Monomeric and Linear Polymeric Samarium(II) Complexes of the 2-(N-Arylimino)pyrrolide Ligand

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The synthesis and structural characterization of monomeric and linear polymeric divalent samarium complexes as well as their related trivalent species supported by an (imino)pyrrolide ligand are described. The divalent samarium 2-(*N*-arylamino)pyrrolide complex [NN]₂Sm(THF)₂ (1) was prepared by the reaction of SmI₂(THF)₂ with 2 equiv of [NN]K ([NN] = [2-(2,6-*i*Pr₂C₆H₃N=CH)-5-*i*BuC₄H₂N]⁻) in THF. Upon treatment of 1 with dry oxygen, the oxo-bridged dimer [NN]₂Sm(μ -O)Sm[NN]₂ (2) was generated. Reaction of [NN]₂SmCH₂SiMe₃ (3) with 3 equiv of AlEt₃ in *n*-hexane gave the samarium aluminate [NN]₂Sm(μ -Et)₂AlEt₂ (4). Reduction of 4 with potassium in toluene yielded the linear polymeric species {[NN]₂SmAlEt₄K(C₇H₈)}_n (5). Compounds 1, 2, 4, and 5 have been characterized by X-ray single-crystal analysis. 5 features a linear polymeric structure, in which the potassium ion links the neighboring monomeric samarium moieties via η^2 and η^5 coordination to the pyrrolide rings in the two different units, with one toluene molecule and one of the ethyl groups of the [AlEt₄] anion being also η^2 coordinated to the potassium to complete its coordination sphere.

Introduction

Since $(C_5Me_5)_2Sm(THF)_2$ was reported in 1981, the organometallic chemistry of Sm(II) has seen remarkable growth and development.¹ Recent developments in organolanthanide chemistry have focused on the use of non-cyclopentadienyl ancillary ligands,² with much of the interest in the synthesis and characterization of lanthanide complexes with unusual reactivity and bonding using nitrogen-based ligand systems.³ In this context, we are interested in exploring bulky 2-(*N*-arylimino)pyrrolide ligands in divalent samarium chemistry. It has been reported by Gambarotta and co-workers that multiple dentate pyrrolide ligands display either a η^1 or η^5 bonding mode and could support interesting polynuclear Sm(II) species capable of activation of small molecules.⁴ Recent studies on pyrrolide transition metal complexes have shown that this family of ligands are promising versatile supporting ligands in transition metal catalysis.⁵ So far, the most extensive studied pyrrolide ligands include methylene (dimethyl and diphenylmethylene) bridged polypyrrolide and 2-(imino)pyrrolide imine systems. The later has been used to prepare a variety of metal complexes including trivalent lanthanide complexes.⁶ However, very little has been carried out to prepare Sm(II) complexes with the (imino)pyrrolide system since the imine moiety could be reduced by Sm(II) in most cases.⁷ We reasoned that it is possible to suppress the reduction of the imino group by Sm(II) atoms by employing bulky substituents on the nitrogen atom of the imino group and introducing a bulky group on the 5-position of the

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pyrrolide ring. Previous studies have shown that the bulky (imino)pyrrolide ligand [NN] ([NN] = $[2-(2,6-iPr_2C_6H_3N=CH)-5-tBuC_4H_2N]^-$) could support rigid C_1 symmetric samarium and yttrium alkyls, which promote polymerization of methyl meth-acrylate to generate highly isotactic polymers.⁸ Herein, we report on the synthesis and structures of stable monomeric and linear polymeric samarium(II) complexes with this bulky (imino)pyrrolide ligand along with the related trivalent species. Interestingly, the polymeric samarium species features an unusual assembly linked by the potassium atom surrounded by two different pyrrolide ligands in the neighboring units in η^2 and η^5 fashions, respectively, and one η^2 toluene molecule as well as an agostic interaction with one ethyl group in the [AlEt₄] anion.

