η^6-Arene(halogenidoaluminato)lanthanoid(III) complexes: Synthesis, characterization and catalytic activity for isoprene polymerization

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Abstract

η^6-Arene(iodido-/bromido-aluminato)lanthanoid(III) complexes, [Ln(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] [Ln = La (**1**), Ce (**2**), Nd (**3**), (Gd) (**4**); C$_6$H$_5$Me = toluene], [Ln(η^6-C$_6$H$_3$Me$_3$-1,3,5)(AlI$_4$)$_3$] [Ln = La (**5**), Ce (**6**), Pr (**7**), Nd (**8**), Sm (**9**), Gd (**10**); C$_6$H$_3$Me$_3$-1,3,5 = mesitylene], and [Ln(η^6-C$_6$H$_5$Me)(AlBr$_4$)$_3$] [Ln = La (**11**), Nd (**12**), Sm (**13**)] were prepared by reactions of aluminium triiodide or aluminium tribromide with the corresponding lanthanoid metals and 1,2-diiodoethane or 1,2-dibromoethane in an arene (toluene or mesitylene) solution (molar ratio : 6:2:3). The first X-ray crystal structures of arene(iodidoaluminato)lanthanoid(III) complexes are reported. The lanthanoid atom is coordinated by an η^6–arene and three chelating κ(I, I′)-tetraiodidoaluminate ligands. The tetrabromidoaluminate complexes have similar structures. The pre-catalyst **3** was treated with AlR$_3$ (R = Me or *i*Bu) to give [Nd(η^6-C$_6$H$_5$Me)(AlI$_3$R)$_3$] species *in situ,* which were then tested for catalytic activity towards isoprene polymerization. Although the resulting polyisoprene had a desirable high *cis*-1,4 content, the catalyst performance was well below known best performing systems and indicates that iodidoaluminates are the least favourable of the halogenidoaluminatolanthanoid(III) complexes.

Keywords

Lanthanoids, η^6-arene complex, Aluminium tribromide, Aluminium triiodide, Iodido- and Bromido-aluminate complexes.

Introduction

Lanthanoid (III) chloridoaluminate η^6-arene complexes [Ln(arene)(AlCl$_4$)$_n$] have been known for more than three decades.[1] These compounds have considerable interest not only for the versatile coordination modes of arenes with lanthanoid metals, but also for the potential applications in catalysis. High catalytic activity of these complexes for the polymerization of ethylene and 1,3-dienes has been reported.[2-3] Recently, the magnetic behavior of [(C$_6$Me$_6$)Dy(AlCl$_4$)$_3$], [(C$_6$H$_5$Me)Dy(AlCl$_4$)$_3$] and [(C$_6$H$_5$Me)Dy(AlBr$_4$)$_3$] has been examined, and they were found to be single-ion magnets.[4, 5] The first structurally characterised chloridoaluminate π-arene complex was [(C$_6$Me$_6$)Sm(AlCl$_4$)$_3$], synthesised by refluxing a mixture of samarium(III) chloride, aluminium chloride and hexamethylbenzene in toluene.[1a] Other chloridoaluminate Ln(III) complexes authenticated by X-ray structure analysis comprise [Ln(η^6-C$_6$H$_6$)(AlCl$_4$)$_3$]·C$_6$H$_6$ (Ln = La, Nd, Sm), [6-9] [Ln(η^6-C$_6$H$_5$Me)(AlCl$_4$)$_3$] (Ln = La, Nd, Sm, Dy, Tm, Yb), [5, 10-14] [Ln(η^6-1,3-C$_6$H$_4$Me$_2$)(AlCl$_4$)$_3$] (Ln = Pr, Sm),[15-16] [Nd(η^6-1,3,5-C$_6$H$_3$Me$_3$)(AlCl$_4$)$_3$]·C$_6$H$_6$, [17] and [Ln(η^6-C$_6$Me$_6$)(AlCl$_4$)$_3$] (Ln = La, Sm, Gd, Tb, Dy, Yb).[1a, 1b, 4, 10, 18-19] Moreover, Ln(III) halogenidogallate complexes [Ln(η^6-arene)(GaX$_4$)$_3$] (Ln = Ce, Yb, Dy; X = Cl, Br) were prepared by the reaction of gallium(III) halides and lanthanoid(III) halides in the presence of alkylated benzenes.[20] A number of η^6-arene(alkyltrihalogenidoaluminato)lanthanoid complexes such as [Ln(η^6-C$_6$H$_5$Me)(AlCl$_3$Me)$_3$] (Ln =Y, Nd, Sm), [Ln(η^6-C$_6$H$_5$Me)(AlCl$_3$Et)$_3$] (Ln = Pr, Nd), [Nd(η^6-Me$_4$C$_6$H$_2$)(AlCl$_3$R)$_3$] (R = Me, Et), [Nd(η^6-MeC$_6$H$_5$)(AlX$_3$Et)$_3$] (X = Br, I) and [Gd(η^6-MeC$_6$H$_5$)(AlBr$_3$Me)$_3$] have been prepared by reaction of the parent Ln(η^6-arene)(AlX$_4$)$_3$ (X = Cl, Br, I) with the corresponding AlR$_3$ (R = Me, Et) compounds.[3] The only structurally characterised [Ln(η^6-arene)(AlBr$_4$)$_3$] complexes are [Gd(η^6-MeC$_6$H$_5$)(AlBr$_4$)$_3$] [13] and [Dy(η^6-MeC$_6$H$_5$)(AlBr$_4$)$_3$],[5] but a number of [Ln(η^6-arene)(AlBr$_4$)$_3$] (Ln = Pr, Nd, Y; arene = MeC$_6$H$_5$; Ln = Nd, arene = durene) complexes

have been characterised analytically and spectroscopically.[13] Three AlI$_4^-$ analogues are known but none have been structurally characterised.[13]

In this work, we explore η^6-arene(iodidoaluminatolanthanoid(III) complexes, and report the synthesis and first X-ray crystal structures of tetraiodidoaluminato-lanthanoid(III) complexes. A number of the iodidoaluminatolanthanoid(III) complexes were prepared by a new one-pot reaction. Besides, three of the bromidoaluminato-lanthanoid(III) complexes were also obtained by the same method. Only [Nd(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] (**3**) and [Nd(η^6-C$_6$H$_5$Me)(AlBr$_4$)$_3$] (**12**) have previously been reported but without structure determinations.[13] The activity of **3** as a pre-catalyst for isoprene polymerization has also been tested.

