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Lanthanum Dibromide Complexes of Sterically Demanding Aminopyridinato and Amidinate Ligands[1)]

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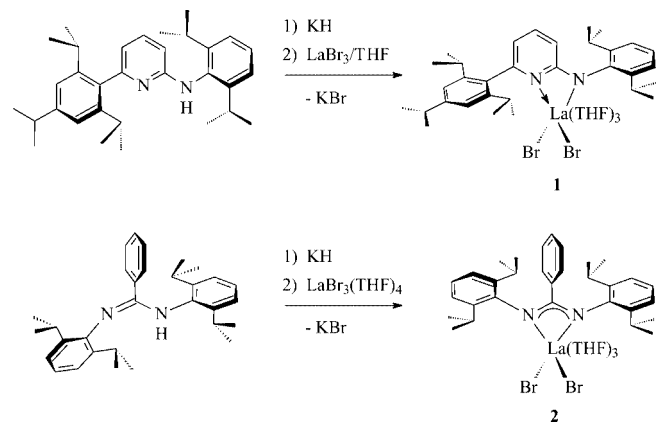
Dedicated to Professor Glen Deacon on the Occasion of his 70th Birthday

Abstract. It is report on synthesis and structure of $Ap^*LaBr_2(THF)_3$ and $Am^*LaBr_2(THF)_3$ (Ap*-H = {(2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine}, Am*-H = N,N′-bis-(2,6-diisopropylphenyl)benzamidine). X-ray crystal structure analyses of the two seven coordinated complexes were carried out to compare the steric demand of the two amido ligands. A similar overall primary coordination site bulkiness for both ligands and distinct differences regarding this bulkiness for different directions were observed. A better shielding of the second coordination sphere was observed for the aminopyridinate.

Keywords: Amidinate ligands; Aminopyridinato ligands; Lanthanides; Lanthanum

Recently, sterically demanding N,N-bidentate anionic ligands became very popular in amido [1, 2] lanthanide chemistry. Among such ligands selected amidinate [3] and aminopyridinato [4, 5] ligands are of special interest since they bind a large variety of rare earth metals forming species of the type $(L)LnX_2(THF)n$ (L = N,N-bidentate mono anionic amido ligands, Ln lanthanide metal, X = halide, n = 1,2,3,...) [6, 7]. In this communication we report on synthesis and structure of $Ap^*LaBr_2(THF)_3$ and $Am^*LaBr_2(THF)_3$ (Ap*-H = {(2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine}, Am*-H = N,N′-bis-(2,6-diisopropylphenyl)-benzamidine).

Both compounds are accessible via salt elimination reaction in moderate to good yields. The reaction of Ap*-H or Am*-H with KH leads to the potassiated aminopyridinate or amidinate, respectively, which then can undergo transmetalation (Schema 1). For **1** no reaction is observed with lithiated Ap*-H. The potassium salt of Ap*-H is a polymer and the lithium salt a three coordinated monomer. Additional coordination of one solvent molecule was found for the lithium salt [8]. This observation is in contrast to the reaction of lithiated Am*-H with $LaBr_3(THF)_4$. We succeeded in the formation of the corresponding lanthanum amidinate, however no complete LiBr separation could be achieved. Furthermore, no formation of a bisaminopyridinato complex could be observed by reacting two equiv. of Ap*K with $LaBr_3$. NMR spectroscopy of the two lanthanum complexes revealed the coordination of three additional THF ligands. Due to the additional coordination of three THF ligands we expected mononuclear seven coordinated compounds in solution. Such complexes should be ideal to compare the steric bulk of the aminopyridinate and the amidinate ligand since the angles between the ancillary ligands are quite sensitive to the steric "pressure" of the amido ligands in at least two directions. Crystals of **1** and **2** suitable for X-ray crystal structure analysis could be grown from hexane (**1**) or THF (**2**) solutions. The molecular structures of **1** and **2** (ORTEP plots) are shown in Figure 1



Scheme 1 Synthesis of **1** and **2**.

