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 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 electropositive metals has met with some success in forming complexes which also provide a convenient route to heterometallic compounds containing a lanthanide metal and a Group 13 metal. This is exemplified by the recent isolation of hexamethylaluminate complexes containing a lanthanide metal and an AlMe₃ group as co-ligand. The first structurally characterized molecular complexes containing a lanthanide and AlMe₃ group were reported by us in 1991,[41 and the chemistry of these materials from molecular precursors is rapidly developing.[43 We also report details of the method for the synthesis of isolable, soluble lanthanide complexes of small ligands Z (Z = Me, Me₃Si) which meet the steric and electronic demands of these large electropositive metals. [42 These complexes will add to lanthanide complexes containing bulky stabilizing co-ligands to form bridged heterometallic species such as those given in Scheme 1.

\[
\begin{align*}
&([\text{C}_4\text{H}_9\text{H}_2\text{Y}(\mu-\text{Me})\text{Al}(\text{Me}_2)_2])^{\text{2-}} \\
&\text{[Yb}[(\mu-\text{SiMe}_3)_2]_2(\mu-\text{Me})\text{MeAlMe}_2]^{\text{2+}} \\
&([\text{C}_4\text{H}_9\text{H}_2\text{Zn}(\mu-\text{C}_2\text{H}_5)_2\text{Al}(\text{Me}_2)_2])^{\text{2+}}
\end{align*}
\]

Scheme 1. Examples of lanthanide heterometallic complexes.

Recently, we have shown that AlMe₃ will also bridge and stabilize metal ligand combinations such as Y(OCMe₃)₂ in [(μ-OCMe₃)(μMe)AlMe₂]₂[91 and [(C₅H₅SiMe₃)Y{(p-OCMe₃)(p-Me)AlMe₃}],[91 which we now report that AlMe₃ 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 NdCl₃ with three equivalents of LiNMe₂ (Z = NMe₂) in THF at room temperature formed a blue material which was identified as 1a [Eq. (a)]. Reaction of AlMe₃ or GaMe₃ with a suspension of 1a in hexane yielded the hexane-soluble products 2a (violet-blue) and 2b (blue, respectively).

\[
\begin{align*}
\text{NdCl}_3 + 3\text{LiNMe}_2 & \rightarrow \text{[Nd(NMe}_2)_3(\text{LiCl})]^{\text{3-}} \text{MeMe}_3 \\
\text{[Nd(NMe}_2)_3(\text{MeMe}_3)]^{\text{3-}} + 3\text{LiCl} & \rightarrow \text{2a, M = Al; 2b, M = Ga}
\end{align*}
\]

The intensely colored solutions of 2 are stable at room temperature. Evaporation of the solvent results in oils which solidify at ~35 °C. These solids slowly decompose at room temperature to form large colorless crystals of \([\text{Me}_2\text{NMe}_2]\text{Nd}(\text{Me}_3\text{Si})\text{Cl}_2\) (M = Al, Ga) 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]

\[
\begin{align*}
\text{NdCl}_3 + 3\text{LiNMe}_2 & \rightarrow \text{[Nd(NMe}_2)_3(\text{LiCl})]^{\text{3-}} \text{MeMe}_3 \\
\text{[Nd(NMe}_2)_3(\text{MeMe}_3)]^{\text{3-}} + 3\text{LiCl} & \rightarrow \text{2a, M = Al; 2b, M = Ga}
\end{align*}
\]

The use of heterometallic bridging moieties to generate tractable lanthanide complexes of small ligands is an emerging area of research. This methodology provides a convenient route to heterometallic complexes which have component combinations of interest with respect to polymerization catalysis and the formation of materials from molecular precursors. We also report details of the first structurally characterized molecular complexes containing a lanthanide and gallium.\[
\text{[Yb}[(\mu-\text{SiMe}_3)_2]_2(\mu-\text{Me})\text{MeAlMe}_2]^{\text{2+}} \\
([\text{C}_4\text{H}_9\text{H}_2\text{Zn}(\mu-\text{C}_2\text{H}_5)_2\text{Al}(\text{Me}_2)_2])^{\text{2+}}
\]

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.

\[
\begin{align*}
&([\text{C}_4\text{H}_9\text{H}_2\text{Y}(\mu-\text{Me})\text{Al}(\text{Me}_2)_2])^{\text{2-}} \\
&\text{[Yb}[(\mu-\text{SiMe}_3)_2]_2(\mu-\text{Me})\text{MeAlMe}_2]^{\text{2+}} \\
&([\text{C}_4\text{H}_9\text{H}_2\text{Zn}(\mu-\text{C}_2\text{H}_5)_2\text{Al}(\text{Me}_2)_2])^{\text{2+}}
\end{align*}
\]

Scheme 1. Examples of lanthanide heterometallic complexes.

** We thank the Division of Chemical Sciences of the Office of Basic Energy Sciences of the Department of Energy for support of this research and the Deutsche Forschungsgemeinschaft for a Postdoctoral Fellowship (to R. A.).

Fig. 1. Molecular structure of 2b; the numbering is identical to that of its structural isomer 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) [2.435(8)], Nd1-C1 2.749(7) [2.708(5)], Nd1-C6 2.749(7) [2.708(5)], Nd1-C10 3.35 [3.23], Nd1-M1 3.276(1) [3.274(2)], Nd2-M2 3.242(1) [3.191(3), Nd1-N1 94.7(2) [96.0(1)], Nd1-C1-M1 84.3(2) [85.7(1)], Nd1-N1-C7 77.3(2) [74.7(1)], Nd1-M1-C1 103.9(3) [102.5(2)], Nd1-N2-M2 94.3(2) [92.6(2)].