Results and Discussion

The iodido- and bromido-aluminato(η^6-arene)lanthanoid complexes have been synthesised by heating a mixture of six molar equivalents of aluminium triiodide or aluminium tribromide with two molar equivalents of the corresponding lanthanoid metals and three molar equivalents of 1,2-diiodoethane in an arene (toluene or mesitylene) solution at about 100°C (Scheme 1). The aluminium triiodide was prepared freshly by heating a mixture of iodine and an excess of aluminium powder and used without isolation to provide a one-pot procedure. Stoichiometric amounts of lanthanoid metal and diiodoethane were then added to the aluminium triiodide solution and the mixture was heated overnight at 100°C. After filtration and evaporation, standing the solution at room temperature for 1-2 days afforded the complexes [Ln(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] (Ln = La (**1**), Ce (**2**), Nd (**3**), (Gd) (**4**)), [Ln(η^6-C$_6$H$_3$Me$_3$-1,3,5)(AlI$_4$)$_3$] (Ln = La (**5**), Ce (**6**), Pr (**7**), Nd (**8**), Sm (**9**), Gd (**10**)). Attempts to prepare complexes of heavier lanthanoid elements did not yield crystalline material suitable for structure determination. Ln(III) bromidoaluminate complexes [Ln(η^6-C$_6$H$_5$Me)(AlBr$_4$)$_3$] (Ln = La (**11**), Nd (**12**), Sm (**13**)) have also been obtained in toluene (Scheme 2) by a similar method. Crystals of **1-13** are insoluble in aromatic solvents like deuterobenzene and decomposed in polar solvents like thf. All complexes are extremely air and moisture sensitive and are difficult to handle. The IR spectra of complexes **1-10** in the solid state show the presence of C–H aromatic absorption of the coordinated toluene molecule at about 3000 cm^{-1} and an sp^3 C-H stretching at around 2900 cm^{-1} as for the reported chloridoaluminate complexes.[9, 10, 21] Due to extreme air sensitivity of the complexes

and low percentage of C and H (only from toluene or mesitylene), H microanalyses were often high and some % C values were somewhat deviant. However, the metal analyses were closer to the expected percentages. They were performed shortly after preparation, whereas C,H microanalyses required international travel before their determination. Surprisingly, compounds **6** and **9** gave reasonable C, Ln analyses for retention of an extra 2/3 mesitylene per molecule of bulk sample and this may have countered decomposition. Although single crystals of some tetrabromidoaluminato-lanthanoid complexes **11-13** were isolated, pure bulk material could not be isolated for microanalyses.
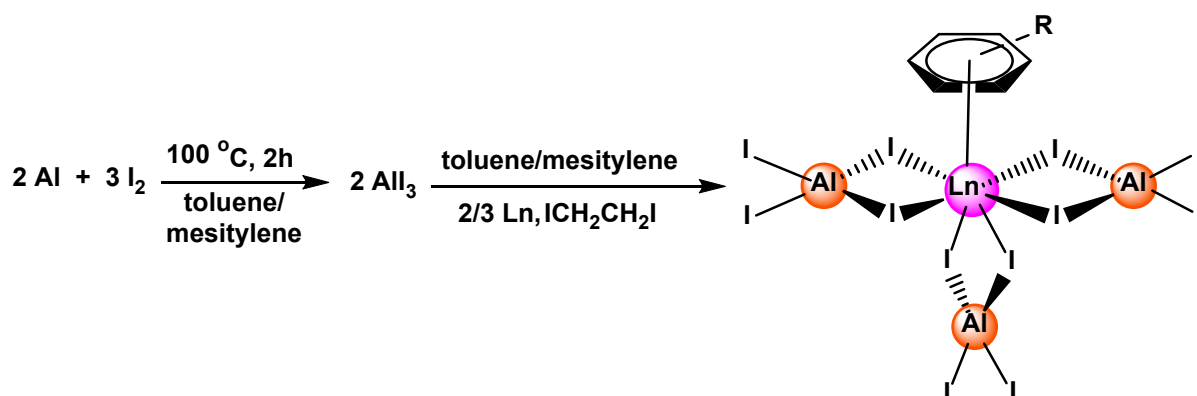
Scheme 1. Synthesis of compounds **1-10** (Yields in parentheses) : R = Me; Ln = La(**1**) (27%), Ce(**2**) (31%), Nd(**3**) (41%), Gd(**4**) (36%); R = 2,4,6-Me$_3$; Ln = La(**5**) (21%), Ce(**6**) (31%), Pr(**7**) (26%), Nd(**8**) (32%), Sm(**9**) (25%), Gd(**10**) (35%).
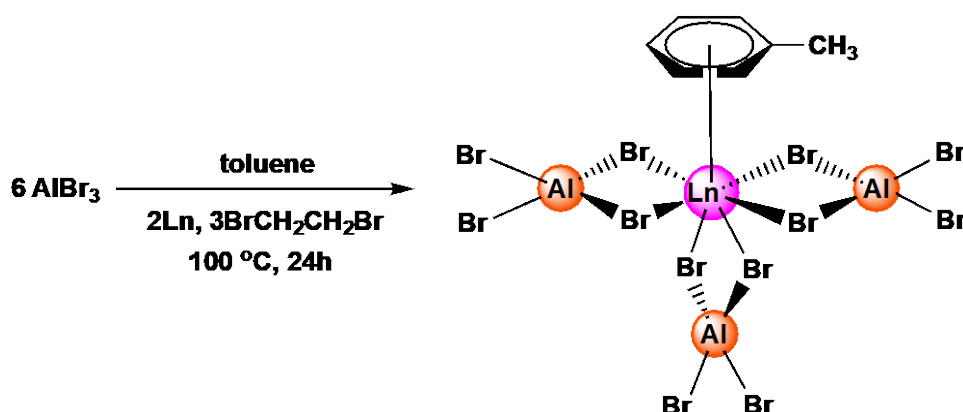
Scheme 2. Synthesis of compounds **11-13**; Ln = La(**11**), Nd(**12**), Sm(**13**). Only identified as single crystals removed from discoloured reaction mixtures.

X-ray Structures

Representative structures of complexes **1–13** are shown in Fig **1–3**. The Ln-C bond lengths and Ln-C-ring (centroid) are in **Table 1**, those for Ln-I/Br are in **Table 2**. Crystal data and refinement details are given in Table S1, and Al-X (X = I or Br) bond lengths are in the Table S2.