Experimental Section

All operations were carried out under an atmosphere of dry argon or nitrogen by using modified Schlenk line and glovebox techniques. All solvents were freshly distilled from Na and degassed immediately prior to use. Elemental analyses were carried out on an Elemental Vario EL analyzer. The ¹H and ¹³C NMR spectroscopic data were recorded on Bruker AV300 and AV400 spectrometers. Infrared spectra were recorded on a Bio-Rad FTS 6000 spectrophotometer. Magnetic susceptibility of the solid sample was measured using a SQUID MPMS XL-7 magnetometer at 300 K and was corrected for diamagnetism by the tabulated Pascal's constants. Effective magnetic moment was calculated by the equation $\mu_{\rm eff} = 2.828(\chi_m T)^{1/2}$, where χ_m is the magnetic susceptibility per formula unit. [NN]₂SmCH₂SiMe₃(THF) was synthesized according to the published procedure.⁸

Synthesis of [NN]₂Sm(THF)₂ (1). THF (150 mL) was condensed to a mixture of [NN]H (3.1 g, 10.0 mmol) and KH (0.40 g, 10.0 mmol) at 0 °C. The mixture was warmed to room temperature and stirred overnight. It was then transferred into the solution of SmI₂(THF)₂ (2.74 g, 5.0 mmol) in THF. After the mixture was stirred at room temperature for 10 h, the solvents were removed and the remaining solid was extracted with toluene (100 mL) at 50 °C. It was filtered and the filtrate was concentrated and stored at -40 °C for 2 days to give black crystals of 1 (6.6 g, 72%). Mp: 190–192 °C. ¹H NMR (C₆D₆, 300 MHz): δ –18.67 (m, 2H), -8.3 (s, 2H), -4.3 (s, 4H), -1.65 (s, 18H, CMe₃), 0.29 (s, 2H), 0.96 (s, 2H), 1.21 (s, 2H), 1.35 (m, 4H), 1.90 (s, 8H, THF), 3.68 (br s, 8H, THF), 4.59 (br s, 6H), 7.02 (m, 6H), 9.64 (br s, 4H), 9.79 (s, 4H), 31.6 (m, 2H). ¹³C NMR: δ 21.4, 23.9, 26.8, 27.8, 28.3, 30.0, 53.7, 92.7, 116.7, 120.6, 123.4, 125.6, 125.7, 128.5, 129.3, 137.9, 208.4. IR: 3061, 2961, 2868, 1629, 1588, 1559, 1497, 1460, 1437, 1364, 1254, 1201, 1124, 1101, 1044, 932, 858, 777, 746, 704, 667, 576, 530. $\mu_{\text{eff}} = 2.53 \ \mu_{\text{B}}$. Anal. Calcd for C₅₀H₇₄N₄O₂Sm (913.51): C, 65.74; H, 8.16; N, 6.13. Found: C, 65.69; H, 7.60; N, 5.67.

Synthesis of [NN]₂Sm(\mu-O)Sm[NN]₂ (2). A solution of [NN]₂Sm(THF)₂ (0.92 g, 1.0 mmol) in toluene (30 mL) was stirred under an atmosphere of purified dioxygen. The color of the solution turned from black to yellow immediately, then the solution was concentrated and stored at -40 °C overnight to give yellow crystals of 2 (0.53 g, 68%). Mp: 262–264 °C. ¹H NMR (C₆D₆, 400 MHz): δ –5.89 (m, 4H, CHMe₂), -3.18 (d, J = 4.4 Hz, 12H, CHMe₂), -1.81 (s, 36H, CMe₃), -0.42 (d, J = 4.4 Hz, 12H, CHMe₂), 3.07 (t, J = 6.4 Hz, 24H, CHMe₂), 4.52 (d, J = 7.2 Hz, 4H, Ar-H), 5.98 (t, J = 7.2 Hz, 4H, Ar-H), 6.83 (d, J = 7.2 Hz, 4H, Ar-H), 7.33 (s, 4H, N=CH), 7.83 (s, 4H, pyrrole-H), 8.94 (s, 4H, pyrrole-H), 11.91 (m, 4H, CHMe₂). ¹³C NMR (C₆D₆): δ 21.2, 22.6, 23.82, 24.3, 29.2, 30.1, 33.8, 34.1, 110.7, 121.6, 122.8, 123.8, 128.8, 135.0, 141.3, 141.7, 149.9, 169.0 (N=CH), 171.3 (N=CH). IR: 3060, 2960, 2868, 1623, 1595, 1577, 1491, 1460, 1440, 1386, 1362, 1320, 140.5 m = 10.5 m