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X-ray crystallography revealed that compounds 2a and 2b are isomorphous, which is somewhat surprising considering the structural differences of the gallium and aluminium 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{μ-OMe₂}₂{(μ-OMe)AlMe₃}₃].[19] Instead, there are only two symmetrically identical [μ-NMe₂]₃{μ-Me}MMe₃ chelating units (involving N1 and N1a) which have planar four-membered Nd-C-M-N metallacyclic rings. The third NMe₃-MMe₃ 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 Nd is slightly disordered. The Nd–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 [Nd{N(SiMe₃)₂}₂(thf)] (2.343(5) Å)[14] and lie in the range found for terminal Nd–N(pyrazolato) bond lengths in the eight-coordinate complex [Nd{3,5-di-tert-butyl]pyrazolato}₃(thf)] (2.443(9) Å).[15] The Nd–N₂ distances are similar to the Nd–N₁ distances (2a, 2.433(4); 2b, 2.374(7) Å) and are similar to the Sm–C(μ-Me) distances in [(C₅Me₅)₂Sm(μ-Me)AlMe₃(μ-Me)₂] (2.734(16) and 2.750(16) Å).[16] In contrast, the Nd–C₁ and Nd–C₇ distances are more in the range of agostic interactions.[17] The bridging M–C(μ-Me) distances (2a, 2.056(4); 2b, 2.073(6), Å) the Nd–N₂ distances are similar to the terminal alkyl distances of 2.515(9) and 2.537(5)-2.651(8) Å in [(C₅Me₅)La(μ-Me)₂Li(thf)].[9] Instead, there are only two symmetrically identical (μ-NMe₂)(μ-OMe)AlMe₃ chelating units (involving N2 and N1a) which have planar four-membered Nd-C-M-N metallacyclic rings. The third NMe₃-MMe₃ 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.

Although solvent-free heterometallic peralkyl compounds like NaBMe₄ and LiAlMe₂ (Z = Me) have been very common reagents for a long time,[17] compounds of the type M₅R₂, containing a transition metal and a main group metal are very rare.[18] Furthermore, the above-mentioned "ate" derivatives like [La(μ-Me₂)Li(tmeda)] are known only in the presence of coordinating donor solvents and are more stable for the late lanthanide elements.

The exchange of NMe₃ groups for methyl in reaction (b) is likely to occur in a stepwise fashion; examination of the analogous lanthanum system in 4b with four equivalents of GaMe₃ 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).[14]

In complex 5, the La–C distances in the two heteroleptic bridging units La–(μ-Me)(μ-NMe₂) are rather long (2.895(5) and 2.992(5) Å) and are similar to those in [La(μ-P₂Ph₃)₂] (2.890(5), 2.790(4), 2.908(5) Å)[25] and even resemble the agostic La–C interactions in [(C₅Me₅)La(μ-C(SiMe₃)₂)₂(thf)] (x = 0). 1.27.9.286(14). The La–C distances in the homoleptic bridging unit La(μ-Me) 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 [La(C₂H₇(THF))₃] and [C₅Me₅La(μ-CH(SiMe₃)₂)₂(thf)]. Respectively. The La–N bond lengths (2.435(4) and 2.444(14) Å) are in the range of those found for terminal
Crystallization of the solution at 3°C yielded 1.221 m; 1.193 m, 1.187 m, 1.142 w, 1.121 w, 1.094 s, 1.064 s, 0.904 s, 0.724 s, 0.664 m, 0.521 (sh), 0.598 s, 0.561 m, 0.539 m, 0.476 m; 0.408 s, 0.272 cm⁻¹.

1H NMR (300 MHz, CD₂Cl₂, 25°C); δ = 2.19 (12H, NMe₂), 2.10 (6H, H₂OCH₃), 2.06 (6H, H₂OCH₃), 0.19 (12H, GaMe₂), -0.19 (12H, GaMe₂). [12]¹H NMR (300 MHz, CD₂Cl₂, 25°C); δ = 4.27 (12H, CH₂), 41.8 (NaMe₂), 41.3 (GaMe₂), -4.1 (GaMe₂).

Elemental analysis [%]: 1a. Caled for Na₂Li₆(NH₂)₃(N₃)₂CN₃: C 7.85; H 0.10; Na 2.15. Found: C 16.2, H 2.06, Na 10.6. 2a. Caled for Na₂Li₆(NH₂)₃(N₃)₂CN₃: C 36.91; H 9.81; Na 8.53; found: C 35.96, H 9.41, Na 6.61. 2b. Caled for Na₂Li₆(NH₂)₃(N₃)₂CN₃: C 39.01; H 7.30; N, 6.67; found: C 37.50, H 7.75, N, 6.44; Na 23.3 a, 3, 3. Caled for Li₆(NH₂)₃(N₃)₂CN₃: Li 27.00, H 8.50; Na 27.0. 265 in cm⁻¹. Reaction of...
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.11 Mesogenic structures can be obtained by self-assembly of two different components by means of selective hydrogen bond formation.12-13 This concept has been extended to side-chain14 and main-chain15,16 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.14 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,13 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-

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

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