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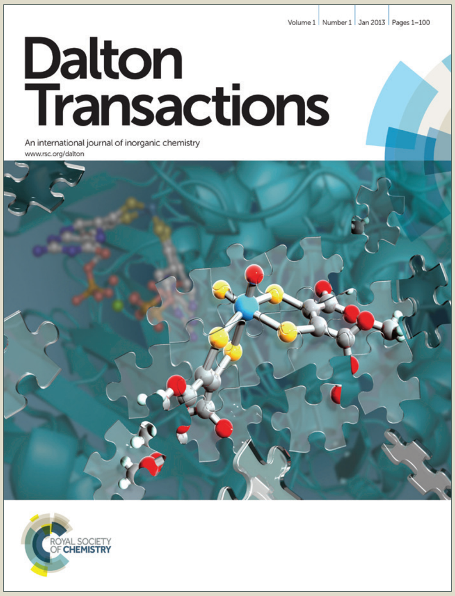

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Carbon Bridged Triphenolate Lanthanide Complexes: Synthesis, Characterization, DFT Studies and Catalytic Activities for Isoprene Polymerization

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The dinuclear lanthanide complexes [Ln_2(**L**)$_2$(THF)$_n$] (Ln=Nd (**1**) n=4, Gd (**2**) n=3, Lu (**3**) n=2) supported by carbon bridged triphenolate ligand [**LH$_3$** = tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane] were synthesized via salt metathesis reaction between lanthanide trichlorides and **L**Na$_3$ in THF. All complexes were characterized by elemental analysis and X-ray crystallography, and complex **3** was characterized by ^{1}H and ^{13}C NMR spectroscopy. Agostic interation was found in these complexes and was further substantiated by DFT calculations of complex **3**. These lanthanide complexes in combination with aluminum alkyls and $[Ph_3C]^+[B(C_6F_5)_4]^-$ generated efficient homogeneous catalysts for the *cis*-1,4 polymerization of isoprene, with complex **1** giving the best catalytic activity.

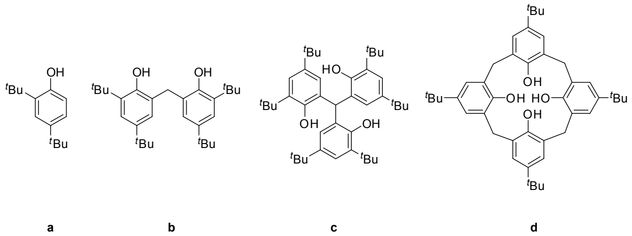
Introduction, Experimental

Lanthanide phenolate complexes are attractive complexes for their relatively chemical stability, steric and electronic tunability and easily availability.[1] They are wildly used in various reactions for their moderated reactivity and solubility.[2] Lanthanide complexes bearing monophenolate[3] (Scheme 1a), bridged bisphenolate ligands[4] (Scheme 1b) and lanthanide calixarene complexes[5] (Scheme 1d) have been synthesized and used to catalyze the polymerization of ethylene, cycle esters, octyloxyallene and isocyanates.

As an intermediate ligand between carbon bridged bisphenol and calixarene, triphenol ligand appears practically attractive. A wide range of transition metal complexes supported by amino trisphenol ligands have been synthesized and used for a variety of applications.[6] Metal complexes supported by triphenoxyl methane have attracted comparatively less attention of researchers.[7] Among the carbon bridged triphenolate complexes, alkali metal and zinc multimetallic complexes show the capability of recognizing molecules with a specific size and shape.[8] To the best of our knowledge, lanthanide complexes bearing the tripodal triaryloxide ligands have not been reported, thus the situation in the chemistry of lanthanide with carbon bridged triphenol ligands would be of interest.

