7(1), Ga2–Nd1–Ga3 121.1(1), Ga1–Nd1–Ga3 122.0(1), C1–Nd1–C2 84.5(3), Nd1–C1–Ga1 82.0(3), C1–Ga1–C2 110.7(4).

hedral lanthanide complexes exist which contain larger bridging groups, for example **2a**, and smaller metals, for example $[Y\{\mu\text{-OCMe}_3\}(\mu\text{-Me})\text{AlMe}_2]_3$,^[9] suggests that the coordination environment around neodymium in **3** is sterically unsaturated. Complex **3** differs from the -ate complexes mentioned earlier in that the lanthanide metal is more electropositive than the other metallic component (electronegativities: Nd $\approx$ 1.1, Ga $\approx$ 1.8^[20]). Therefore **3** is better described as a gallate ($[\text{GaMe}_4]^-$) rather than a neodymate ($[\text{NdMe}_6]^{3-}$) complex, although the most important aspect of this difference will be in the reactivity.

The Nd–C distances in **3** are close to that of the Nd–C bond length of 2.65 Å expected in the unknown $[\text{Nd}\{(\mu\text{-Me})_2\text{Li}(\text{tmeda})\}_3]$ on the basis of Shannon radii^[21] and the known Ho and Er structures.^[2a, b] Other relevant Nd–C distances are 2.53(2) and 2.70(2) Å in $[(\text{C}_5\text{H}_4\text{CMe}_3)_2\text{Nd}(\mu\text{-Me})_2]$,^[22] 2.517(7) Å in $[(\text{C}_5\text{Me}_5)_2\text{Nd}\{\text{CH}(\text{SiMe}_3)_2\}]$,^[23a] and 2.506(7) Å in $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{Nd}\{\text{CH}(\text{SiMe}_3)_2\}]$.^[23b] The Ga–C distances in **3** are similar to those in **2b**.

The exchange of NMe₂ groups for methyl in reaction (b) is likely to occur in a stepwise fashion; examination of the analogous lanthanum system **1b** with four equivalents of GaMe_3 provided the partially exchanged complex **5** [Eq. (c)], which was characterized by elemental analysis, NMR spectroscopy, IR spectroscopy, and X-ray structural analysis (Fig. 3).^[24]

In complex **5**, the La–C distances in the two heteroleptic bridging units $\text{La}(\mu\text{-Me})(\mu\text{-NMe}_2)$ are rather long (2.891(5) and 2.992(5) Å) and are similar to those in $[\text{La}\{(\text{Ph}_2\text{P})_2\text{CH}\}_3]$ (2.890(5), 2.790(4), 2.908(5) Å)^[25] and even resemble the agostic $\text{La} \cdots \text{C}$ interactions in $[(\text{C}_5\text{Me}_5)\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_2(\text{thf})_x]$ ($x = 0, 1$; 2.978(6)–3.265(14) Å).^[16] The La–C distances in the homoleptic bridging unit $\text{La}(\mu\text{-Me})_2$ are also relatively long in comparison to the Nd–C distances in **3**. In comparison, La–C (terminal alkyl) distances of 2.515(9) and 2.537(5)–2.651(8) Å are found in $[\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_3]$ ^[26] and $[(\text{C}_5\text{Me}_5)\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_2(\text{thf})_x]$,^[16] respectively. The La–N bond lengths (2.451(4), 2.444(4) Å) are in the range of those found for terminal

Fig. 3. Molecular structure of **5** with probability ellipsoids drawn at the 50% level. Selected distances [Å] and angles [°]: La1–C1 2.891(5), La1–C6 2.992(5), La1–C11 2.776(5), La1–C12 2.742(5), La1–N1 2.451(4), La1–N2 2.444(4), La1–Ga1 3.187(1), La1–Ga2 3.112(1), La1–Ga3 3.291(1), Ga1–C1 2.058(5), Ga2–C6 2.033(5), Ga3–C11 2.084(5), Ga3–C12 2.096(5), Ga–C, 1.978(7); C11–La1–C12 78.4(2), C1–La1–N1 71.2(1), C6–La1–N2 68.9(1).

La–N bonds in $[\text{La}\{\text{N}(\text{SiMe}_3)_2\}_3(\text{PPh}_3\text{O})]$ (2.41(2) Å)^[27a] and $[(\text{C}_5\text{Me}_5)_2\text{La}(\text{NHMe})(\text{H}_2\text{NMe})]$ (2.323(10) Å).^[27b] A consequence of this irregular bonding pattern is that Ga1 and Ga2 lie closer to the La center than Ga3, and the La–C–Ga–N rings are nonplanar. The orientation of Ga1 and Ga2 toward the Ga3 unit and the arrangement of the methyl groups of the amido ligands with respect to the other methyl moieties appear to optimize the steric packing.

