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New Bulky Allyl Complexes of Lanthanide Metals: Role of Alkali-Metal Cations in Controlling Solid-State and Solution Assemblies in Precatalysts

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Summary: The reaction of the bulky allyl anion [1,3-$C_3H_3(SiMe_3)_2$]$^-$ with $SmI_2(THF)_2$ gives the allyl-bridged dimer [$Sm(C_3H_3(SiMe_3)_2)_3\{\mu\text{-}K(THF)_2\}]_2$, the first structurally authenticated Sm(II) allyl complex. The compound is a highly effective single-component catalyst for the polymerization of methyl methacrylate and ϵ-caprolactone.

Allyl complexes of lanthanide metals are important catalyst precursors, particularly for the stereospecific polymerization of butadiene.[1,2] A number of anionic allyl lanthanate complexes of the type Li[Ln(allyl)$_4$] have been structurally characterized and were found to contain discrete ions.[3] In an effort to prepare more stable complexes with improved solubility characteristics, we have become interested in the chemistry of bulky silyl-substituted allyl complexes[4−7] and have recently reported a series of complexes containing the mono(silyl)- and bis(silyl)-substituted ligands [1-C_3H_4-$SiMe_3$]$^-$ and [1,3-$C_3H_3(SiMe_3)_2$]$^-$ and the *ansa*-bis(allyl) ligand [$(Me_3SiC_3H_3)_2SiMe_2$]$^{2-}$.[8,9] We describe here the synthesis of [1,3-$C_3H_3(SiMe_3)_2$]$^-$ complexes of neodymium and the first structurally authenticated example of a samarium(II) allyl complex. The compounds are highly active single-component catalysts for the polymerization of methyl methacrylate and ϵ-caprolactone.

The reaction of $NdI_3(THF)_{3.5}$ with 2 equiv of K{1,3-$C_3H_3(SiMe_3)_2$} (**1**) in THF gives a mixture of products. In addition to the mono(allyl) complex $NdI_2(A'')(THF)_{1.25}$ isolated earlier (A'' = 1,3-$C_3H_3(SiMe_3)_2$),[8] we now found that, on further concentration and cooling of the solution, the bis(allyl) product $NdI(A'')_2(THF)_2$ (**2**) can be obtained as green crystals.[10] In contrast, the reaction of **1** with $SmI_2(THF)_2$ with 3 equiv of **1** gave a dark green solution from which a compound of composition $KSm(A'')_3(THF)_2$ (**3**) was isolated. Single-crystal X-ray diffraction showed that **3** possesses a cyclic structure, comprising two samarium and two potassium ions bridged by four η^3-allyl ligands (Scheme 1).[11] To the best of our knowledge, **3** is the first structurally authenticated example of a Sm(II) allyl complex.[12]

There are two different molecules in the unit cell. In one of the molecules one potassium atom is coordinated to two tetrahydrofuran ligands, while the other is only bonded to one, with a further THF molecule in close