1272, 1234, 1202, 1180, 1124, 1101, 1047, 999, 933, 858, 821, 801, 778. 749, 730, 704, 654, 592, 569. Anal. Calcd for $C_{84}H_{116}N_8OSm_2$ (1556.77): C, 64.90; H, 7.52; N, 7.21. Found: C, 64.28; H, 7.62; N, 6.88.

Synthesis of [NN]₂Sm(AlEt₄) (4). To a solution of 3 (4.65 g, 5.0 mmol) in *n*-hexane (60 mL) was added AlEt₃ (1.71 g, 15.0 mmol) in n-hexane (20 mL). The mixture was stirred at room temperature for 4 h. All volatiles were removed, and the remaining solid was extracted with toluene (10 mL). After filtration, n-hexane (15 mL) was carefully added to the filtrate. The solution was stored at -40 °C for 3 days to give orange crystals of 4 (2.93 g, 64%). Mp: 168 °C (dec). ¹H NMR (C₆D₆): δ -4.13 (s, 18H, CMe₃), -0.56 (d, 6H, J = 8.0 Hz, CHMe₂), 0.80 (d, 6H, J = 8.0 Hz, CHMe₂), 1.36 (d, 6H, J = 8.0 Hz, CHMe₂), 1.43 (d, 6H, J = 8.0 Hz, CHMe₂), 2.14 (m, 2H, CHMe2), 2.51 (m, 18H, CH2CH3), 3.38 (m, 2H, CHMe₂), 5.46 (m, 2H, Ar-H), 5.93–6.06 (m, 4H, Ar-H), 6.53 (d, 2H, J = 4.8 Hz, pyrrole-H), 8.90 (d, 2H, J = 4.8 Hz, pyrrole-H), 9.17 (s, 2H, CH = N), 18.63 (m, br, 2H, CH_2CH_3). ¹³C NMR (C₆D₆, 300 MHz): δ 14.3, 20.8, 21.5, 23.0, 26.5, 26.7, 27.1, 27.6, 29.3, 30.5, 31.9, 109.7, 122.3, 122.6, 124.6, 129.1, 138.3, 139.6, 142.9, 149.8, 165.3, 175.3. IR: 3060, 2960, 2866, 1919, 1861, 1796, 1624, 1588, 1560, 1495, 1460, 1437, 1382, 1364, 1318, 1271, 1253, 1233, 1201, 1179, 1124, 1101, 1046, 1004, 980, 955, 932, 885, 858, 777, 746, 703, 655. Satisfactory elemental analysis were not obtained for the aluminates 4 and 5 due to the easy loss of the ethyl groups upon the exposure to air.

Synthesis of [NN]₂SmAlEt₄K(C₇H₈) (5). Toluene (50 mL) was condensed into the mixture of L₂SmAlEt₄ (0.46 g, 0.5 mmol) and K (0.23 g, 0.6 mmol) at room temperature. The mixture was stirred at room temperature for 2 days, and the color turned from orange to black. It was filtered, and the filtrate was concentrated (ca. 20 mL) and then stored at -40 °C for 2 days to yield dark brown crystals of **5** (0.44 g, 84%). Mp: 197–199 °C. IR: 3060, 2960, 2865, 1625, 1581, 1560, 1496, 1460, 1438, 1382, 1363, 1319, 1275, 1255, 1234, 1201, 1179, 1123, 1101, 1045, 997, 983, 932, 857, 777, 746, 653. $\mu_{\rm eff} = 3.77 \ \mu_{\rm B}$.

X-ray Structural Determination. All intensity data were collected with a Bruker SMART CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were resolved by direct methods and refined by full-matrix least-squares on F^2 . Hydrogen atoms were considered in calculated positions. All non-hydrogen atoms were refined anisotropically. Crystals of 1 suitable for X-ray analysis were grown from THF at room temperature, and 2, 4, and 5 were obtained from toluene at room temperature.