The synthesis of polyisoprene has attracted great attention from both academic and industrial researchers for the pursue of high performance of synthetic rubbers and numerous industrial applications. Among numerous catalytic studies of the homopolymerization of isoprene, lanthanide complexes have showed their superiority in the preparation of *cis*-1,4[9], *trans*-1,4[10] and 3,4-polyisoprenes[11] as well as polyisoprenes with different microstructures[12]. In particular, complexes $[Ln(CH_2SiMe_3)(PNP^{Ph})(thf)_2][B(C_6F_5)_4]$ (PNP^{Ph}=$[\{2\text{-}(Ph_2P)C_6H_4\}_2N]$; Ln=Sc, Y, Lu)] afforded a high *cis*-1,4 selectivity (>99%) and excellent livingness for isoprene polymerization[13]; complexes [(S,S)-BOPA]$Ln(CH_2SiMe_3)_2$ (BOPA=(S,S)-bis(oxazolinylphenyl)amido; Ln=Sc, Lu) have been reported to exhibit very high activities and *trans*-1,4 selectivity (up to 100%) in the presence of activator.[14]

In this context, we set out to investigate the chemistry of lanthanide complexes supported by a carbon bridged triphenol ligand (Scheme 1c). This work details the synthesis and characterization of lanthanide complexes bearing the tripodal triaryloxide ligand. The structure of the complex **3** was further studied via DFT calculations. In addition, data concerning the catalytic activity toward the initiation for isoprene polymerization combined with aluminum alkyls and $[Ph_3C]^+[B(C_6F_5)_4]^-$ are reported herein.



Scheme 1 Monophenolate, bisphenolate, triphenolate and calix[4]arene ligands.

Results and discussion

Synthesis and characterization of lanthanide complexes 1-3

The tripodal triaryloxide ligand **L**H$_3$ was prepared according to the literature.[15] The molecule is C_3 symmetric with the central methine C–H bond as C_3 axis. Scott group[7d] widely studied this type of ligand, and they reported the two extremes of conformation of this C_3 symmetric ligand (Type 1 *syn* form and Type 2 *anti* form,

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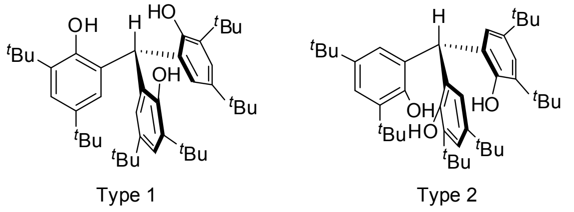
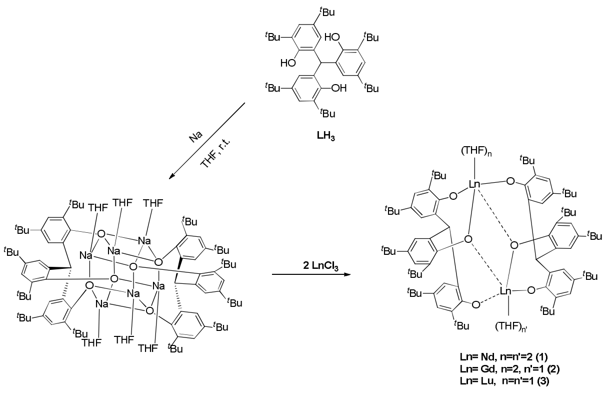
† Electronic Supplementary Information (ESI) available: cif files of complexes 1-3 and **L**Na$_3$. See DOI: 10.1039/x0xx00000x

Scheme 2). Extensive studies show that the type 1 conformer, with the central methine hydrogen oriented in line with all three hydroxide groups, is the preferred conformer. The ligand can be coaxed into type 2 conformer to bind atoms such as phosphorus and arsenic.[7d,8b] Kawaguchi reported titanium and zirconium complexes of the tripodal ligand and the rearrangement of the *syn*- to *anti*-complexes.[7g,i]

The sodium salt of the tripodal triphenol (**L**Na_3) was prepared by the reaction of **L**H_3 with an excess of sodium metal in THF at room temperature for 12 h. Suitable crystals for X-ray analysis were grown from THF solvent. Single crystal X-ray diffraction study of sodium salt revealed that it forms hexanuclear aggregate, with Na_6O_6 core stacked by three aryl groups on each side. The same structure was reported by Scott through the NaH method.[8a]



Scheme 2 Extremes of Conformation of the C_3 Symmetric Ligand.