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[10] Preparation of **2**: solid portions of $NdI_3(THF)_{3.5}$ (3.80 g, 4.89 mmol) were slowly added to a solution of K{1,3-$C_3H_3(SiMe_3)_2$} (**1**; 2.20 g, 9.79 mmol) in tetrahydrofuran (150 mL) over 30 min. The reaction mixture rapidly became light green, with a large amount of precipitate. After the mixture was stirred for 16 h at 20 °C, the volatiles were removed. The green residue was extracted with light petroleum (2 × 100 mL), concentrated, and cooled to −20 °C to give dark green crystals (2.71 g, 70.5%). Anal. Calcd for $C_{26}H_{58}INdO_2Si_4$: C, 39.72; H, 7.44. Found: C, 39.34; H, 7.01. ^1H NMR (benzene-d_6, 20 °C): δ −8.67 (br s, 8 H, THF), −4.00 (br s, 8 H, THF), 3.41 (br s, 36 H, $SiMe_3$), 4.76 (br s, 4 H, allyl), 11.89 (br s, 2 H, allyl). Preparation of **3**: following the procedure given for **2**, solid $SmI_2(THF)_2$ (0.95 g, 1.73 mmol) was added slowly to a solution of **1** (1.17 g, 5.21 mmol) in THF (50 mL). After the mixture was stirred for 16 h, extraction with light petroleum, concentration, and cooling to −20 °C afforded **3** as dark green crystals (0.96 g, 62.3%). Anal. Calcd for $C_{35}H_{79}KO_2Si_6Sm$: C, 47.23; H, 8.95. Found: C, 46.98; H, 8.76. ^1H NMR (toluene-d_8, 20 °C): δ −25.84 (br s, 8 H, μ-allyl), −0.25 (br s, 36 H, $SiMe_3$), 1.32 (s, 8 H, *m*-THF), 2.65 (br s, 72 H, $SiMe_3$), 3.63 (s, 8 H, *o*-THF), 5.16 (br s, 4 H, μ-allyl), 8.75 (br s, 2 H, term. allyl), 13.88 (br s, 4 H, term. allyl).

[11] X-ray crystal data for **3**: $C_{70}H_{158}O_4Si_{12}K_2Sm_2$, M_r = 1779.94, monoclinic, space group $P2/c$, a = 21.324(4) Å, b = 22.942(5) Å, c = 22.402(5) Å, β = 111.01(3)°, V = 10231(4) Å^3, Z = 4, D_c = 1.156 g cm^{-3}, $F(000)$ = 3760, T = 140(1) K, λ(Mo Kα) = 0.71073 Å. wR2 = 0.0833 and R1 = 0.0837 for all 17 038 reflections weighted with $w = [\sigma^2(F_o^2) + (0.0244P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the “observed” data only, R1 = 0.0390. There are two independent molecules in the crystal, one with a potassium atom coordinated to only one THF molecule and one disordered noncoordinating molecule of THF. In the other ring both potassium atoms are coordinated to two THF molecules.

[12] Samarium(II) complexes formulated as $(1,3\text{-}C_3H_3R_2)_2Sm(THF)_2$ (R = Ph, $SiMe_3$) have been reported, although they were not fully characterized: Ihara, E.; Koyama, K.; Yasuda, H.; Kanehisa, N.; Kai, Y. *J. Organomet. Chem.* **1999**, *574*, 40. These compounds exhibited only low activity toward methyl methacrylate over a period of hours.