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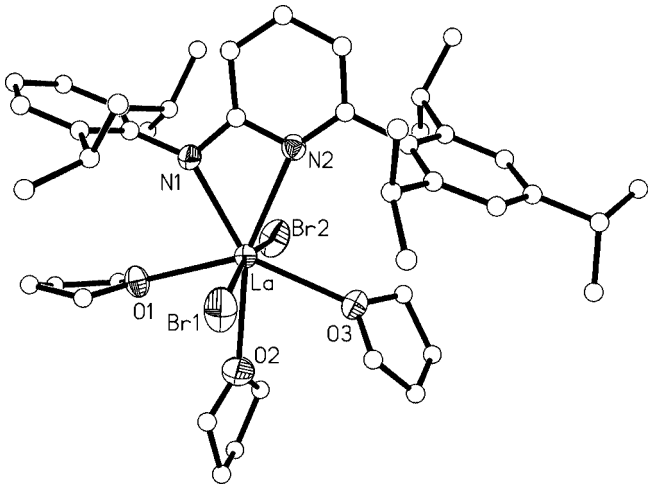
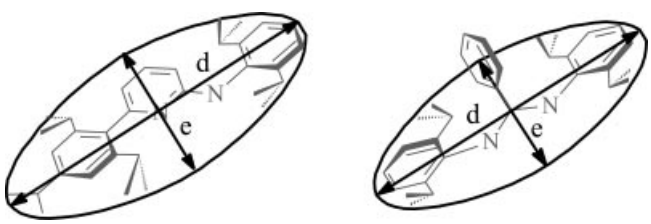


Figure 1 Molecular structure of **1** (ellipsoids [non carbon atoms] correspond to the 50 % probability level).

Selected bond lengths/Å and angles/°: La-N1 2.447(3), La-O1 2.560(2), La-O3 2.579(2), La-O2 2.634(3), La-N2 2.645(3), La-Br1 2.9028(6), La-Br2 2.9116(6); N1-La-O1 76.60(9), N1-La-O3 142.25(9), O1-La-O3 140.96(8), N1-La-O2 146.27(10), O1-La-O2 69.68(10), O3-La-O2 71.44(10), N1-La-N2 52.98(8), O1-La-N2 129.56(8), O3-La-N2 89.31(9), O2-La-N2 160.75(9), N1-La-Br1 96.58(7), O1-La-Br1 91.08(6), O3-La-Br1 87.98(7), O2-La-Br1 83.62(10), N2-La-Br1 95.61(6), N1-La-Br2 96.55(7), O1-La-Br2 88.29(6), O3-La-Br2 83.95(7), O2-La-Br2 83.38(10), N2-La-Br2 95.29(6), Br1-La-Br2 166.342(17), O1-La-O3 140.96(8).

and 2, respectively. Both compounds are monomeric in the solid state and the coordination can be described best as pentagonal bipyramides in which the two bromo ligands occupy the axial positions. The equatorial sites are populated by the three oxygen atoms of the THF ligands as well as the two N-atoms. The two N-atoms in **2** are equally bonded to the metal center [La-N 2.5254(18) Å], while the La-N distances of **1** [La-N1 2.447(3) Å; La-N2 2.645(3) Å] indicate a localization of the anionic function at the amido N-atom. The binding of Ap* to the lanthanum atom is described best as a donorfuntionalized amido metal bond. The maximum atom to atom distances in accordance to Scheme 2 express the overall steric bulk of the two amido ligands or the second coordination sphere bulkiness. These distances are: d = 15.1 Å, e = 8.8 Å for **1** and d = 11.9 Å, e = 8.6 Å for **2**. Which means **1** is the more demanding in this regard.



Scheme 2 Description of the steric demand of the amido ligands by using the parameter d and e (maximum H-atom-H-atom distances perpendicular to each other).

Furthermore, the Br-La-Br bond angles and the nearly linear O-La-O angle can be used to describe the steric "pressure" which is put on the ancillary ligands (bromo and THF ligands). We call this the primary coordination site bulkiness. For **1** these angles are: Br1-La-Br2 166.342(17)°, O1-La-O3 140.96(8)° and for **2**: Br-La-Br′ 159.24(1)°, O1-La-O1′ 146.77(6)°. The aminopyridinato ligand is

