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A Lanthanide−Gallium Complex Stabilized by the N-Heterocyclic Carbene Group

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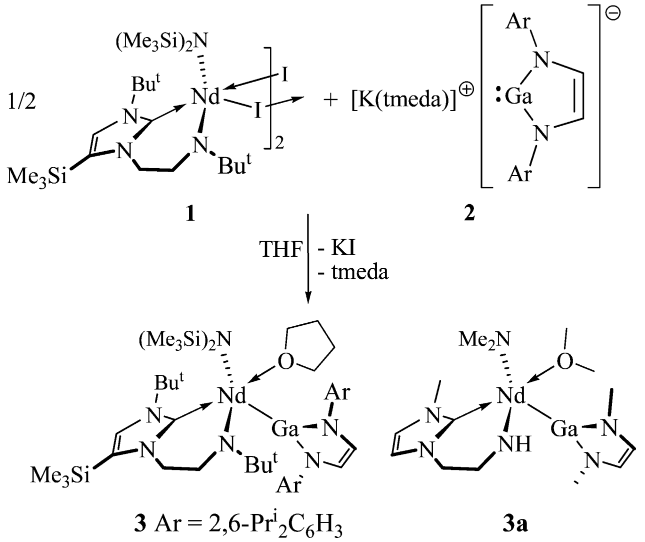
The synthesis of molecular metal−metal bonds is fundamentally important to the understanding of chemical bonding,[1,2] catalysis, the chemistry of metal surfaces, and of magnetic devices.[3−5] Since the report of quadruple bonds in salts of $[\mathrm{Re_2Cl_8}]^{2-}$,[6] the study of transition metal−metal bonds has generated significant new knowledge, the most recent milestone exemplified by a Cr(I)−Cr(I) dimer which formally features a quintuple bond.[7] However, in contrast to transition metals, lanthanide complexes featuring a metal−metal bond are virtually unknown. The only reported lanthanide complexes that contain unsupported metal−metal bonds are $[\mathrm{(THF)(Cp)_2Lu{-}Ru(Cp)(CO)_2}]$[8] and $[\mathrm{(Cp^*)_2Ln{-}Al(Cp^*)}]$ (Ln = Eu, Yb).[9] In the former, the Lu−Ru bond may be regarded as a polarized covalent bond, whereas in the latter pair the dative Ln−Al bonds have been shown to be essentially ionic, with negligible charge transfer or covalent contributions from the Ln and Al fragments.

Recently, we in the Arnold group reported the facile, one-pot, high yield synthesis of $[\mathrm{Nd(L')(N'')(\mu\text{-}I)}]_2$ (**1**)[10] [$\mathrm{L' = Bu^tNCH_2CH_2\{C(NCSiMe_3CHNBu^t)\}}$; $\mathrm{N'' = N(SiMe_3)_2}$] from $[\mathrm{Nd(L)(N'')_2}]$ and $\mathrm{Me_3SiI}$ [$\mathrm{L = Bu^tNCH_2CH_2\{C(NCHCHNBu^t)\}}$]. Compound **1** is an excellent synthon for exploring N-heterocyclic carbene (NHC)-supported lanthanide chemistry by salt elimination routes, since the NHC is tethered covalently to the lanthanide center and the iodide ligand is easily substituted. The NHC in **1** is softer than in non-silylated analogues.[10,11] Thus, the NHC in **1** renders a potentially reducible neodymium center very resistant to reduction.[10] In parallel, we in the Jones group have been exploring the coordination chemistry of the gallium diyl, $[\mathrm{Ga(NArCH)_2}][\mathrm{K(tmeda)}]$ (**2**)[12] [$\mathrm{Ar = 2,6\text{-}Pr^i_2C_6H_3}$; $\mathrm{tmeda = Me_2NCH_2CH_2NMe_2}$]. **2** contains an anionic gallium heterocycle which is valence iso-electronic to NHCs, and strong parallels between the chemistry of **2** and NHCs have been observed.[13] The utility of **2** in salt elimination chemistry has begun to be demonstrated.[14] In some reactions the insertion of **2** into metal−halide bonds followed by reductive elimination to afford gallium(II)−halide species may occur.[15] Given the documented reluctance of **1** to engage in reduction chemistry,[10] we identified **1** and **2** as ideal precursors from which to prepare a compound containing a lanthanide−gallium bond. Herein, we report the synthesis and structure of the first f-element−gallium bond.