Scheme 3 Synthesis of Triphenolate Lanthanide Complexes.

Treatment of **L**Na_3 with 1 equiv of lanthanide chlorides in THF at 70 °C for 3 days afforded the lanthanide triphenolate complexes at moderate yields (Scheme 3). The complexes are air- and moisture-sensitive. Complexes **1-3** were characterized by X-ray diffraction and elemental analyses. Suitable crystals for X-ray diffraction were grown from concentrated THF solution. The X-ray structures revealed that the dinuclear lanthanide complexes were formed: two triphenoxymethane units incorporated two lanthanide centers as shown in Scheme 3. The ligand adopted a *syn*-conformation when coordinated to lanthanides, with hydrogen on methine pointing to metal atoms. Interestingly, the number of coordination THF molecules in the complexes decreased as the radius of the lanthanide ion decreased. Complexes **1-3** showed high solubility in toluene and hexane at room temperature in contrast to poor solubility of **L**H_3, which was comparable with the calixarene lanthanide complexes.[5]

The ORTEP diagram of **1** which is centrosymmetric, is depicted in Fig. 1 with their selected bond lengths and bond angles. The structure shows a dimeric feature containing a four-membered Nd_2O_2 core bridging through the oxygen atoms of phenoxy groups which is structurally similar as found in complex [Nd(calix[4]H)(thf)]$_2$.[16] The two bridging oxygen atoms and two lanthanide atoms are exactly coplanar as required by the crystallographic symmetry. The central metal atom is six-coordinated by two terminal phenoxy groups and two bridging phenoxy groups from two triphenol ligands, and two THF molecules in a distorted octahedron. O(1), O(1A), O(4) and O(5) can be considered to occupy equatorial positions of the octahedron and the lanthanide center with Σ(O-Nd-O) 360.2°. O(2) and O(3A) occupy axial positions and the angle of O(2)-Nd-O(3A) is distorted away from the idealized 180° to 162°. The distance between two Nd atoms is 3.867 Å, which is slightly shorter than the value (3.933 Å) in [$Nd_2(dbp)_6(thf)_2$]•$2C_7H_8$ (dbpH=2,4-di-tert-butylphenol).[17] The average terminal Nd-O(Ar) bond length is 2.235 Å, falling in the range in previously reported literatures.[4i,18] As expected, the bridging Ln-O(Ar) bond lengths (2.379 Å) are longer than that of the average terminal one, and this feature is also found in other dinuclear lanthanide complexes.[4f,19] In these complexes, some solvent molecules THF are trapped by the bulky aromatic rings and their alphatic groups, which have been detected by X-ray analysis.

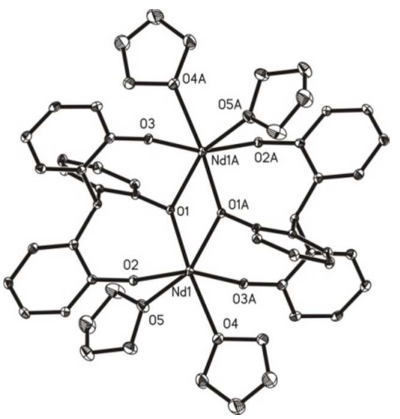


Fig. 1 X-ray structure of complex **1** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Nd-O1 2.379(2), Nd-O2 2.267(2), Nd-O3A 2.206(2), Nd-O4 2.595(2), Nd-O5 2.502(2), O1-Nd1-O1A 72.11(7), O1-Nd-O2 101.35(7), Nd1-O1-NdA 107.89(7).