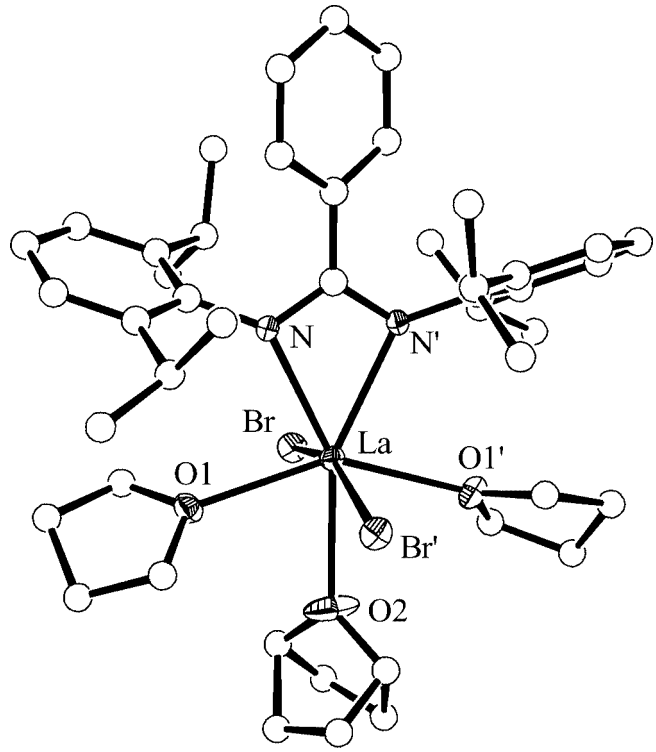


Figure 2 Molecular structure of **2** (ellipsoids [non carbon atoms] correspond to the 50 % probability level).

Selected bond lengths/Å and angles/°: La-N 2.5254(18), La-O1 2.5571(17), La-O2 2.620(3), La-Br 2.9053(2); N-La-Br 99.18(4), N′-La-Br 99.44(4), N-La-O1 80.46(6), N-La-O2 153.84(4), N-La-O1′ 132.77(6), N′-La-O1 132.77(6), N′-La-O2 153.84(4), O1-La-O2 73.38(4), O1-La-O1′ 146.77(6), N-La-N′ 52.33(6), O1-La-Br 85.62(4), O2-La-Br 79.62(1), Br-La-Br′ 159.24(1).

sterically more demanding in d-direction which could be understood by the fact that the 2,6-isopropyl-phenyl substituent linked to the pyridine ring is pointing downwards (Figure 1). In e-direction the amidinate ligand is bulkier. The differences in the Br-La-Br und O-La-O angles are similar 7.1° and 5.8°, respectively. Thus we assume a similar overall primary coordination site bulkiness for both ligands but distinct differences in the d- and e-directions. The consequences of these differences in terms of the reactivity of the corresponding early transition metal and lanthanide complexes are going to be investigated.

Experimental Section

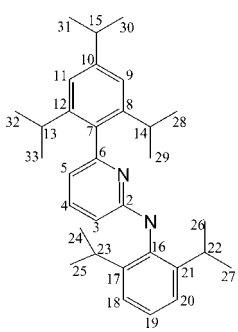
All reactions and manipulations with air-sensitive compounds were performed under dry argon, using standard Schlenk and drybox techniques. Solvents were distilled from sodium benzophenone ketyl. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried (CaH_2) and distilled prior to use. NMR spectra were obtained using either a Bruker ARX 250, Bruker DRX 500, Varian Unity Inova 400 or VXR 300 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses were carried out using an Elementar Vario EL III. Ap*-H [8] and Am*-H [7b] were synthesised following literature procedures. $LaBr_3(THF)_4$ was prepared by continuous extraction of anhydrous $LaBr_3$ [9]. All other starting materials were purchased from commercial suppliers. X-ray crystal structure analyses were performed using a STOE-IPDS II (**1**) or a Brucker SMART APEX CCD (**2**) equipped with a low temperature

Table 1 Details of the X-ray crystal structure analyses of **1** and **2**.

compound	**1**	**2**
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$	Pbcn
a, Å	14.455(3)	17.0544(9)
b, Å	17.772(4)	17.393(1)
c, Å	18.361(4)	14.6421(8)
β, deg	95.13(3)	
V, Å^3	4697.9(16)	4343.2(4)
Z	4	4
crystal size, mm	0.48 x 0.36 x 0.34	0.49 x 0.46 x 0.39
ρ_{calcd}, g cm^{-3}	1.372	1.460
μ, mm^{-1} (Mo Kα)	2.647	2.862
T, K	193(2)	100(1)
θ range, deg	1.60 to 26.31	2.34 to 29.68
no. of reflecions unique	9341	5384
no. of reflections obs. [I > 2σ (I)]	8148	4661
no. of parameters	469	358
wR^2 (all data)	0.0849	0.0618
R value [I>2σ (I)]	0.0333	0.0286

unit. Structure solution and refinement was accomplished using SIR97 [10], SHELXL97 [11] and WinGX [12]. Crystallographic details are summarized in Table 1. CCDC-602184 (compound **1**) and -602602 (compound **2**) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge at **www.ccdc.cam.ac.uk/conts/retrieving.html** (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Preparation of the lanthanide complexes Ap*LaBr$_2$(THF)$_3$ (1)