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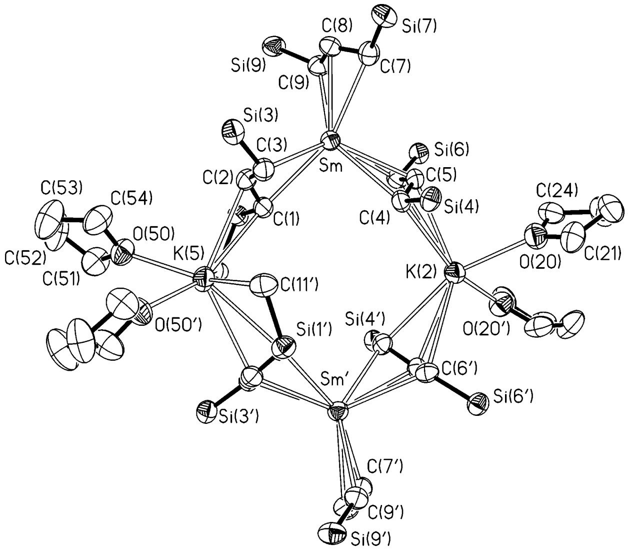
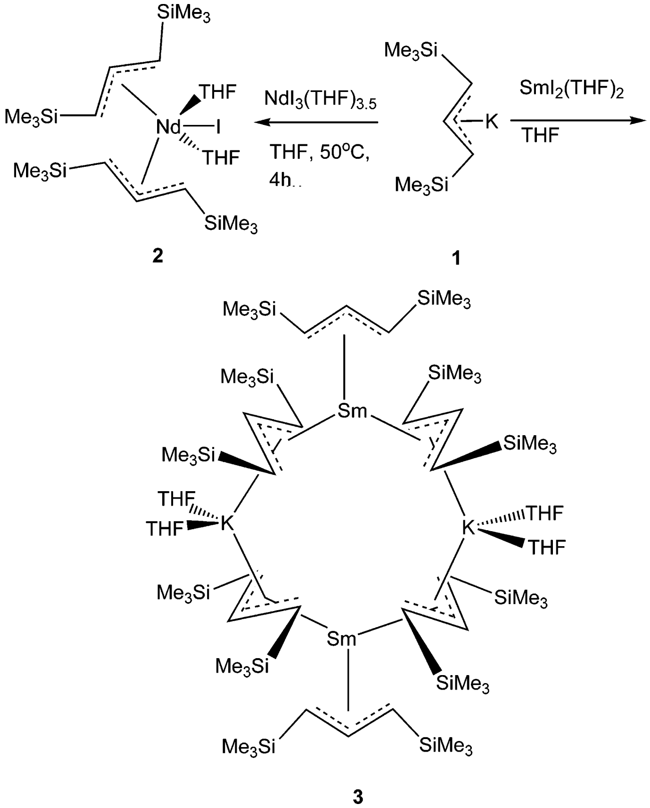


Figure 1. One of the two independent molecules of **3**, showing the atomic numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and methyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sm−C(1) = 2.833(4), Sm−C(2) = 2.804(4), Sm−C(3) = 2.875(4), Sm−C(7) = 2.814(5), Sm−C(8) = 2.801(4), Sm−C(9) = 2.789(5); C(1)−C(2)−C(3) = 131.4(4), C(7)−C(8)−C(9) = 130.9(4), O(50)−K(5)−O(50′) = 77.25(14), C(2)−K(5)−C(2′) = 129.77(15), K(5)−H(11A)−C(11) = 114(4).