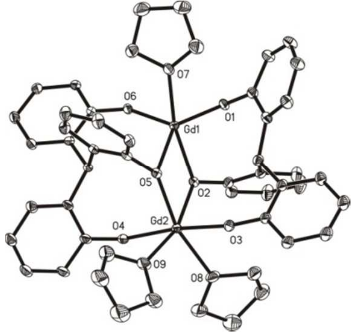


Fig. 2 X-ray structure of complex **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Gd1-O1

2.171(3), Gd1-O2 2.321(3), Gd1-O5 2.378(3), Gd1-O6 2.097(3), Gd1-O7 2.427(4), Gd2-O2 2.309(3), Gd2-O3 2.206(3), Gd2-O4 2.220(3), Gd2-O5 2.290(3), Gd2-O8 2.444(4), Gd2-O9 2.472(4) O1-Gd1-O2 82.69(11), O5-Gd1-O6 110.51(11), O5-Gd1-O2 72.69(11), O5-Gd2-O2 74.55(11), O4-Gd2-O5 94.23(12), O2-Gd2-O3 95.55(12).

The ORTEP of **2** is depicted in Fig. 2 with their selected bond lengths and bond angles. It is also a dinuclear complex containing a Gd_2O_2 core bridging through the oxygen atoms of phenoxy groups as found in complex **1**. Unlike complex **1**, complex **2** is unsymmetric with a six coordinated Gd atom and a five coordinated one. The six coordinated Gd(2) atom is coordinated by two terminal phenoxy groups, two bridging phenoxy groups and two THF molecules, the geometry of Gd(2) can be described as a distorted octahedron with O(3) and O(4) occupying the axial position. The five coordinated Gd(1) atom is coordinated by two terminal phenoxy groups, two bridging phenoxy groups and one THF molecule. The geometry of Gd(1) can be described as a distorted trigonal bipyramid with O(2) and O(7) occupying the axial position. The average Gd(2)-O distance (2.134 Å) of terminal phenoxy group is shorter than the value (2.226 Å) of Gd(1)-O. The average Gd(2)-O distance (2.300 Å) of bridging phenoxy group is slightly shorter than the value (2.350 Å) of Gd(1)-O. Like complex **1**, Gd_2O_2 core are also coplanar with ∑(O-Gd-O) 360.2°. The angle of Gd_1-O_5-Gd_2 bond is 105.7°, differentiates the Gd_1-O_2-Gd_2 bond angle of 107.0°.

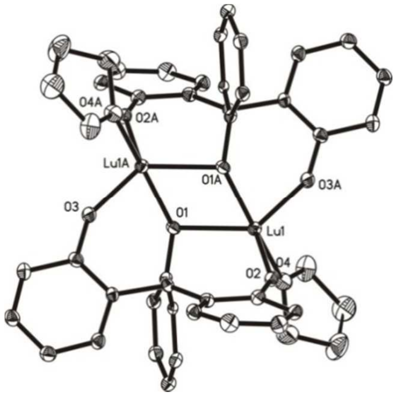


Fig. 3 X-ray structure of complex **3** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Lu1-O1 2.213(3), Lu1-O2 2.054(3), Lu1-O3A 2.050(3), Lu1-O4 2.297(3), O1-Lu1-O2 112.00(12), O1A-Lu1-O3A 88.24(12), O1-Lu1-O1A 74.41(12), Lu1-O1-LuA 105.59(12).

The ORTEP of **3** is depicted in Fig. 3 with their selected bond lengths and bond angles. It is a central symmetric dinuclear complex containing a Lu_2O_2 four member core bridging through the oxygen atoms of phenoxy groups as found in complex **1**. The metal center Lu displays five-coordinated and distorted trigonal-bipyramidal geometry, with O(4) and O(1A) occupying the axial positions. The major difference between complex **3** with the previous two complexes is that both of the Lu centers are five-coordinated for it has a smaller radius. The Lu-O length of terminal phenoxy group is 2.052 Å which is consistent with the literature.[20] The decreasing bond length from Nd-O to Lu-O is in good agreement with lanthanide contraction (the ionic radius decreases from La to Lu).