Single crystals of [Ln(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] (Ln = La **1**, Ce **2**, Gd **4**) are isomorphous and crystallize in the monoclinic space group P2$_1$/c with two similar molecules in the asymmetric unit (**Fig 1** for molecule 1 of **1**). [Nd(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] (**3**) crystallizes in the monoclinic space group P2$_1$/n with a single molecule in the asymmetric unit. Although **3** is not isomorphous with **1, 2** and **4**, all four complexes showed a nine coordinate arrangement where the Ln(III) centre is ligated by six iodides from three chelating AlI$_4^-$ ligands and an η^6-bound arene (**Fig 1**). The coordination polyhedron of all complexes can be described as a distorted pentagonal bipyramid with the η^6-arene located in an axial position. The other axial position opposite to the arene centroid is occupied by I10 (the centroid-Ln-I10 angle in **1-4** is around 180°). For all complexes, Ln1-I10 is the shortest Ln-I bond, hence I10 is the most strongly bound to the Ln^{3+} centre. This feature can be attributed to a weak *trans* influence [22] of the uncharged arene ligand compared with the charged tetraiodidoaluminate ligands. Iodidoaluminate complexes **1**, **3** and **4** are isostructural with the corresponding chloridoaluminate complexes [Ln(η^6-C$_6$H$_5$Me)(AlCl$_4$)$_3$] (Ln = La, Nd, Sm, Dy, Tm, Yb) [5, 10-14] and the tetrabromidoaluminate [Gd(η^6-C$_6$H$_5$Me)(AlBr$_4$)$_3$],[10] but they are not isomorphous. Compound **2** is the first reported cerium η^6-arene tetrahalogenidoaluminate complex. The Ln-C bond lengths and Ln-C-ring (centroid) show the effect of ionic radius[23] as La-C > Ce-C > Nd-C > Gd-C (Table 1), while Ln-I bond lengths show irregular behaviour as the average La-I > Nd-I > Ce-I > Gd-I (Table 2).The irregular behaviour of Nd-I compared to the others results in two bond length breaks in the Ln series.

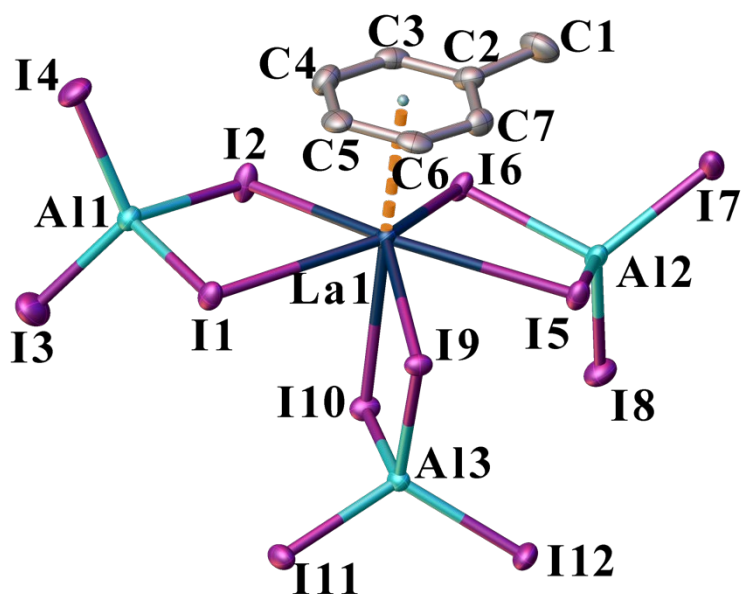**Fig 1**. Molecular diagram of [La(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] (representative of La, **1**, Ce, **2**, Nd, **3**, Gd, **4**) represented by 50% thermal ellipsoids. The molecule 2 for **1, 3, 4** and hydrogen atoms have been omitted for clarity.

Single crystals of [Ln(η^6-1,3,5-Me$_3$C$_6$H$_3$)(AlI$_4$)$_3$] (**5-8, 10**) are isomorphous as they have similar unit cell parameters. The complexes **5-8** and **10** crystallize in the monoclinic space group P2$_1$/c. Owing to the poor crystal quality of **5** and **8**, only unit cell data are provided (see Experimental). [Sm(η^6-1,3,5-Me$_3$C$_6$H$_3$)(AlI$_4$)$_3$] (**9**) crystallizes in the monoclinic space group C2/c. Complexes [Ln(η^6-1,3,5-Me$_3$C$_6$H$_3$)(AlI$_4$)$_3$] (**6, 7, 9, 10**) of the bulkier mesitylene have nine-coordinate structures (**Fig. 2**) similar to **1-4** and the tetrachloridoaluminate analogue [Nd(η^6-1,3,5-Me$_3$C$_6$H$_3$)(AlCl$_4$)$_3$].[17] Despite the difference in steric and donor ability between toluene and mesitylene, the average Ln-C bond distances of the same metal are similar (**Table 1**, Ce-C: **2** 2.986 Å, **6** 2.981 Å; Gd-C: **4** 2.906 Å, **10** 2.906 Å) and this is particularly evident from the Ln-centroid values (e.g. Ce-C: **2** 2.639 Å, **6** 2.634 Å; Gd-C: **4** 2.547 Å, **10** 2.548 Å (Table 1). Evidently the increased bulk is offset by the increased donor ability with greater methyl substitution. In this regard the tetraiodidoaluminate complexes differ from analogous tetrachloridoaluminates where for [Nd(η^6-arene)(AlCl$_4$)$_3$] (arene = C$_6$H$_6$, C$_6$H$_5$Me, 1,3,5-Me$_3$C$_6$H$_3$), the Nd-C bond length decreases with increased methyl substitution[17] hence the electronic effect of Me outweighs the steric factor. Again, the *trans* (to the centroid) Ln-I10 bond is the shortest for **6, 7, 9, 10** (**Table 2**), but here mesitylene substitution has an effect in that Ln-I10

values for **6** and **10** are slightly longer (0.01-0.02 Å) than in their toluene counterparts **2** and **4**. Thus, the *trans* influence of mesitylene is greater than toluene. The Ln-C bond lengths of **1-4** and **6, 7, 9, 10** and their Ln-centroid distances generally correspond well with the corresponding reported values for $[Ln(\eta^6\text{-arene})(AlCl_4)_3]$ complexes.[7-9, 12, 17, 19] On the other hand the arene bonding in **4** and **10** is much weaker than that in the zerovalent $[Gd(1,3,5\text{-}t\text{Bu}_3C_6H_3]$ where Gd-C is 2.585-2.660 Å and Gd-centroid is 2.219 Å.[24] The decrease in Ln-C bond lengths (or Ln-centroid distances) from **1-4** and from **6, 7, 9, 10** (La → Gd) is *ca*. 0.1 Å which corresponds to the decrease in the nine coordinate ionic radii (0.11 Å).[23] The average bond lengths of Ln-I for complexes **6, 7, 9** and **10** show Ce-I > Pr-I > Sm-I > Gd-I, also corresponding to the ionic radii difference.