Scheme 1



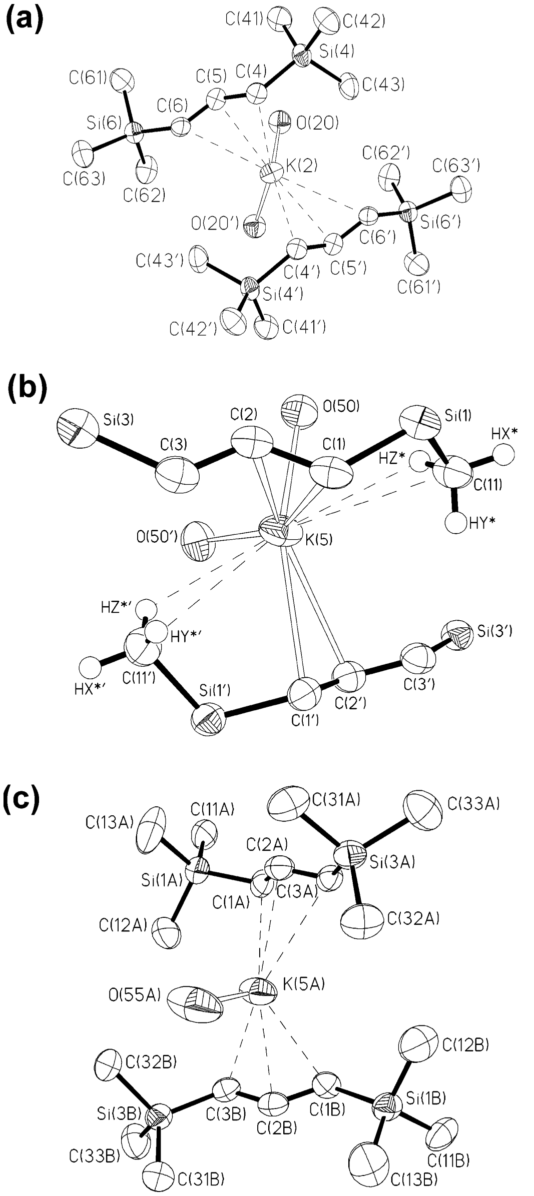


Figure 2. Bonding of allyl ligands and THF to potassium in **3**: (a) atom K(5) in molecule 1; (b) atom K(2) in molecule 1; (c) atom K(5A) in molecule 2. All nonessential atoms are omitted for clarity. Selected interatomic distances (Å): (a) K(2)−O(20) = 2.717(3), K(2)−C(4) = 3.115(5), K(2)−C(5) = 3.095(4), K(2)−C(6) = 3.442(5), C(4)−C(5) = 1.412(5), C(5)−C(6) = 1.382(6); (b) K(5)−C(1) = 3.089(4), K(5)−C(2) = 3.171(4), K(5)−C(3) = 3.679(5), K(5)−O(50) = 2.712(3), K(5)−C(11) = 3.385(6), K(5)−H(11A) = 2.91(5); (c) K(5A)−O(55A) = 2.604(6), K(5A)−C(1A) = 3.122(5), K(5A)−C(2A) = 3.029(4), K(5A)−C(3A) = 3.179(5), C(1A)−C(2A) = 1.399(6), C(2A)−C(3A) = 1.397(6).

proximity. In the second molecule both potassium atoms are coordinated to two THF ligands; this molecule is depicted in Figure 1.

Complex **3** is very soluble in aromatic solvents. At 20 °C in C_6D_6 there are two sets of signals for the bridging and the terminal allyl ligands, in a 2:1 ratio. At elevated temperatures (ca. 80 °C) these two signals coalesce. Surprisingly, addition of THF-d_8 to the toluene solution had very little effect on the spectra, and even in neat tetrahydrofuran-d_8 at 20 °C the spectrum remains essentially unchanged, suggesting that the cyclic structure remains intact in solution.[13]

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(13) A reviewer suggested that ion pairs might be formed which would still show allyl signals in a 2:1 ratio. This would imply that benzene or toluene bind to potassium strongly enough to disrupt the dimeric structure. However, the poor solubility of closely related polymeric potassium-bridged allyl lanthanates[9] suggests that aromatic solvents do not solvate K^+ strongly enough to disrupt the structural framework.

Table 1. Polymerization of Polar Monomers Catalyzed by Lanthanide Allyl Complexes[a]

run	cat.	amt of Ln, 10^{-5} mol	monomer	additive	time, min	temp, °C	yield, g	conversn, %	TON[b]	M_n[c]	M_w/M_n
1	**3**	1.87	MMA	tol	0.5	0	1.296	69.2	83 100	43 800	2.0
2	**3**	1.87	MMA	tol	130	−78	1.865	99.6	460	78 800	3.2
3	**3**	1.87	MMA	thf	0.5	0	1.097	58.4	68 800	35 700	2.2
4	**3**	1.87	MMA	thf	0.33	−78	1.038	55.3	97 700	68 200	4.7
5	**2**	3.61	CL		1	50	1.768	85.8	25 700	127 000	1.3
6	**3**	3.61	CL		0.5	20	2.010	97.6	58 500	24 200	1.6
7	**3**	3.61	CL		0.5	−78	1.950	94.7	56 800	54 500	1.5

[a] Polymerization conditions: Sm, 1.87×10^{-5} mol; Nd, 3.61×10^{-5} mol. MMA:Ln = 1000; CL:Ln = 500. [b] TON in units of mol of monomer (mol of Ln)$^{-1}$ h^{-1}. [c] Determined by ^{1}H NMR in $CDCl_3$. [d] Determined by GPC relative to polystyrene standards.