The paramagnetism of complex **1** and **2** precludes $^1H(^{13}C)$ NMR spectroscopic identification, but the solution state of complex **3** can be identified by $^1H(^{13}C)$ NMR. The resonance of the bridging methine proton occurs at 5.55 ppm and the resonance of methine carbon at 32.79 ppm. The chemical shift of the ^1H NMR spectrum moves toward upfield of the free ligand (δ 5.91 in toluene-d_8) suggesting a characteristic of agostic interaction. Another support of some agostic interactions from X-ray analysis includes that the ligand positions the central methine hydrogen proximal to Lu atom at a distance of 2.596 Å, as well as the distance of 3.496 Å between Lu and the carbon atoms, and the Lu···H-C angle of 149.5°, which are the possible parameters of agostic bond of Lu and C-H σ bond.[21] The interactions may also exist in complexes **1-2** via X-ray diffraction analysis. For complex **2** which is asymmetric, both of the methine H point towards the Gd(1) atom. The distances between the Gd atom and the carbon atoms are 3.278 and 3.403 Å respectively, and the corresponding Gd-H distance of 2.605 and 2.762 Å with Gd···H-C angle of 124.6 and 122.3°. For the larger radius Nd atom, the Nd-H distance is 2.927 Å and the distance between Nd atom and the carbon atom is 3.694 Å with the Nd···H-C angle of 135.9°. Brookhart pointed out that "the word agostic will be used to refer specifically to situation in which a hydrogen atom is covalently bonded simultaneously to both a carbon atom and a transition metal atom."[22] Agostic interactions exist in the complexes of Ti, Ta, etc. bearing the tripodal ligands and are proved by X-ray diffraction analysis, DFT calculations and NMR analysis.[7g,h,m,n]

Theoretical calculations

The interaction of C-H···Lu was investigated by DFT calculations for further understanding. With the same ligand of $\mathbf{L}H_3$, mononuclear Ta complex[7g] which had been certified bearing agostic interactions and structurally similar tetranulcear Zn complexes[7d] were calculated for comparison. The DFT structure for complex **3** is shown in Fig. 4 and comparisons of selected parameters of X-ray structures and DFT calculations are listed in Table 1. As can be seen from Table 1, the optimized DFT geometries are in good agreement with the solid state structures. The calculation of Ta complex validates the DFT calculation at B3LYP level.[7g] The calculated distance between methine H and metal is 2.797 Å for Lu, 2.268 for Ta and 2.227 for Zn, which is comparable to those X-ray structure data 2.596 for Lu, 2.131 for Ta and 2.225 for Zn. Calculated infra-red frequency shows the C-H stretch (unscaled) occurs at a higher value compared with the free ligand. It can be rationalized on the constrained cage structure around the C-H bond.[7g,n]

Table 1 Selected parameters of X-ray structures and DFT calculations with bond lengths (Å) and angles (°) for the free ligand, Lu, Ta and Zn complexes, where C* and H* denote as methine group.

Structure	Free ligand DFT	Lu DFT	Lu X-ray	Ta DFT	Ta X-ray	Zn DFT	Zn X-ray
M-O(1)		2.066	2.050	1.955	1.951	1.851	1.977
M-O(2)		2.233	2.216			1.986	1.852
M···H*		2.797	2.596	2.268	2.131	2.227	2.225
M···C*		3.725	3.496	3.327	3.156	3.145	3.098
C*-H*	1.103	1.091	1.000	1.059	1.045	1.087	1.000
M-O(1)-C		157.4	151.3	150.8	147.5	123.3	123.4
M-O(2)-C		136.7	136.0			137.4	137.7
C(1)-C*-C(2)	113.7	106.2	103.6	118.2	116.2	109.1	109.3
C(2)-C*-C(3)	113.6	119.3	117.5	118.2	121.0	114.9	115.5
C(1)-C*-C(3)	113.6	114.8	117.0	118.3	116.2	118.6	117.8
O(1)-M-H*		54.7	59.4	55.9	61.1	66.2	66.1
O(2)-M-H*		55.8	60.9			71.7	71.5
M···H*-C*		142.8	149.5	179.9	166.4	140.7	145.1
H*-C*-C(1)	104.9	106.2	105.9	97.7	87.9	105.3	104.2
H*-C*-C(2)	104.9	105.2	105.9	97.7	103.5	105.0	104.2
H*-C*-C(3)	104.9	104.0	105.9	97.7	103.5	102.5	104.1
υ(C*^{a}-H*) cm^{-1}	2962	3096		3452		3142	