By contrast with the Ln-I bond lengths, the Al-I bonds show little variation (Table S1). Terminal Al-I bonds of **1-10** lie in the narrow range 2.471(3) – 2.517(4) Å whilst the bridging Al-I(-Ln) bonds are longer as expected in the range 2.559(2) – 2.619(7) Å. Although Al-I9,10 are marginally longer than Al-I1,2,5,6, I10- which forms the shortest Ln-I bonds, has similar Al-I bond lengths to I9 (Table S1). Change of Ln has little effect on the Al-I bonds.
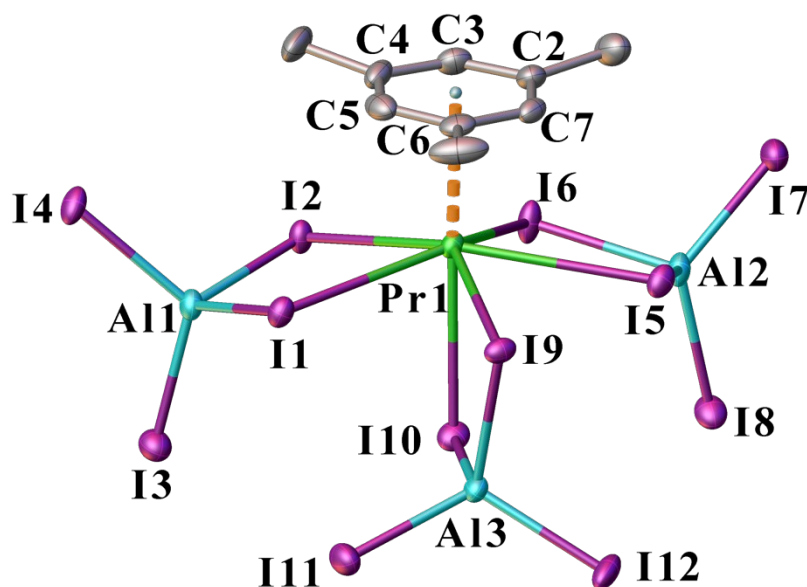

Fig 2. Molecular diagram of $[Pr(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(AlI_4)_3]$ (representative of Ce, **6**, Pr, **7**, Sm, **9**, Gd, **10**) represented by 50% thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

Table 1: A comparison of Ln-C(arene) and Ln-Centroid(arene)distances Å

Complex	Ln1-C	Ln1-C$_{avg}$	Ln1-C$_{centroid}$
[La(η^6-C$_6$H$_5$Me)(AlCl$_4$)$_3$] [10]	2.927- 3.035	2.981	2.633
[Nd(η^6-C$_6$H$_5$Me)(AlCl$_4$)$_3$] [12]	-	2.926	2.577
[Sm(η^6-C$_6$H$_5$Me)(AlCl$_4$)$_3$] [11]	-	2.910	2.540
[La(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] **1**	2.975(10) - 3.054(10)	3.009	2.666
[Ce(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] **2**	2.951(11) - 3.041(11)	2.986	2.639
[Nd(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] **3**	2.885(6) - 3.015(5)	2.932	2.578
[Gd(η^6-MeC$_6$H$_5$)(AlCl$_4$)$_3$] **4**	2.867(8) - 2.970(8)	2.906	2.547
[Ce(η^6-C$_6$H$_3$Me$_3$)(AlI$_4$)$_3$] **6**	2.952(7) - 3.009(9)	2.981	2.634
[Pr(η^6-C$_6$H$_3$Me$_3$)(AlI$_4$)$_3$] **7**	2.940(6) -2.993(7)	2.969	2.618
[Sm(η^6-C$_6$H$_3$Me$_3$)(AlI$_4$)$_3$] **9**	2.902(15) - 2.957(12)	2.930	2.579
[Gd(η^6-C$_6$H$_3$Me$_3$)(AlI$_4$)$_3$] **10**	2.878(6) - 2.943(6)	2.906	2.548
[La(η^6-C$_6$H$_5$Me)(AlBr$_4$)$_3$] **11**	2.943(6) - 3.054(6)	2.992	2.645
[Nd(η^6-C$_6$H$_5$Me)(AlBr$_4$)$_3$] **12**	2.877(4) - 3.003(4)	2.934	2.577
[Sm(η^6-C$_6$H$_5$Me)(AlBr$_4$)$_3$] **13**	2.867(6) - 2.962(6)	2.906	2.547

Table 2: Ln-X (I or Br) bond lengths (Å)

X = I	La **1**	Ce **2**	Nd **3**	Gd **4**	Ce **6**	Pr **7**	Sm **9**	Gd **10**
Ln1-X1	3.2805(11)	3.2634(11)	3.2294(10)	3.1990(9)	3.3024(13)	3.2910(13)	3.2758(17)	3.2358(8)
Ln1-X2	3.3332(9)	3.3203(10)	3.3295(8)	3.2724(8)	3.3027(9)	3.2933(8)	3.3644(19)	3.3555(13)
Ln1-X5	3.3671(9)	3.3561(10)	3.2754(8)	3.3087(8)	3.3872(14)	3.3830(14)	3.252(2)	3.2499(8)
Ln1-X6	3.3148(9)	3.3004(9)	3.2651(7)	3.2416(7)	3.2917(9)	3.2790(8)	3.2468(19)	3.2486(13)

Ln1-X9	3.2812(10)	3.2646(11)	3.3293(8)	3.2069(9)	3.2519(9)	3.2441(8)	3.2750(17)	3.1942(8)
Ln1-X10	3.2494(10)	3.2290(11)	3.1370(6)	3.1512(9)	3.2496(9)	3.2325(8)	3.1549(18)	3.1786(8)
Ln-X (average)	3.3044	3.2396	3.2610	3.2299	3.2976	3.2872	3.2615	3.2438

