Organolanthanides

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Heteroleptic Samarium(II) Complexes by Base-Induced Reduction

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bulky ligands · C–H activation · lanthanides · reduction · samarium

In memory of Herbert Schumann

Divalent samarium was first discovered as the chloride, $SmCl_2$, about one century ago.[1] Subsequent work over many decades revealed that the crystal chemistry of samarium(II) is that of divalent strontium, or in other words, there are divalent lanthanide ions with electronic configurations of $[Xe]6s^05d^04f^n$ that behave as pseudo alkaline earth ions.[2] These lanthanides are the elements europium, ytterbium, samarium, thulium, dysprosium, and neodymium, in order of ascending (negative) standard electrode potentials E^o for the half cells M^{2+}/M^{3+}. Potentials start at -0.35 V (M = Eu) and approach the reduction potentials of alkali metals, with $E^o = -2.6$ V for R = Nd.[3] Figure 1 shows a comparison of the standard electrode potentials for divalent lanthanides along with a number of non-noble metals.

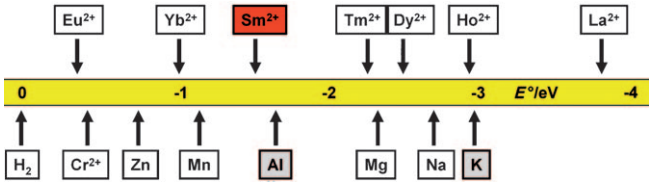

Figure 1. Standard electrode potentials $E^0(M^{2+}/M^{3+})$ (symbolized as M^{2+}, top) and a comparison with a variety of common reducing agents (bottom).

In solids, these six elements form, for example, diiodides MI_2, which have crystal structures that are well-known for other salts of that formula type. There are, however, a number of other lanthanide diiodides for La, Ce, Pr, and Gd.[4] In these compounds, the electronic configuration $[Xe]6s^05d^14f^{n-1}$ is favored (under standard conditions), which gives rise to special properties, such as electronic conductivity or cluster formation, because the "large" 5d orbital may delocalize or take part in chemical bonding. Delocalization of 5d electrons is, of course, only possible in extended solids. In molecular organometallic compounds, however, the electrons need to be localized, and the favored electronic configuration is $[Xe]6s^05d^04f^n$. Much progress has been made in recent years to synthesize true organometallic compounds of Eu, Yb, Sm, Tm, Dy, and Nd.[5] Ligands for these coordination compounds are mostly bulky (substituted) cyclopentadienide anions.[6]

Quite recently, it was shown that lanthanum and cerium can also be secured in the divalent state, although with the electronic configuration $[Xe]6s^05d^14f^0$ (for M = La), with a localized (!) 5d electron, in $[K([2.2.2]crypt)][LaCp''_3]$.[7]

Syntheses using samarium(II), usually involving Kagan's reagent, which is solvated SmI_2 with $E^o(Sm^{2+}/Sm^{3+}) = -1.55$ V, has a great impact on synthetic organic chemistry.[8] This reduction potential is high enough to reduce dinitrogen, as attested by the existence of compounds such as $[Sm_2Cp_4N_2]$ (Cp = cyclopentadienyl).[9] It is also high enough to reduce certain ligands or activate C–H bonds. Paramount for the further development of organometallic/coordination chemistry of low-valent lanthanides is, therefore, the development of novel synthetic routes that avoid these side reactions, which is synonymous with the development of new ligands that are stable to reduction. An important step forward was the observation that $C_5Me_5^-$ (Cp^{*-}) in sterically overcrowded $[Sm(Cp^*)_3]$ may spontaneously induce reduction (SIR) of Sm^{3+} to Sm^{2+}, leaving over a $(Cp^*)^\bullet$ radical, which dimerizes.[10]

As the SIR concept depends on (super-)bulky ligands, other bulky ligands have been and need to be tested to aid the reduction of trivalent to divalent lanthanides. Such a bulky, non-Cp ligand is the tetramethylaluminate anion, $[AlMe_4]^-$. Chemistry with this complex anion had been developed to secure new catalysts for polymerization reactions.[11] It has now been shown that $[AlMe_4]^-$, in combination with a bulky multi-N donor molecule, namely the Lewis base 1,3,5-tricyclohexyl-1,3,5-triazacyclohexane (TCyTAC) in the present case, may serve as a powerful reducing agent.[12] $[Sm(AlMe_4)_3]$ is converted into $[(TCyTAC)_2Sm(AlMe_4)_2]$ (**1**; Figure 2) with toluene as the solvent. Surprisingly, in benzene the dimeric species $[(TCyTAC)_2Sm_2(AlMe_4)_4]$ (**2**) is observed. In both cases, ethane is released, which attests to the formation of a methyl radical from one methylide anion present in $[AlMe_4]^-$. Therefore, CH_3^- is the actual reductant, which is strong enough to reduce Sm^{3+} to Sm^{2+}. The released Lewis acid $AlMe_3$ reacts with the Lewis base TCyTAC, as the the structure determination of single crystals of (TCyTA-