The isolation and characterization of complexes **2**, **3**, and **5** demonstrates that insoluble, oligomeric lanthanide complexes of small ligands can be “cracked” under very mild conditions (room temperature, hexane) by the attack of strong, soluble Lewis acids to form alkane-soluble, tractable compounds. This approach to developing the chemistry of lanthanide complexes of small ligands should be general; preliminary results show that species such as “Ln(OMe)₃” and InR₃ fit in this scheme.

Experimental Procedure

1: Addition of LiNMe₂ (2.22 g, 43.5 mmol) under nitrogen in a glovebox to a suspension of NdCl₃ (3.63 g, 14.5 mmol) in THF (50 mL) caused a spontaneous reaction indicated by a color change from pink to violet. After stirring the mixture at room temperature for two days, the solvent was removed to give a powder of composition **1a**. IR (Nujol): $\tilde{\nu}$ = 1205 m, 1126 s, 1113 s, 1052 m, 973 w, 893 vs, 459 m cm^{−1}. **1b** is prepared similarly.

2: Addition of MMe₃ (3 mmol) to a pink suspension of **1a** (0.40 g, 0.99 mmol) in hexane resulted in the extraction of soluble products into the hexane phase; this steadily darkened in color. After 12 h, the mixtures were centrifuged, concentrated, and crystallized. Analytical and spectroscopic data were collected on crystals grown from hexane solutions. **2a** (0.39 g, 80%): IR (Nujol): $\tilde{\nu}$ = 1220 sh, 1193 vs, 1145 w, 1113 s, 1091 s, 1043 s, 1024 w, 901 s, 695 vs, 580 vs, 537 m, 510 m, 480 m, 423 m, 311 m cm^{−1}. **2b** (0.51 g, 83%): IR (Nujol): $\tilde{\nu}$ = 1218 m, 1196 s, 1140 w, 1116 s, 1086 w, 1040 s, 971 w, 901 s, 724 s, 675 w, 650 w, 590 m, 556 s, 532 m, 495 w, 456 m, 411 s, 265 m cm^{−1}. Reaction of **1a** with one or two equivalents of MMe₃ also gave the homoleptic compounds **2**, but in lower yield.

3: To a suspension of **1a** (0.43 g, 1.05 mmol) in hexane (20 mL) was added GaMe₃ (0.63 mL, 6.30 mmol). After stirring this mixture for 36 h at room temperature, a white precipitate was separated from a blue hexane soluble product by centrifugation. After stirring for an additional 48 h, **3** can be separated from **4** by fractional crystallization at −35 °C as blue pyramidal crystals. **3** (0.47 g, 84%): IR (Nujol): $\tilde{\nu}$ = 1413 m, 1191 s, 736 s, 716 s, 582 s, 564 s, 527 s, 416 s, 289 s cm^{−1}.

5: A suspension of **1b** (0.75 g, 1.88 mmol) in hexane (20 mL) was extracted with GaMe₃ (0.75 mL, 7.52 mmol). The mixture was stirred overnight and centrifuged. Crystallization of the solution at −35 °C provided **5** as colorless crystals in 65%

yield. IR (Nujol): $\tilde{\nu}$ = 1221 m, 1199 m, 1193 m, 1187 m, 1142 w, 1121 s, 1090 w, 1044 s, 904 s, 724 s, 664 m, 621 (sh) m, 598 m, 561 m, 530 m, 476 m, 408 s, 272 m cm^{−1}. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 2.19 (s, 12 H, NMe₂), 2.10 (s, 6 H, μ -CH₃), 2.06 (s, 6 H, μ -CH₃), −0.19 (s, 6 H, GaMe₃), −0.23 (s, 12 H, GaMe₂). ¹³C{¹H} NMR (300 MHz, C₆D₆, 25 °C): δ = 42.7 (μ -CH₃), 41.8 (NMe₂), 41.3 (μ -CH₃), −3.1 (GaMe₃), −4.1 (GaMe₂).