In compound **3**, as well as in the related polymeric allyl complex $[La\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2\{\mu\text{-}K(THF)\}\cdot 0.5THF]_\infty$,[9] potassium fulfills a structurally important role as bridging atom by means of π and agostic interactions. There are in fact three clearly distinct coordination environments of potassium in compound **3**; these are illustrated in Figure 2.

Generally potassium ion binding in organometallic "ate" complexes is found if electron-rich heteroatoms are available and in potassium salts of cyclopentadienyl-type anions which tend to form coordination polymers.[14,15] In contrast, π complexes of alkali-metal cations to allyl anions are very rare,[15] while allyl lanthanate complexes with lithium cations exist as discrete ions, with Li^+ preferring binding to ethers.[3b−d,9] In **3**, K^+ displays a variety of coordination modes. K(2) is slightly asymmetrically η^3-bound to two allyl ligands, as well as to two THF molecules (Figure 2a). In contrast, the second potassium atom K(5) shows strongly asymmetric allyl bonding, i.e., η^2 coordination, with short K−C distances to C(1) and C(2) of less than 3.2 Å, and a long nonbonding distance to C(3), 3.679 Å. In addition, K(5) is supported by agostic interactions with two methyl groups, one from each of the two neighboring silyl substituents Si(1) and Si(1′), with a K(5)−H(11A) distance of 2.91 Å. This is slightly longer than the interionic bond length in KH, 2.85 Å,[16] but compares well with agostic C−H bonding to potassium;[17] for example, in the coordination polymer $K[AlBu^i{}_4]$ the K···H−C interactions range from 2.60 to 3.05 Å.[18] Such agostic interactions are absent for K(2). The second independent molecule of **3** contains one potassium atom, K(5A), bonded to only one THF ligand placed on the molecular C_2 axis. Although this metal center might be considered coordinatively less saturated (viz. the short K(5A)−O(55A) bond of 2.604(6) Å!), agostic CH···K interactions are absent. Potassium bonding therefore seems to fall into two categories, η^2-allyl stabilized by agostic bonding, and η^3-allyl without additional C−H interactions. Presumably the energy difference between these coordination modes is small; however, the persistence of the cyclic structure of **3** in solution highlights the strength of π bonding to potassium and its preference over O-donor coordination in the case of heavier alkali metals.

The samarium(II) complex proved to be an extremely active catalyst for the polymerization of methyl methacrylate in toluene at 0 °C, with turnover numbers (TON) of >80 000 h^{-1} (Table 1). The polymerization also proceeds at −78 °C, albeit much more slowly (entry 2). At 0 °C there was little difference when the polymerization was carried out in THF; however, at −78 °C the more polar reaction medium led to a *more than 200-fold increase* in activity, with >50% conversion in only 20 s (cf. entries 2 and 4). The polymer molecular weight remained essentially unaffected, and in both solvents cooling led to substantially higher molecular weights. The polymers are most probably produced by an anionic coordination mechanism[19] and show essentially random tacticity, although cooling and the use of THF as solvent increased the *rr* triad content (e.g. entry 4: *rr* 45.8%, *mr* 43.4%, *mm* 10.8%). MMA polymerization with Sm(III) cyclopentadienyl and related complexes has been reported.[20]

Complex **2** was slow to react with ϵ-caprolactone at 20 °C, but warming to 50 °C led to rapid polymerization (85−95% conversion in 60 s) to give high-molecular-weight polymer with narrow polydispersity (entry 5). Although a number of neutral samarium and related lanthanide complexes have been shown to polymerize ϵ-caprolactone,[21,22] the reactions with anionic **3** proceeded unexpectedly smoothly, with essentially quantitative conversion being reached within seconds, even at −78 °C.

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Supporting Information Available: Tables of crystallographic data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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