Results and Discussion

The samarium(II) complex $[NN]_2Sm(THF)_2$ (1, [NN] = $[2-(2,6-iPr_2C_6H_3NCH)-5-tBuC_4H_2N]^-)$ was prepared by salt elimination reaction of SmI₂(THF)₂ with 2 equiv of K[NN] in THF. 1 is inert to CO and N₂ under normal conditions. Attempts to prepare the THF-free [NN]₂Sm by sublimation were unsuccessful. Addition of AlEt₃ (2, 3, and 4 equiv) to 1 in toluene resulted in the formation of the corresponding aluminate $[NN]_2Sm(\mu-Et)_2AlEt_2$ (4) in low yield. Alternatively, 4 can be prepared reproducibly in good yield by the reaction of [NN]₂SmCH₂SiMe₃(THF) (**3**) with 3 equiv of AlEt₃ in *n*-hexane. Reduction of 4 with 1.1 equiv of K in toluene furnished the linear polymeric species $\{[NN]_2SmAlEt_4K(C_7H_8)\}_n$ (5) in high yield. Reduction of 4 with K in cyclohexane presumably also vielded polymeric Sm(II) species. Unfortunately, direct crystallization of the product from cyclohexane under different conditions failed. However, crystallization of the solid from toluene after removal of cyclohexane also yielded 5, indicating that toluene seems to be essential for the formation of the linear polymeric chain.

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Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sm1–N1 2.7218(19),Sm1–N22.5224(18),Sm1–O12.6624(15);N2–Sm1–N2A 145.92(8), N2–Sm1–O1 83.45(5), N2A–Sm1–O1 125.01(5), O1–Sm1–O1A 76.69(7), N2–Sm1–N1 66.51(6).

Compound 1 was isolated as black crystals and represents a rare example of a stable Sm(II) complex with an imino functionality. Gambarotta and co-workers have investigated the reactions of pyrrole-based and salen-type tetradentate Schiff base ligands with Sm[N(SiMe₃)₂]₂(THF)₂ and SmI₂(THF)₅. Only in one case was a samarium(II) species isolated as a dimer linked by two Sm-pyrrole π interactions. The structure of **1** determined by X-ray single-crystal analysis (Figure 1) showed that **1** is a monomer with the two [NN] ligands and two THF molecules being coordinated to the samarium ion. The molecule has a crystallographic C_2 axis. The two (imino)pyrrolide ligands adopt an η^2 coordination with acute N-Sm-N angles (66.51(6)°). The largest angles around the samarium atom observed in 1 are those of O1-Sm1-N1A and O1A-Sm1-N1 (158.08(6)°). The Sm-N bond lengths (2.5224(18) and 2.7218(19) Å) are longer than those found in the trivalent samarium compound [NN]2SmCH2SiMe3(THF) (average $Sm-N_{pyrolide} = 2.46$ and $Sm-N_{imino} = 2.60$ Å),⁸ in accordance with relatively large Sm(II) ionic radius. The Sm-O distance (2.6624(15) Å) is longer than those found in the six-coordinate (C12H8N)2Sm(THF)4 (2.560-2.602 Å)9 and even marginally longer than those found in the formally eight-coordinated samarium species $(C_5Me_5)_2Sm(THF)_2$ (2.62 and 2.64 Å)¹⁰ probably due to the bulkiness of the (imino)pyrrolide ligand.