$LaBr_3$ (0.80 g, 2.10 mmol), [K(Ap*)] (1.04 g, 2.10 mmol) and THF (40 cm^3) were added to a flask, and the mixture was stirred for 15 h. The solvent was removed under vacuum and hexane was added (30 cm^3). The yellow reaction mixture was filtered and on standing at room temperature for 24 h, yellow crystals (partially suitable for X-ray analysis) of **1** were formed (0.80 g, 40 %). Analysis: C, 54.03; H, 6.70; N, 2.70 %; $C_{44}H_{67}Br_2LaN_2O_3$ requires C, 54.44; H, 6.96; N, 2.89 %.

^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 1.17 (d, 6H, H^{28,29,32,33}), 1.22 (d, 6H, H^{30,31}), 1.29 (d, 6H, H^{24,25,26,27}), 1.44 (br, 4H, β-CH_2, THF), 1.49 (d, 6H, H^{24,25,26,27}), 1.57 (d, 6H, H^{28,29,32,33}), 2.78 (sept, 1H, H^{15}), 3.44 (sept, 2H, H^{13,14}), 3.58 (br, 12H, α-CH_2, THF), 4.22 (sept, 2H, H^{22,23}), 5.78 (d, 1H, H^3), 6.03 (d, 1H, H^5), 6.86 (t, 1H, H^4), 7.18 (m, 2H, H^{18,20}), 7.24 (m, 1H, H^{19}), 7.29 ppm (m, 2H, H^{9,11}). **^{13}C NMR** (C_6D_6, 298 K): δ = 21.36 (C^{28,29,32,33}), 24.39 (C^{24,25,26,27}), 24.64 (C^{28,29,32,33}), 25.23 (β-CH_2, THF), 25.98 (C^{24,25,26,27}), 26.17 (C^{30,31}), 28.64 (C^{22,23}), 30.81 (C^{13,14}), 34.75 (C^{15}), 70.65 (α-CH_2, THF), 107.70 (C^3), 111.18 (C^5), 121.04 (C^{9,11}), 124.10 (C^{18,20}), 125.60 (C^{19}), 137.83 (C^7), 138.75 (C^4), 144.45 (C^{17,21}), 147.13 (C^{16}), 148.66 (C^{8,12}), 149.07 (C^{10}), 155.92 (C^6), 170.77 (C^2) ppm.

Am*LaBr$_2$(THF)$_3$] (2)

Am*-H (0.88 g, 2.00 mmol) was added to a slurry of KH (0.08 g, 2.00 mmol) in THF (25 mL) and stirred to become a clear solution. After adding $LaBr_3(THF)_4$ (1.33 g, 2.00 mmol) the mixture was heated under reflux for several minutes to become slurry again. The hot mixture was filtered and slowly cooled to room temperature. After a few hours yellow crystals of the title complex were formed which were filtered of and dried under reduced pressure (1.68 g, 88 %). Analysis: C, 51.94; H, 6.39; N, 2.82 %. $C_{43}H_{63}Br_2LaN_2O_3$ requires C, 54.10; H, 6.65; N, 2.93 %).

^{1}H NMR (400 MHz, THF-d_8, 298 K): δ = 0.70 (d, 12H, ^3J(H,H) = 6.6 Hz, CH_3), 1.18 (d, 12H, ^3J(H,H) = 6.6 Hz, CH_3), 1.72 (br, 12H; β-CH_2, THF), 3.56 (br, 12H; α-CH_2, THF), 3.71 (sept, 4 H, ^3J(H,H) = 6.6 Hz, CHMe$_2$), 6.69 – 6.97 (m, 11H, C_6H_5, C_6H_3) ppm. **^{13}C NMR** (100 MHz, THF-d_8, 298 K): 25.19 (CH_3), 26.56 (CH_3), 27.34 (THF), 29.68 (CHMe$_2$), 69.22 (THF), 124.98 (Ar *C*), 125.14 (Ar *C*), 127.93 (Ar *C*), 130.23 (Ar *C*), 133.23 (Ar *C*), 143.56 (Ar *C*), 147.40 (Ar *C*), 174.25 (N*C*N) ppm.

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