X = Br	La 11	Nd 12	Sm 13
Ln1-X1	3.0890(9)	3.0434(7)	3.0250(8)
Ln1-X2	3.0476(8)	3.0033(7)	2.9873(8)
Ln1-X5	3.0724(11)	3.0282(9)	3.0124(10)
Ln1-X6	3.0574(9)	3.0102(7)	2.9906(8)
Ln1-X9	3.0745(8)	3.0318(7)	3.0154(8)
Ln1-X10	3.0051(8)	2.9493(7)	2.9201(8)
Ln-X (average)	3.0577	3.0110	2.9918

The tetrabromidoaluminate complexes $[Ln(\eta^6\text{-}C_6H_5Me)(AlBr_4)_3]$ (**11-13**) are isomorphous and have unit cell parameters in agreement with the reported X-ray data for $[Gd(\eta^6\text{-}C_6H_5Me)(AlBr_4)_3]$[13] and $[Dy(\eta^6\text{-}C_6H_5Me)(AlBr_4)_3]$.[5] $[Ln(\eta^6\text{-}C_6H_5Me)(AlBr_4)_3]$ (**11-13**) crystallize in the monoclinic $P2_1/n$ space group with one toluene and three $[AlBr_4]^-$ ligands (**Fig. 3**). The stereochemistry of the Ln(III) ion is close to pentagonal bipyramidal with the centroid of toluene and the Br10 atom in the apical positions. The average Ln-C bond distances and the Ln-centroid values of the same metal are similar to those of the tetraiodidoaluminates [La-C: **1** 3.009 Å, **11** 2.992 Å; Nd-C: **3** 2.932 Å, **12** 2.934 Å; Ln-C(centroid) La-C: **1** 2.666 Å, **11** 2.645 Å; Nd-C: **3** 2.578 Å, **11** 2.577 Å]. The bond lengths of Ln-C(average) and Ln-C (centroid) of **11-13** are longer than those of Dy (2.860, 2.503 Å),[5] and the average bond lengths of Ln-Br in **11-13** are significantly longer, as expected, than those of Ln-Cl in $[Ln(\eta^6\text{-}C_6H_5Me)(AlCl_4)_3]$ (Ln = La, Nd, Sm).[10-12]

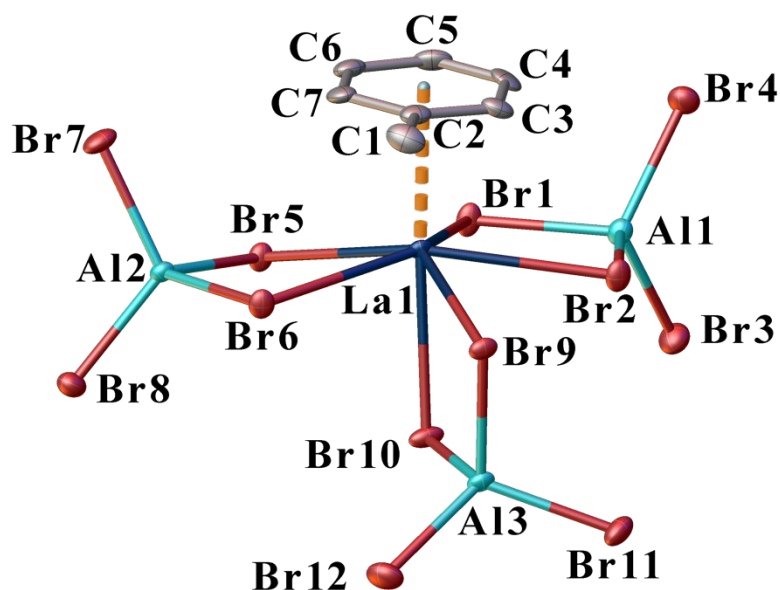**Fig 3**. Molecular diagram of [La(η^6-C$_6$H$_5$Me)(AlBr$_4$)$_3$] (representative of La, **11**, Nd, **12, Sm, 13**) represented by 50% thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

Raman spectra

The Raman spectra of three complexes **1, 3** and **5** were recorded in an attempt to locate skeletal stretching frequencies. All gave strong band at 170-140 cm^{-1} together with a weaker feature at 150-140 cm^{-1} (**Table 3**). These can be confidently assigned to Al-I stretching as Al-I symmetric stretching (ν_1) of AlI$_4$$^-$ is observed at 144 cm^{-1}.[25] In the structures, there are two terminal and two bridging Al-I bonds in the AlI$_4$$^-$ units hence the symmetry is lowered from T$_d$ in AlI$_4$$^-$ to at least C$_{2v}$ thereby activating more than one Al-I stretching vibration in the Raman spectra.[26]

Table 3   Al-I stretching frequencies of 1, 3, and 5 in Raman spectra

Compound	Raman bands
[La(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] (**1**)	150m, 144sh
[Nd(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] (**3**)	152s, *ca.* 140sh
[La(η^6-C$_6$H$_3$Me$_3$)(AlI$_4$)$_3$] (**5**)	166s, 150w,sh

Catalytic activity of [Nd(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] (3) for the polymerization of isoprene

Arene(alkyltrihalogenidoaluminato)lanthanoid(III) complexes, as described by Biagini *et al.*, displayed promising activity in butadiene and ethylene polymerization.[2] Considering solubility criteria and the neodymium effect,[3b] complex **3** [Nd(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] was selected as a potential precatalyst. Accordingly, **3** was converted *in situ* into the corresponding neodymium alkyltriiodidoaluminate complexes [Nd(η^6-C$_6$H$_5$Me)(AlI$_3$R)$_3$] (R = methyl or isobutyl) and their performance in isoprene polymerization tested (Scheme 3).