The interaction of divalent lanthanide complexes with dioxygen has been less investigated in comparison with that of late transition metal complexes. Takats and co-workers reported the first lanthanide superoxo complex (TpMe₂)₂Sm(η^2 -O₂) (TpMe₂ = HB(3,5-Me₂pz)₃) via the reaction of (TpMe₂)₂Sm with O₂.¹¹ Following this work, several other lanthanide superoxo and peroxo complexes were obtained by reactions of divalent lanthanide complexes with O₂.¹² This work demonstrated that suitable ligand sets are essential for the stabilization of these activated dioxygen complexes. The successful isolation of monomeric 1 with the bulky 2-(imino)pyrrolide ligand [NN] prompts us to study its interaction with dioxygen, in the hopes of generating novel species. Upon exposure of a solution of 1 in toluene to one atmosphere of dry dioxygen, a yellow solution was obtained immediately, indicating the rapid oxidation process. The oxidation product was isolated as yellow crystals after crystallization from toluene. Its structure was identified as the oxo-bridged dimer $[NN]_2Sm(\mu-O)Sm[NN]_2$ (2) by ¹H NMR, ¹³C NMR, and IR spectroscopy, elemental analysis, and X-ray single-crystal analysis. The structure of 2 is shown in Figure 2 alone with a list of relevant bond lengths and angles. The molecule resides on a C_2 axis in the space group P-42₁c, resulting in the disorder of the oxygen atom by occupying two positions (O1-O1A = 1.29(3) Å). The short O1–O1A contact, significantly shorter than a single O–O bond (1.46 Å) and those of lanthanide peroxo complexes (1.46-1.65 Å),¹² excludes the possibility of a peroxo complex. The Sm1-O1 and Sm1A-O1 bond lengths (2.222(15) and 2.269(16) Å) are significantly longer than those found in the linear or almost linear Sm-O-Sm species [(C₅Me₅)₂Sm]₂(µ-O) (2.094(1) Å),¹³ $[(C_5Me_4iPr)_2Sm]_2(\mu - O) (2.116(3) \text{ Å})$, and $[(C_5Me_5)_2Sm(NC_5H_5)]_2(\mu-O) (2.151(2) \text{ Å}),^{14}$ in which the short Sm-O bond lengths are explained by possible multiple bonding between the samarium atom and the oxygen atom. The Sm1-O1-Sm1A angle (138.4(7)°) is significantly deviated from linearity, like those observed in the reported Sm-O-Sm species mentioned above. The complete cleavage of the dioxygen double bond by 1 along with the formation of 2 is unexpected. A few reported complexes containing a Sm-O-Sm unit were not generated by dioxygen reactions but prepared by reactions of Sm (II) or Sm(III) species with nitroarenes, epoxybutane, pyridine N-oxide, and Ph₃PO.¹³⁻¹⁵ The formation of 2 may involve the peroxo intermediate [NN]₂Sm(µ- O_2)Sm[NN]₂, which was immediately trapped by the highly reactive 1. However, we were unable to monitor the rapid reaction by spectroscopic methods and isolate the intermediate.

Complex 4 was initially obtained by the reaction of 1 with AlEt₃. The reaction proved to be unpractical due to its low yield. It can be prepared in good yield by reaction of the trivalent alkyl 3 with AlEt₃. Single crystals of 4 amenable for X-ray diffraction analysis were obtained from toluene. The ORTEP diagram of 4 is shown in Figure 3, and the crystallographic data are summarized in Table 1. The C_2 symmetric structure of 4 is monomeric with the Et₄Al anion coordinated to the samarium atom via two bridging methylene carbon atoms. This coordination mode has been previously observed in $(C_5Me_5)_2$ SmA1Et₄.¹⁶ The Sm $-C(\mu$ -CH₂) distances (2.781(5) Å) in 4 are longer than those observed in (C₅Me₅)₂SmA1Et₄ (2.662(4) Å) and L₂SmMe(THF) (2.625(2) Å).⁸ The Al-C(μ -CH₂) distance (2.099(7) Å) is only marginally longer than the Al-C (CH₂) terminal distances (2.063(12) Å), and these Al-C distances are in the range of those found in (C₅Me₅)₂SmA1Et₄ $(Al-C(\mu-CH_2) = 2.106(5) \text{ and } Al-C(CH_2) = 2.032(6) \text{ Å}).$ The long Sm-C distances and almost average Al-C distances in 4 indicate the relatively weak bonding of the Et₄Al anion to the