The reaction between **1** and **2** in cold THF proceeds smoothly, with concomitant elimination of KI, to give a dark red solution. Workup and recrystallization from toluene affords **3** as large red blocks in moderate yield (Scheme 1).[16] The spectroscopic and elemental analysis data for **3** are consistent with the proposed formulation. We were unable to isolate a product containing a Ln−Ga bond from treatment of $\mathrm{LnCl_3}$ with 3 equiv of **2**, or of $\mathrm{Ln(\eta\text{-}C_5H_5)_2Cl}$ with **2** (Ln = Nd, Sm, Gd, or Er).

Scheme 1. Synthesis of **3**



Notably, **3** is stable in solution, in contrast to $[\mathrm{(Cp^*)_2Ln{-}Al(Cp^*)}]$ (Ln = Eu, Yb),[9] which immediately dissociate in solution to $[\mathrm{(Cp^*)_2Ln}]$ and $[\mathrm{Al(Cp^*)}]$. A toluene solution of **3** does not decompose until heated to 100 °C for 16 h. This results in deposition of elemental gallium and an unidentified compound, which we suggest contains a Nd-bound diazabutadienide anion.

A single-crystal X-ray diffraction experiment was performed;[17] the molecular structure of **3** is depicted in Figure 1. The neodymium center adopts a distorted trigonal bipyramidal geometry, such that the two neutral donors O(1) and C(2) are axially disposed, and the anionic donors N(2), N(4), and Ga(1) reside in the equatorial plane. The Nd−Ga bond length of 3.2199(3) Å is without precedent and so cannot be compared with other data, but it is slightly longer than the sum of covalent radii (Nd−Ga = 2.89 Å).[18] The Nd−Ga bond length is about 0.15 Å shorter than the Eu−Al bond length of 3.3652(10) Å reported for $[\mathrm{(Cp^*)_2Eu{-}Al(Cp^*)}]$.[9] Divalent Eu is slightly larger than trivalent Nd, and the covalent radii of Al(I) and Ga(I) are very similar (1.30 vs 1.25 Å, respectively),[19] so the two bonds seem fairly similar in length, considering the differences in their components. The Nd(1)−C(2) bond length of 2.669(2) Å is toward the higher end of the range of Nd−NHC bonds[20] and reflects the presence of the nucleophilic, anionic gallium heterocycle.

DFT calculations were carried out on the model geometry **3a** (Scheme 1) to probe the nature of the Nd−Ga bond in **3**. The DFT geometry optimization of **3a** reproduces successfully the principal

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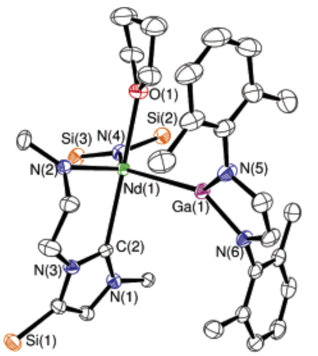

Figure 1. Molecular structure of **3** (thermal ellipsoids at 40% probability levels, H atoms and Me groups omitted). Selected bond lengths (Å) and angles (deg): Nd(1)−Ga(1), 3.2199(3); Nd(1)−C(2), 2.669(2); Nd(1)−N(2), 2.223(2); Nd(1)−N(4), 2.357(2); Nd(1)−O(1), 2.5578(19); Ga(1)−N(5), 1.932(2); Ga(1)−N(6), 1.932(2); C(2)−N(1), 1.365(3); C(2)−N(3), 1.367(3); N(2)−Nd(1)−N(4), 120.37(8); N(2)−Nd(1)−O(1), 89.64(7); N(4)−Nd(1)−O(1), 91.43(7); N(2)−Nd(1)−C(2), 82.45(7); N(4)−Nd(1)−C(2), 100.53(8); O(1)−Nd(1)−C(2), 167.84(7); N(2)−Nd(1)−Ga(1), 104.76(6); N(4)−Nd(1)−Ga(1), 134.69(5); O(1)−Nd(1)−Ga(1), 84.59(4); C(2)−Nd(1)−Ga(1), 88.49(5); N(5)−Ga(1)−N(6), 83.89(9); N(1)−C(2)−N(3), 102.8(2).