Elemental analysis [%]: **1a**: Calcd for NdLi₃Cl₃N₃C₆H₁₈: C 17.85, H 4.49, N 10.41, Nd 35.73; found: C 16.42, H 4.26, N 10.96, Nd 35.0. **2a**: Calcd for NdAl₃N₃C₁₅H₄₅: C 36.56, H 9.21, N 8.53; found: C 35.86, H 9.41, N 6.61. **2b**: Calcd for NdGa₃N₃C₁₅H₄₅: C 29.01, H 7.30, N 6.77, Nd 23.23; found: C 27.50, H 7.25, N 5.44, Nd 22.3. **3**: Calcd for C₁₃H₃₆Ga₃Nd: C 27.00, H 6.80, Nd 27.0; found: C 26.81, H 6.54, Nd 26.5. **5**: Calcd for C₁₄H₂₄Ga₃LaN₂: C 28.67, H 7.22, N 4.78, La 23.7; found: C 27.16, H 7.00, N 4.82, La 21.8.

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- [12] a) The complexes **2** crystallize from hexane in the monoclinic space group C2/c. **2a** (−110 °C): $a = 16.437(4)$, $b = 11.194(2)$, $c = 15.219(3)$ Å, $\beta = 116.38(2)^\circ$, $V = 2508.8(10)$ Å³, $\rho_{\text{calc}} = 1.304$ g cm^{−3} for $Z = 4$; 2743 reflections ($I \geq 4 \sigma(I)$), $R_f = 0.037$. **2b** (−110 °C): $a = 16.215(3)$, $c = 11.2890(10)$ Å, $\beta = 116.760(10)^\circ$, $V = 2487.8(6)$ Å³, $\rho_{\text{calc}} = 1.537$ g cm^{−3} for $Z = 4$; 3167 reflections ($I \geq 4.0 \sigma(I)$), $R_f = 0.061$. Both molecules lie on a twofold axis and are disordered. b) Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-58236. c) The SmGa analogue was prepared similarly and is isostructural with **2a** and **2b**.
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A Liquid-Crystalline Polymer Network Built by Molecular Self-Assembly through Intermolecular Hydrogen Bonding**

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The use of noncovalent interactions such as hydrogen bonds for materials design has attracted much attention.^[1] Mesogenic structures can be obtained by self-assembly of two different components by means of selective hydrogen bond formation.^[2–5] This concept has been extended to side-chain^[3] and main-chain^[4, 5] liquid-crystalline polymers.

We demonstrate here that a mesogenic three-dimensional network can be constructed by self-assembly through noncovalent interactions. Hydrogen-bonded cross-linked polymers were prepared by complexation of a polyacrylate (**1**) containing a benzoic acid moiety (H-bond donor) with various ratios of bifunctional 4,4'-bipyridine (**2**) and the monofunctional stilbazole **3** as

H-bond acceptors.^[6] Compound **2** is capable of recognizing and binding carboxylic acid fragments of the polymer at each of its pyridyl ends and functions as a cross-linker. The hydrogen-bonded complexes were prepared by the evaporation method,^[2, 3] and the stoichiometry of the H-bond donor and H-bond acceptors was maintained. For the ternary complex of **1**, **2**, and **3**, a mixture of H-bond acceptors ($x/2$ mol of **2** corre-

sponding to x mol of the pyridyl unit, and y mol of **3**) was complexed with an amount of **1** containing $x + y$ mol of the H-bond donor moiety. The mol fraction of the pyridyl moiety of **2** relative to the all of the pyridyl units in the complex is represented as $\bar{x} = x/(x + y)$.

The proposed structure of the hydrogen-bonded 1:1 complex (containing an equimolar amount of H-bond donor and acceptor) prepared from H-bond donor polymer **1** and H-bond acceptors **2** and **3** is shown in Figure 1. The self-assembly of a cross-linked mesogen for the polymeric networks was expected.

Differential Scanning Calorimetry (DSC) thermograms of the polymeric complexes containing various ratios of **2** and **3**

on heating scans are shown in Figure 2. Plots of transition temperatures of the polymeric complexes against $\bar{x}$, the mol fraction of pyridyl units of **2** in the mixture of **2** and **3**, are shown in Figure 3. The 1:1 complex of **1** and **3** behaves like a side-chain liquid-crystalline polymer^[3d, 7] and exhibits

Fig. 1. Proposed molecular structure of the polymeric complex consisting of **1**, **2**, and **3**.

Fig. 2. DSC thermograms of polymeric complexes: A: $\bar{x} = 0$; B: $\bar{x} = 0.3$; C: $\bar{x} = 0.5$; D: $\bar{x} = 0.7$; E: $\bar{x} = 1.0$.

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