The conversion of the neodymium iodidoaluminate η^6-arene complex **3** into its alkylated variant **3-R** was accomplished using 1.5 equivalents trimethylaluminium (TMA) and triisobutylaluminium (TIBA), respectively. A clear blue solution was obtained after ten minutes for the TIBA-reaction, while it took 1.5 hours for the reaction with TMA to turn into a clear solution. Afterwards, the solutions were combined with a solution mixture containing di*iso*butylaluminium hydride (DIBAH) and isoprene. It is vital for the polymerization to be conducted in *n*-hexane. Although the polymerization in *n*-hexane gives only low yields of polyisoprene after 5 h, only traces of polymer were observed when the polymerization was conducted in toluene. As compiled in Table 1, the obtained polymers exhibit a high *cis*-1,4 content, similar to study by Biagini *et al.*, describing the fabrication of high *cis*-1,4 polybutadiene.[2]
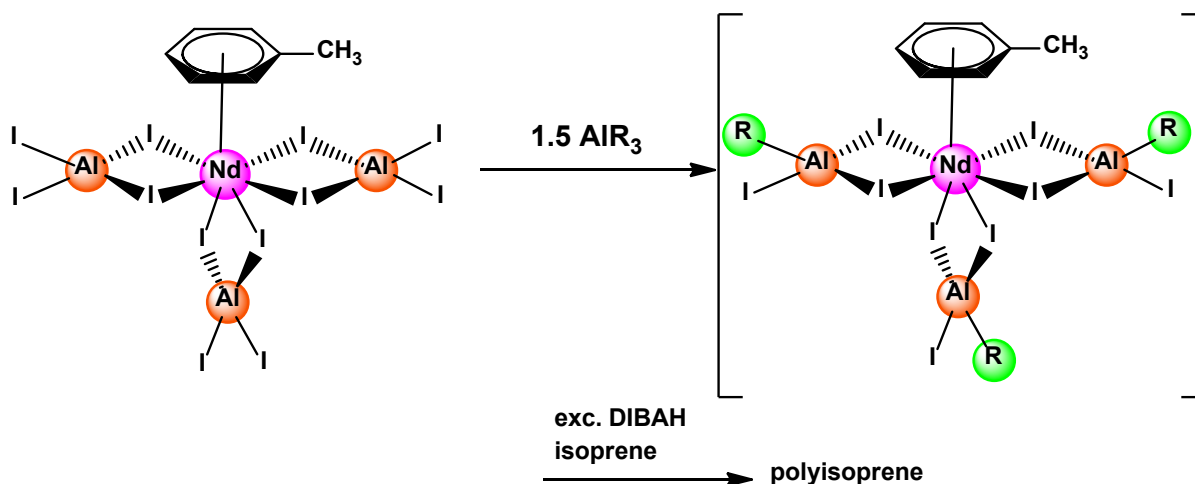
Scheme 3. Experimental conditions used for the polymerization of isoprene using [Nd(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$] (**3**) as precatalyst.

Table 4 Polymerization results of isoprene with [Nd(η^6-C$_6$H$_5$Me)(AlI$_3$R)$_3$] (3)

entry	precatalyst	cocatalysts	yield (%)	cis-1,4[a]	$trans$-1,4[a]	3,4[a]	M_n[b] (x 10^4)	M_w/M_n[b]	T_g[c]	ref.
1[d]	**3**	TIBA/DIBAH	16	83.3	5.3	11.4	2.9	6.74	-59.2	-
2[d]	**3**	TMA/DIBAH	25	86.4	0.0	13.6	2.7	7.67	-60.0	-
3[d]	**3**	TIBA/MgBu$_2$	tr.	-	-	-	-	-	-	-
4[e]	Nd(AlBr$_4$)$_3$	TIBA/DIBAH	34	98.6	1.1	0.3	-	-	-	[2]
5[f]	Nd(AlCl$_4$)$_3$	TIBA/MgBu$_2$	73	97.4	1.8	0.8	14.2	7	-	[2]

[a] Determined by ^{1}H, ^{13}C NMR spectroscopy in CDCl$_3$. [b] Determined by GPC against polystyrene standards. [c] Determined by DSC at 10 K/min heating and cooling rate. [d] Polymerization conditions vary and are shown in the experimental section. [e] Polymerization of butadiene: hexane 150 ml, butadiene 15 g, [Nd] = 3*10^{-4} mol/L, DIBAH/[Ln] = 50 molar ratio, T = 50 °C, 2 h. [f] Polymerization of butadiene: hexane 150 ml, butadiene 15 g, [Nd] = 3*10^{-4} mol/L, Mg/[Ln] = 6 molar ratio, T = 50 °C, 15 min.

Due to partial solubility in THF, only the soluble part (36% in entry 1; 42% in entry 2) of the obtained polyisoprenes were analyzed by GPC. Most likely, the molecular weight of the polymers are much higher but only the polymer part with a low molecular weight was soluble in THF. Biagini *et al.* obtained polybutadienes, which are also insoluble in THF. Using di-*n*-butylmagnesium (DBM) as a cocatalyst instead of DIBAH they obtained polybutadienes which are soluble in THF.[2] In our hands, the ternary system [Nd(η^6-C$_6$H$_5$Me)(AlI$_4$)$_3$]/TIBA/DBM gave only traces of polyisoprene. Overall the sequence [Nd(AlX$_4$)$_3$(arene)]/AlMe$_3$/DIBAH seems way less efficient than the binary system Nd(AlMe$_4$)$_3$/AlMe$_2$Cl described previously.[27]

Conclusions

Lanthanoid(III) arene complexes **1-13** extend the structures attainable within the arene(tetrahalogenidoaluminato)lanthanoid(III) series with the first structural characterization of tetraiodidoaluminate coordinated complexes **1-10**. The latter were synthesised by a convenient one pot procedure from lanthanoid metals with a straightforward isolation procedure, All complexes **1-13** are nine coordinate monomers with an η^6-arene and three bidentate tetrahalogenidoaluminate ligands. The catalytic activity of **3** after pretreatment with trialkylaluminium compounds for isoprene

polymerization was investigated at ambient temperature. However, it was not effective as expected as a catalyst, hence the introduction of the softest and largest halogen in tetrahalogenidoaluminate ligands has an adverse effect in catalysis. Although this could be tested with further examples, the results for **3** are sufficiently disappointing to discourage further investigation of the iodide class in catalysis.