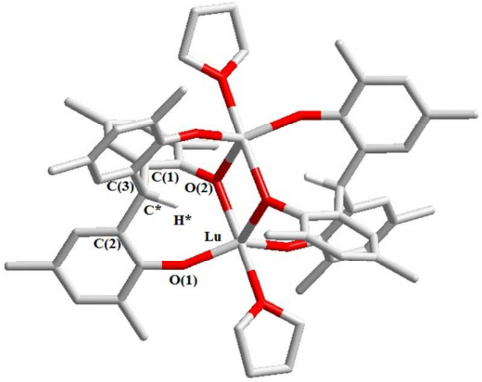


Fig. 4 DFT-optimized geometry of complex **3**.

Table 2 Comparison of calculated spectroscopic, Wiberg bond indices and NBO analysis for the C-H···M interaction.

Structure	Free ligand DFT	Lu DFT	Ta DFT	Zn DFT
H*[a] charge NBO	0.269	0.252	0.255	0.240
C* charge NBO	-0.313	-0.256	-0.277	-0.262
M charge		1.849	1.050	1.398
WBI[b] M···H*		0.018	0.050	0.025
WBI[b] C*-H*	0.861	0.862	0.818	0.853
WBI[b] M···C*		0.015	0.019	0.013
Occupancy C*-H* σ bond	1.956	1.940	1.923	1.944
Energy	-0.492	-0.465	-0.375	-0.488
Occupancy C*-H* σ* bond	0.027	0.025	0.050	0.037
Energy	0.418	0.539	0.665	0.481
E(2) CH σ to M LP*[c]		2.16	11.88	2.18
E(2) M LP to CH σ* bond[c]		22.07	3.53	1.04

[a] C* and H* denote as the methine group. [b] WBI means Wiberg bond index. [c] Most significant interaction.

A natural bonding orbital (NBO) analysis was carried out to investigate the nature of the interaction between C-H σ bond and the metal valence orbitals (Table 2). The NBO analysis gives the methine H charge as +0.252 for Lu, +0.255 for Ta and +0.240 for Zn, reduced in comparison with the free ligand as +0.269. Charges on methine C atoms are -0.256 for Lu, -0.277 for Ta and -0.262 for Zn, deviated from the free ligand of -0.313. These indicate some interaction of C-H bond with metal. The calculated average occupancy of 5d orbital on Ta is 0.53 and the energy is negative. The relative occupancy of 4s orbital on Zn is 1.98 with the energy -0.488 hartree. However, the occupancy of 5d orbital on Lu is only 0.16 with energy of 0.140 hartree. It does not support much favorable electron donation of C-H σ bond to Lu d orbital. The magnitude of the interactions E(2), the C-H σ bonding orbital to metal as 2.16 kcal mol^{-1} for Lu and 2.18 for Zn which is small compared with 11.88 for Ta. The occupancy of the C-H σ bonding NBO of the three metal complexes decreases compared with the free ligand which also reflects the donation of the C-H σ bond to the metal. It is possible for back donation of electron in metal d orbitals to the C-H σ* orbital and the magnitude of this effect is 22.07 kcal mol^{-1} for Lu, 3.53 for Ta and 1.04 for Zn. The interaction could also be reflected by the Wiberg bond order. The values of H···Ta interaction and the C-H bond are 0.050 and 0.818, respectively, indicating the electron density of C-H bond weakens and the electron density accumulates between Ta and H atoms in comparison with 0.861 for the C-H bond in free ligand. The Wiberg bond orders of H···Zn and H···Lu are comparatively small and the changes of C-H bond compared with the free ligand are negligible. The calculated data suggest strong agostic interactions of C-H···M in the Ta complex[7g] and quite weak agostic bond in the Lu and Zn complex.