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Figure 2. Molecular structure of **2**. The oxygen atom is disordered in two positions related by a C_2 axis; the other half and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sm1–O1 2.222(15), Sm1A–O1 2.269(16), Sm1–N2 2.493(9), Sm1–N4 2.498(10), Sm1–N3 2.521(9), Sm1–N1 2.562(11), O1–Sm1–N2 87.3(4), O1–Sm1–N2A 120.1(5), O1–Sm1–N4A 86.0(5), O1–Sm1–N4 118.9(4), N2–Sm1–N4 153.8(3), O1–Sm1–N3A 107.6(5), O1–Sm1–N3 121.1(6), N2–Sm1–N3 97.3(3), N4–Sm1–N3 70.7(3), O1–Sm1–N1 143.6(6), O1–Sm1–N1A 131.0(6), N2–Sm1–N1 70.4(3), N4–Sm1–N1 89.8(3).



Figure 3. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sm1–N2 2.425(3), Sm1–N1 2.544(3), Sm1–C22 2.781(5), Al1–C22 2.099(7), Al1–C24 2.063(12), N2–Sm1–N2A 140.72(16), N2–Sm1–N1A 86.25(11), N2–Sm1–N17 0.39(11), N1–Sm1–N1A 106.74(14), N2–Sm1–C22 129.76(17),N2–Sm1–C22A 83.13(17),N1–Sm1–C22 154.90(17), N1–Sm1–C22A 91.00(16), C22–Sm1–C22A 78.7(3), C22–Al1–C22A 114.2(3).

samarium atom and the partial ion pair structure. In **4**, the Sm1–N1 and Sm1–N2 bond lengths (2.544(3) and 2.425(3) Å) and the N–Sm–N angles in the bidentate ligand (70.39(11)°) are comparable to those found in [NN]₂SmCH₂SiMe₃(THF).

The crystal structure of **5** is shown in Figure 4 along with selected bond parameters. The most striking feature of **5** is that each unit is linked by a potassium atom to form a linear polymeric structure, in which each of the potassium ions is surrounded by one η^2 -coordinated pyrrolide ring in one unit and the other pyrrolide ring in the neighboring unit in η^5 fashion and one toluene molecule and one ethyl group of the [AlEt₄]⁻ moiety in η^2 modes. The K-C_{arene} distances range from 3.026(3) to 3.263(4) Å, comparable

 Table 1. Crystallographic Data for 1, 2, 4, and 5

	1	2	4	5
formula	$C_{50}H_{74}N_4O_2Sm$	C84H116N8OSm2	C50H76AlN4Sm	C57H85AlKN4Sm
fw	913.48	1554.59	909.38	1042.72
T (K)	113(2)	113(2)	113(2)	113(2)
space group	C2/c	P-42 ₁ c	Cc	$P2_1/n$
a (Å)	13.591(3)	18.045(3)	13.485(3)	11.576(2)
b (Å)	20.265(4)	18.045(3)	27.386(5)	35.840(7)
c (Å)	18.043(4)	26.868(5)	15.247(3)	13.549(3)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	90.00(3)	90.00	99.66(3)	99.62(3)
γ (deg)	90.00	90.00	90.00	90.00
$V(Å^3)$	4969.4(18)	8748(3)	5550.9(19)	5542.2(19)
Z	4	8	4	4
d_{calcd} (g/cm ³)	1.221	1.183	1.088	1.250
F(000)	1920	3248	1888	2196
GOF	1.094	1.074	1.058	1.066
R_1 , wR_2	0.0241, 0.0611	0.0823, 0.2355	0.0587, 0.1573	0.0372, 0.0841

 $(I \ge 2\sigma(I))$ R_1, wR_2 0.0254, 0.0618 0.0993, 0.2544 0.0628, 0.1605 0.0464, 0.0881 (all data)

to those in K[Nd(OC₆H₃*i*Pr₂-2,6)₄] (3.097(10)-3.473(11) Å) and KBPh₄ (3.191(5) Å).¹⁷ Additional K-C short contacts (3.486(5) and 3.421(5) Å) are found in **5** involving the η^2 agostic interaction with one of the ethyl groups coordinated to the samarium in the [AlEt₄]⁻, leading to the lengthening of the Sm-C distance (2.982(4) Å) compared to the other Sm–C distance (2.904(4) Å). The K–N distance (3.044(3) Å) and the short K-C distances (3.062(3)-3.172(4) Å) observed in the K(η^5 -pyrrolide) fragment are comparable to those found in other transition metal pyrrolide ate complexes.¹⁸ In each of the monomeric samarium units, the samarium atom is six-coordinated and the coordination geometry resembles that of 4. However, the bond distances around the samarium are quite distinct from those found in 4 due to the interactions of the two pyrrolide rings with the two different potassium atoms and the different oxidation states of the samarium atoms in 4 and 5. Especially, Sm1-N3A (to the nitrogen atom of