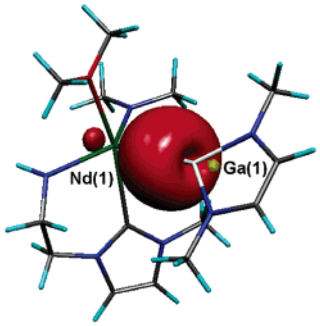

Figure 2. The Nd−Ga bond NBO in **3a**.

features of the structure of **3** as determined by X-ray crystallography; the Nd(1)−Gd(1) and Nd(1)−C(2) distances are 3.227 and 2.682 Å, respectively, ca. 0.01 Å longer than in the X-ray crystal structure of **3**. A notable difference between the experimental geometry of **3** and the calculated geometry **3a** is the relative orientation of the $[Ga(MeNCH)_2]^-$ and $\{Nd\}^+$ fragments. In **3a** the angle between the planes defined by Nd(1)N(2)N(4) and Ga(1)N(5)N(6) is 24.7° whereas in **3** this angle is 60.2°. The calculated structure converged at this geometry irrespective of the relative orientations of the $[Ga(MeNCH)_2]^-$ and $\{Nd\}^+$ fragments used in the input geometry. Thus, it appears that the steric bulk of the pendant substituents in **3** controls the relative orientation of the $[Ga(NArCH)_2]^-$ and $\{Nd\}^+$ fragments in **3**. However, given the spherical symmetry and composition of the Nd−Ga bond in **3a** (see below) it is likely that the electronic structure and Nd−Ga bond energy of **3a** provide good models for those of **3**.

A natural bond orbital (NBO) analysis of **3a** reveals natural charges for Nd(1) and Ga(1) of +2.40 and +0.38, respectively, consistent with charge transfer from a formal Ga(I) center to a Nd(III) center to form a Nd−Ga bond with a Wiberg bond order of 0.827. A NBO analysis of the Nd−Ga bond shows that this bond is 87% Ga and 13% Nd in character (Figure 2) and involves Nd $6s6p^{0.01}5d^{0.36}$ and Ga $4s4p^{1.67}$ hybrid orbitals, the latter corresponding to the expected sp^2 hybridization of the formally Ga(I) center.

The calculated Nd−Ga bond energy, corrected for thermal and zero point energies, the preparation energies for the $[Ga(MeNCH)_2]^-$ and $\{Nd\}^+$ fragments, and for basis set superposition errors, is 386 kJ mol^{-1}. This energy is similar to that for the reaction $[M(OMe_2)_5\{Ga(MeNCH)_2\}]^+ + [Ga(MeNCH)_2]^- \rightarrow [M(OMe_2)_5\{Ga(MeNCH)_2\}_2] + Me_2O$ (M = Ca, $\Delta E = 348.9$ kJ mol^{-1} and M = Sr, $\Delta E = 358.4$ kJ mol^{-1})[21] and an order of magnidude greater than the bond energy of the Ln−Al bonds in $[(Cp^*)_2Ln^{II}-Al^{I}(Cp^*)]$ (Ln = Eu, Yb, ca. 30 kJ mol^{-1}).[9] Thus, **3** is considerably more stable than $[(Cp^*)_2Ln-Al(Cp^*)]$ in solution because of the stronger Ln−M bond in **3.** The relatively strong Nd−Ga bond involves charge transfer from a more polarizable Ga(I) center to a more polarizing Nd(III) center leading to a bond with Nd−Ga covalent character.

In summary, we have described the synthesis and structure of the first f-element−gallium bond in a complex which is stable in solution as well as in the solid state. We are currently investigating the reactivity of **3** since it contains a lanthanide center bonded to both an NHC and an isoelectronic anionic gallium−NHC analogue, both of which have potentially ambiphilic character.

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Supporting Information Available: Experimental, X-ray, and computational data for **3**/**3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Crystallographic data for **3** at 150 K with Mo Kα radiation ($\lambda = 0.71073$ Å): orthorhombic, space group $P2_12_12_1$, $a = 14.0875(5)$, $b = 19.1557(6)$, $c = 22.0078(7)$ Å, $V = 5938.9(3)$ Å^3, $Z = 4$, $R_1 = 0.0259$ for 12575 ($I > 2\sigma(I)$) data, wR_2 (all data) = 0.0632.
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