Table 3 Polymerization of isoprene initiated by lanthanide complexes **1**-**3**[a].

entry	Ln complex	$\mathrm{AlR_3}$	[Ln]/[B]/[Al] (molar ratio)	temp(°C)	t (h)	yield(%)[b]	$10^{-5}M_n$	PDI[c]	microstructure[d](%)		
									cis-1,4(%)	*trans*-1,4(%)	3,4(%)
1	**1**	-	1/1/0	25	16	97	0.02	1.59		>90[e]	
2	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/0/30	25	16	0					
3	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/1/30	25	16	53	5.7	5.82	77.6	3.4	19.0
4	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/2/30	25	16	87	5.8	1.41	89.7	2.7	7.6
5	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/3/30	25	16	93	5.0	1.61	85.7	4.3	10.0
6	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/4/30	25	16	99	3.5	1.67	85.5	3.0	11.5
7	**1**	$\mathrm{AlMe_3}$	1/2/30	25	16	82	2.8	2.00	73.2	18.3	8.5
8	**1**	$\mathrm{AlEt_3}$	1/2/30	25	2	91	8.8	1.22	73.1	11.5	15.4
9	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/2/20	25	48	60	5.4	2.17	78.7	4.2	17.1
10	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/2/40	25	16	35	5.4	2.34	80.2	4.7	15.1
11	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/2/30	25	3	14	11.6	1.31	90.8	5.8	3.4
12	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/2/30	25	6	28	8.5	1.46	92.6	4	3.4
13	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/2/30	25	13	59	6.6	1.59	90.5	3.4	5.0
14	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/2/30	25	24	92	7.5	1.55	92.4	4.2	3.4
15	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/2/30	40	24	95	1.7	4.35	87.7	4.3	8
16	**1**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/2/30	50	24	91	1.7	4.15	89.1	3.3	7.6
17	**2**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/2/30	25	24	38	4.6	1.71	73.2	5.9	20.9
18	**3**	$\mathrm{Al}^i\mathrm{Bu}_3$	1/2/30	25	24	7	3.8	2.21	70.6	12.1	17.3

[a] General polymerization conditions: toluene as the sovlent (2 mL), complex **1**-**3** (10 μmol), isoprene (5 mmol). [b] Yield: (weight of polymer obtained)/(weight of monomer used). [c] Determined by GPC with respect to a polystyrene standard. [d] Determined by ^{1}H NMR and ^{13}C NMR spectroscopy in $\mathrm{CDCl_3}$. [e] The *trans*-1,4 unit is the major component.

Polymerization of isoprene

All the complexes were evaluated in the initiation of isoprene polymerization activated by $[\mathrm{Ph_3C}]^+[\mathrm{B(C_6F_5)_4}]^-$ and trialkyl aluminum. Table 3 summarizes the results of polymerization performed in toluene at various temperatures. High molecular polymers containing different *cis*-1,4, *trans*-1,4 and 3,4-polyisoprene units were obtained. The activity of these complexes was moderate and the specialty of these complexes could be found in high molecular weight polymers with relative narrow molecular weight distribution.

The catalytic system composed of complex **1** and borate (enrty 1) could initiate the *trans*-1,4 polymerization of isoprene, and the exactly same result (low molecular weight and high *trans*-1,4 content) of the polymerization initiated by borate alone[11c] indicating that complex **1** was the spectator in the polymerization without participating of aluminum alkyls. The alkylated lanthanide metal center without borate was inactive toward isoprene polymerization (entry 2), suggesting that the generation of a cationic Nd alkyl species was essential for isoprene polymerization. The amount of activator $[\mathrm{Ph_3C}]^+[\mathrm{B(C_6F_5)_4}]^-$ exerted much influence on the activity and selectivity of the polymerization (entries 3-6). The polymerization data of entry 3 were typical of a poorly controlled process with 1 equiv of activator. However, when 2 equiv of activator was added, the performance of activity and selectivity improved much along with very high molecular weight and quite narrow dispersities. Increasing amount of activator facilitated the polymerization of isoprene and moderate activity and the highest *cis*-1,4 selectivity were achieved by adding 2 equiv of activator.