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Figure 4. Extended structure of **5.** Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sm1–N1 2.586(3), Sm1–N3A 2.630(3), Sm1–N2A 2.664(3), Sm1–N4A 2.731(3), Sm1–C43 2.904(4), Sm1–C45 2.982(4), Al1–C47 1.993(4), Al1–C43 2.024(4), Al1–C45 2.030(4), Al1–C49 2.042(5), K1–C2 3.219(4), K1–C3 3.263(4), K1–N3 3.044(3), K1–C22 3.102(3), K1–C23 3.172(4), K1–C24 3.170(4), K1–C25 3.062(3), K1–C55, 3.233(4), K1–C56 3.156(4), K1–C45A 3.486(5), K1–C46A 3.421(5), N1–Sm1–N3 143.01(9), N1–Sm1–N2 67.49(8), N3–Sm1–N2 91.55(8), N1–Sm1–N4 92.55(8), N3–Sm1–N4 66.45(8), N2–Sm1–N4 111.88(9), C56–K1–C55 24.62(10), C2–K1–C3 24.88(9), C46–K1–C45 25.92(9).

the K(η^5 -pyrrolide), 2.630(3) Å) is longer by ca. 0.1 Å than those found in the divalent species 1, but Sm1-N4A (to the imino nitrogen, 2.731(3) Å) is comparable to those observed in 1. The samarium atom to the other ligand nitrogen atom distances (Sm1-N1A = 2.586(3) and Sm1-N2A = 2.664(3) Å) are slightly different from the corresponding distances found in 1: the former is longer and the latter is shorter than those in 1, probably resulting from the relatively strong conjugation of the imino group with the pyrrolide ring due to the η^2 -coordinated potassium atom. Thus, the overall samarium coordination can be viewed as one neutral potassium (imino)pyrrolide and one monoanionic (imino)pyrrolide ligand as well as one [AlEt₄] anion. The divalent nature of the samarium atom is indicated by its black color and significantly shifted and very broad proton NMR resonances. The high stability of the (imino)pyrrolide ligand [NN] in the presence of potassium is noteworthy since imino groups could be easily reduced by alkali metals, resulting in reductive C-C coupling. The stability may be attributed to the strong conjugation of the imino group with the aromatic pyrrole ring in the presence of bulky substituents. A few examples of linear polymeric divalent samarium species linked by an alkali ion with arene π interactions are known.^{4g,19} Compound 5 is unique in that both the η^2 - and η^5 -bonded pyrrolides to the potassium ion and only the N-coordination to samarium ion are observed; especially the η^2 -bonded pyrrolide ring to the potassium ion has no precedent.

Conclusion

Novel stable divalent samarium complexes **1** and **5** with the bulky 2-(*N*-arylimino)pyrrolide ligand [NN] ([NN] = [2-(2,6- $iPr_2C_6H_3N=CH$)-5- $tBuC_4H_2N$]⁻) have been synthesized and structurally characterized. These compounds do not undergo intramolecular electron transfer reactions between the divalent samarium and the imino group under normal conditions. The results indicate that the bulky (imino)pyrrolide ligand [NN] may be used for the preparation of other divalent lanthanide

Scheme 1. Synthesis and Reaction of 1



Scheme 2. Synthesis of the Linear Polymeric 5



complexes. Further investigations of the reactivity and properties of **1** and **5** as well as the synthesis of other divalent lanthanide derivatives with this ligand are currently in progress.

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Supporting Information Available: CIF files giving X-ray structural information on **1**, **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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