Experimental

General

The lanthanoid compounds described here are highly air and moisture sensitive, and were prepared and handled with vacuum-nitrogen line techniques and in a dry box in an atmosphere of purified nitrogen. Lanthanoid metals were from Santoku/Molycorp/Eutectix. Large chunks were filed in the drybox before use. All other chemicals were purchased from Sigma Aldrich. Toluene was pre-dried over sodium metal and distilled over sodium before being stored under an atmosphere of nitrogen. IR spectra were recorded as Nujol mulls between NaCl plates using either a Perkin Elmer 1600 Series FTIR instrument or a Perkin Elmer Spectrum RX I FTIR Spectrometer within the range 4000-600 cm^{-1}. Raman spectra of crystals sealed in a micro pipette were recorded using a Renishaw inVia Raman Microscope spectrometer (Renishaw Pty Ltd., Wotton-under-edge, UK). Microanalyses were determined by the Elemental Analysis Service, London Metropolitan University, and all the samples were sealed in tubes under nitrogen. Meatal analyses were performed by complexometric titration using EDTA after digestion with dilute HCl, buffering with hexamine, and masking Al with a 5% aqueous solution of sulfosalicylic acid. Crystals were immersed in crystallography oil, and were measured on the MX1 beamline at the Australian Synchrotron. Crystal data and refinement details are given in Table S1. CCDC 2122735-2122745 for compound **1-4**, **6**, **7**, **9**, **10** and **11-13**, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of iodidoaluminate complexes in toluene

A mixture of excess Al (0.162 g, 6,0 mmol) and I$_2$ (1.90 g, 7.5 mmol) in a Schlenk flask charged with toluene (40 mL) was heated with stirring for 2 h at 100°C. The solution turned to colourless from red indicating the consumption of all iodine. After cooling the

solution to room temperature, stoichiometric amounts Ln filings and ICH_2CH_2I were added to the solution under a nitrogen atmosphere in the glove box. The mixture was heated at 100°C for 24 h, filtered and allowed to crystallize over 2 days at room temperature.

$[La(\eta^6\text{-}C_6H_5Me)(AlI_4)_3]$ (**1**): La filings (0.232 g, 1.67 mmol) and ICH_2CH_2I (0.704g, 2.5 mmol) were added to the aluminium iodide solution. Colourless crystals (0.82g, 27%). Metal analysis ($C_7H_8Al_3I_{12}La$); calc. (%) C 4.58, H 0.44, La 7.57; found C 4.95, H 1.14, La 7.54. IR (Nujol, υ/cm-1): 2925(s), 1582(m), 1490(m), 1210(m), 1178(w), 1077(w), 1033(w), 786(m), 728(w), 682(w).

$[Ce(\eta^6\text{-}C_6H_5Me)(AlI_4)_3]$ (**2**): Ce filings (0.234 g, 1.67 mmol) and of ICH_2CH_2I (0.704 g, 2.5 mmol,) were added to the aluminium iodide solution. Red crystals (0.94g, 31%). Elemental analysis ($C_7H_8Al_3I_{12}Ce$): calc. (%) C 4.58, H 0.44, Ce 7.63; found C 4.57, H 0.47, Ce 7.59. IR (Nujol, υ/cm-1): 2923 (s), 1581(w), 1211(w), 1176(w), 1078(w), 1030(w), 787(m), 723(w), 682(w).

$[Nd(\eta6\text{-}C_6H_5Me)(AlI_4)_3]$ (**3**): Nd filings (0.241 g, 1.67 mmol) and ICH_2CH_2I (0.704g, 2.5 mmol) were added to the aluminium iodide solution. A light blue solution was obtained and light blue crystals were formed in 24 h (1.27g, 41%). Elemental analysis ($C_7H_8Al_3I_{12}Nd$): calc. (%) C 4.57. H 0.44, Nd 7.84; found C 4.02, H 2.03, Nd 7.90. IR (Nujol, υ/cm-1): 2924(s), 1581(w), 1211(w), 1177(w), 1078(w), 1031(w), 789(s), 726(w), 680(w).

$[Gd(\eta^6\text{-}C_6H_5Me)(AlI_4)_3]$ (**4**) : Gd filings (0.263 g): 1.67 mmol) and of ICH_2CH_2I (0.704 g, 2.5 mmol) were added to the aluminium iodide solution. Yellow-orange crystals (1.12g, 36%). Elemental analysis ($C_7H_8Al_3I_{12}Gd$): calc.(%) C 4.54, H 0.44, Gd 8.49; found C 4.57, H 0.50, Gd 8.46. IR (Nujol, υ/cm-1): 2923(s), 1578(w), 1306(w), 1156(w), 1074(w), 1027(w), 793(s), 722(w), 672(w).

Preparation of iodidoaluminate complexes in mesitylene

A mixture of excess Al (0.162 g, 6.0 mmol) and I_2 (1.90 g, 7.5 mmol) in a Schlenk flask charged with 40 mL of mesitylene was heated with stirring in oil bath for 2 h at 100°C. The solution turned to colourless from red indicating the consumption of all iodine. After cooling the solution to room temperature, stoichiometric amounts of Ln filings and ICH_2CH_2I (0.704 g, 2.5 mmol) were added to the solution under a nitrogen atmosphere in the glove box. The mixture was heated overnight at 100°C giving a

colourless solution, which was filtered and allowed to crystallize at room temperature generally for two days.

[La(η^6-C$_6$H$_3$Me$_3$)(AlI$_4$)$_3$] **(5):** La filings (0.232 g, 1.67 mmol) and ICH$_2$CH$_2$I (0.704 g, 2.5 mmol) were added to the aluminium iodide solution. Colourless crystals (0.65g, 21%). Metal analysis (C$_9$H$_{12}$Al$_3$I$_{12}$La); calc. (%) La 7.46; found La 7.37. IR (Nujol, υ/cm^{-1}): 3186(w), 2918(s), 2724(m), 2667(m), 1302(m), 1262(m), 1154(m), 1090(w), 1029(m), 967(w), 869(m), 722(m), 672(w). Unit cell: monoclinic P2$_1$/c, a=18.609(4) Å, b=10.119(2) Å, c=20.373(4) Å, β = 113.25(3).

[Ce(η^6-C$_6$H$_3$Me$_3$)(AlI$_4$)$_3$] **(6):** Ce filings (0.234 g, 1.67 mmol) and ICH$_2$CH$_2$I (0.704g, 2.5 mmol) were added to the solution of aluminium iodide. Red crystals (0.95g, 31%). Elemental analysis (C$_9$H$_{12}$Al$_3$I$_{12}$Ce); calc. (%) C 5.80, H 0.65, Ce 7.52; found C 9.41, H 1.82, Ce 7.31. The microanalysis sample contained an additional 2/3 mesitylene: C$_{15}$H$_{20}$Al$_3$CeI$_{12}$ calc. C, 9.27; H, 1.04; Ce, 7.21.

[Pr(η^6-C$_6$H$_3$Me$_3$)(AlI$_4$)$_3$] **(7):** 1.67 mmol of Pr filings (0.235 g) and 2.5 mmol ICH$_2$CH$_2$I (0.704g) were added to the aluminium iodide solution. Red crystals (0.82g, 26%). Elemental analysis (C$_9$H$_{12}$Al$_3$I$_{12}$Pr); cal. (%) C 6.16, H 0.69, Pr 7.56; found C 6.27, H 1.56, Pr 7.48.