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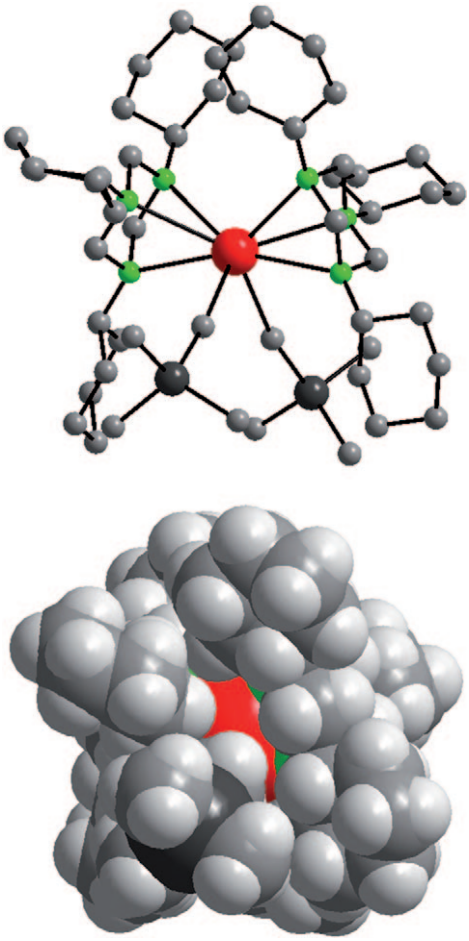

Figure 2. The crystal structure of $[(TCyTAC)_2Sm(AlMe_4)_2]$ (**1**). Top: ball-and-stick model with hydrogen atoms omitted; bottom: space-filling model. Sm red, Al dark gray, N green, C light gray.

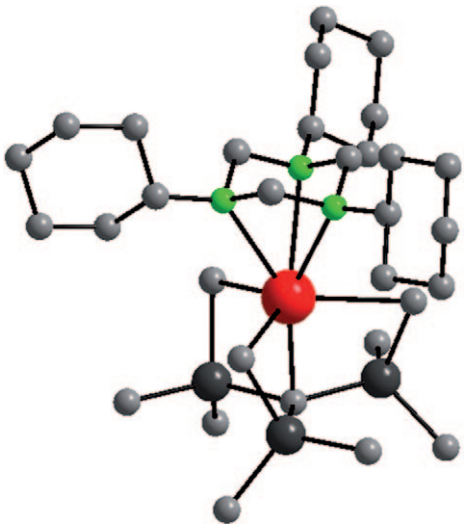

Figure 3. The crystal structure of $[(TCyTAC)Sm\{CH(AlMe_3)_3\}]$ (**4**). Sm red, Al dark gray, N green, C light gray.

C)$AlMe_3$ (**3**) shows. C–H activation also plays a role, as attested by the formation of methane and the minor product $[(TCyTAC)Sm\{CH(AlMe_3)_3\}]$ (**4**; Figure 3).

In the heteroleptic complex $[(TCyTAC)_2Sm(AlMe_4)_2]$ (**1**), samarium(II) is well-shielded by rather bulky ligands. Sm^{2+} has the coordination number eight, with six Sm–N bonds of 283.2 pm (on average) and two Sm–C bonds of 294.8 pm. Both the coordination number and bond lengths are reasonable, especially when viewed in context with $[(TCyTAC)Sm\{CH(AlMe_3)_3\}]$ (**4**). In this samarium(III) compound, Sm–N bonds are 271.8 pm, and the Sm–C bonds to the methyl groups average to 263.6 pm with one rather short Sm–C distance to the C–H group (234.0 pm). For the shortening of the Sm–N and Sm–C bond lengths from **1** to **4** the ionic radii of Sm^{2+} and Sm^{3+} are of course responsible.

The novel base-induced reduction (BIR) of trivalent lanthanides presented herein, which was first observed by Mitzel et al.,[12] has only been tested for Sm^{3+}/Sm^{2+} to date, but it provides a larger number of synthetic possibilities, which are apparently more widespread than the routes to known divalent organolanthanide compounds. First, other weakly coordinating bulky ligands exist or can be developed. Second, the size and donor strength of the bases appear to be unlimited. Third, the formation of "ate-complexes", that is, salts, may further add to the stabilization of compounds through lattice energy. Fourth, there is a large variety of solvents that can be tested. Fifth, this concept may be easily applied to other lanthanides, provided that the ligands, anions and bases are stable to reduction and that C–H activation does not become the prime or only process. The only obvious disadvantage of the base-induced reduction route may be that only heteroleptic complexes can be synthesized, but this issue may be solved in time and with further vigorous research.

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