[Nd(η^6-C$_6$H$_3$Me$_3$)(AlI$_4$)$_3$] **(8):** Nd filings (0.241 g, 1.67 mmol) and ICH$_2$CH$_2$I (0.704g, 2.5 mmol) were added to the AlI$_3$ solution. Red crystals (0.10 g, 32%). Elemental analysis (C$_9$H$_{12}$Al$_3$I$_{12}$Nd); calc. (%) C 5.79, H 0.65, Nd 7.72; found C 5.10, H 1.86, Nd 7.58. IR (Nujol, υ/cm^{-1}): 3155(w), 2924(s), 2733(m), 2667(m), 1608 (m), 1296(m), 1261(m), 1173(w), 1090(w), 1027(m), 986(w), 868(m), 722(m), 676(w). Unit cell: monoclinic space group P2$_1$/c, a=18.645(4) Å, b=10.117(2) Å, c=20.399(4) Å, β = 113.35(3).

[Sm(η^6-C$_6$H$_3$Me$_3$)(AlI$_4$)$_3$] **(9):** Sm filings (0.375 g, 2.5 mmol) and ICH$_2$CH$_2$I (0.704g, 2.5 mmol) were added to the aluminium iodide solution. Dark orange-red crystals (0.88 g, 25%). Elemental analysis (C$_9$H$_{12}$Al$_3$I$_{12}$Sm): calc. (%) C 5.77, H 0.65, Sm 8.02; found C 9.29, H 1.86, Sm 7.94. The microanalysis sample contained an extra 2/3 mesitylene C$_{15}$H$_{20}$Al$_3$I$_{12}$Sm calc. (%) C 9.22, H 1.03, Sm 7.69.IR (Nujol, υ/cm^{-1}): 3170(m), 2923(s), 2726(m), 2670(m), 1301(m), 1261(m), 1155(m), 1078(w), 1026(m), 967(w), 869(m), 722(m), 672(w).

[Gd(η^6-$C_6H_3Me_3$)(AlI_4)$_3$] **(10):** Gd filings (0.263 g, 1.67 mmol) and 2.5 mmol of ICH_2CH_2I (0.704g) were added to the aluminium iodide solution. Yellow-orange crystals (1.06 g, 35%). Elemental analysis ($C_9H_{12}Al_3I_{12}Gd$): calc. (%) C 5.75, H 0.64, Gd 8.36; found C 4.47, H 2.75, Gd 8.45. IR (Nujol, υ/cm^{-1}): 3177(w), 2923(s), 2726(m), 2670(m), 1301(m), 1268(m), 1155(m), 1074(w), 1026(m), 967(w), 870(m), 722(m), 672(w).

Preparation of bromidoaluminate complexes in toluene

A mixture of $AlBr_3$ (1.6 g, 6.0 mmol), Ln filings (2.0 mmol; 0.278 g La for **11**, 0.288 g for **12** and 0.30 g Sm for **13**) and $BrCH_2CH_2Br$ (0.6 g, 6 mmol) was taken in a Schlenk flask charged with 40 mL toluene. The mixture was heated overnight at 100°C giving a dark muddy solution, which was filtered to remove the unreacted solid. The solution was kept at room temperature for crystallization and dark crystals covered with muddy solution were obtained next day. Crystals suitable for X-ray study were separated and identified by X-ray crystallography. No pure material could be isolated for elemental analysis.

Polymerization Studies

General

Isoprene was dried over trioctylaluminium and distilled prior to use. Size exclusion chromatography (SEC) was performed on a *Viscotek GPCmax* with a GPCmax apparatus and a model *TDA 302 triple detector array*. Sample solutions (1.0 mg polymer per mL thf) were filtered through a 0.45 μm syringe filter prior to injection. The flow rate was 1 mL/min. dn/dc and dA/dc data were determined by means of the integrated *OmniSec* ™ software. The glass transition temperature (T_g) of the polyisoprenes was determined on a Perkin-Elmer DSC 8000 with heating rates of 10 K/min and cooling rates of 10 K/min.

Polymerization of Isoprene using 3/TMA/DIBAH. TMA (14.42 μL, 0.15 mmol) was added to a suspension of Nd(AlI_4)$_3$ (18.40 mg, 0.01 mmol) in 0.5 ml toluene. The mixture was aged at ambient temperature for 90 minutes and then added to a solution of DIBAH (90.01 μL, 0.50 mmol) and isoprene (1.01 mL, 10 mmol) in 3 ml *n*-hexane. The polymerization was carried out at ambient temperature for 5 h. The reaction was terminated by pouring the polymerization mixture into 20 mL of methanol containing

0.1% (w/w) 2,6-di-tert-butyl-4-methylphenol as a stabilizer. The polymer was dried under vacuum at ambient temperature to constant weight.

Polymerization of Isoprene using 3/TIBA/DIBAH. TIBA (37.85 µL, 0.15 mmol) was added to a suspension of $Nd(All_4)_3$ (18.40 mg, 0.01 mmol) in 0.5 ml toluene. The mixture was aged at ambient temperature for 10 minutes and then combined with a solution of DIBAH (90.01 µL, 0.50 mmol) and isoprene (1.01 mL, 10 mmol) in 3 ml *n*-hexane. The polymerization was carried out at ambient temperature for 5 h. The reaction was terminated by pouring the polymerization mixture into 20 mL of methanol containing 0.1% (w/w) 2,6-di-tert-butyl-4-methylphenol as a stabilizer. The polymer was dried under vacuum at ambient temperature to constant weight.

Polymerization of Isoprene using 3/TIBA/MgBu₂. TIBA (37.85 µL, 0.15 mmol) was added to a suspension of $Nd(All_4)_3$ (18.40 mg, 0.01 mmol) in 0.5 ml toluene. The mixture was aged at ambient temperature for 10 minutes and then added to a solution of $MgBu_2$ (11.66 µL, 0.06 mmol) and isoprene (1.01 mL, 10 mmol) in 3 ml *n*-hexane. The polymerization was carried out at ambient temperature for 5 h. The reaction was terminated by pouring the polymerization mixture into 20 mL of methanol containing 0.1% (w/w) 2,6-di-tert-butyl-4-methylphenol as a stabilizer. The polymer was dried under vacuum at ambient temperature to constant weight.

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