Various aluminum alkyls had been tested to the ternary catalytic system. $\mathrm{AlR_3}$ types and the aluminum to lanthanide molar ratio significantly influenced the activity and selectivity. $\mathrm{AlMe_3}$ and $\mathrm{Al}^i\mathrm{Bu}_3$ showed similar activities but differentiated in selectivity for *cis*-1,4 unit of the polyisoprenes. When $\mathrm{Al}^i\mathrm{Bu}_3$ was replaced by $\mathrm{AlEt_3}$, the activity of complex **1** raised with the yield achieving 91% within 2 h and the value of molecular weight distribution decreased to 1.22 (entry 8). However, the selectivity for *cis*-1,4 unit decreased to 73.1%, far below that cocatalyzed with $\mathrm{Al}^i\mathrm{Bu}_3$. The **1**/$\mathrm{Al}^i\mathrm{Bu}_3$/borate catalytic system appeared to be less successful in less or excess than 30 equiv of aluminum alkyl.

The GPC curves of the polyisoprenes obtained at 25 °C were all unimodal with moderate molecular weight distribution, consistent with the predominance of a homogeneous single-site catalytic species. However, the GPC curves of the polymers obtained above room temperature (entries 15,16) became bimodal which suggested the unstability of the cationic alkyl species generated at higher temperatures. With time extending, the yield of polyisoprene increased, but the molecular weight decreased and the molecular weight distribution widened, and this phenomenon might attribute to the chain transfer in polymerization. Besides the types of cocatalysts, the metal center also played a vital role in the catalytic performances. The highest *cis*-1,4 selectivity was observed by Nd catalytic system (*cis*-1,4 content: 92.6%). For the smaller metallic radii Gd and Lu complexes, the activity and selectivity decreased with the decreasing value of the metal radius in the order Nd > Gd> Lu.

Conclusions

A series of lanthanide complexes supported by carbon bridged triphenol ligand are synthesized and their structural features have been characterized by X-ray diffraction. The structures of complex **1** and **3** are centrosymmetric. With the contraction of the metal radius (Nd > Gd > Lu), the coordination number around the metal center reduces. The smallest metal radius Lu complex is five-coordinated. Results of DFT calculations show agostic interaction between the metal center Lu and H are quite weak compared with that in transition-metal complexes (Ti, Zn) which bear the same ligand. Nd and Gd complexes can also be assumed to bear the agostic interaction. Complexes **1**-**3** exhibit moderate activity towards isoprene polymerization coactivated by $[Ph_3C]^+[B(C_6F_5)_4]^-$ and aluminum alkyls. Nd complex with the largest metal radius among the three shows a good activity and selectivity for *cis*-1,4 unit. The results may provide new insights into the design of lanthanide complexes.

Experimental Section

General Procedures.

All manipulations were performed under argon using standard Schlenk techniques. THF, hexane and toluene were distilled from sodium benzophenone ketyl before use. Anhydrous lanthanide trichlorides were prepared according to the literature procedures.[23] The other reagents were commercial available and used without further purification. Lanthanide analyses were performed by EDTA titration with xylenol orange indicator and hexamine buffer. Carbon, hydrogen and nitrogen analyses were performed by direct combustion with a Flash EA-1112 instrument. NMR spectra were recorded on a Bruker Avance DMX 400 spectrometer or Agilent 600 MHz Direct Drive 2. Molecular weight and molecular weight distribution were measured by size exclusion chromatograph equipped with RI (Waters 2414) detector and a Waters 1525 isocratic high performance liquid chromatography pump at 40 °C with THF as the eluent at a flow rate of 1.0 mL/min.

Synthesis of $\mathbf{LNa_3}$. LH_3 (2.5 g, 4 mmol) was dissolved in 40 mL THF and then excess sodium metal was added at room temperature. After stirring at room temperature for 12 h, white precipitate formed and the reaction mixture turned to be slurry. The precipitate was filtrated and stored in argon. The product was characterized by ^1H NMR to make sure the successful synthesis of **L**Na_3. ^1H NMR(600 MHz, toluene-d_8) δ 8.35(3H, d, Ar-H), 8,27(1H, s, C-H), 7.26(3H, d, Ar-H), 3.13(12H, t, THF), 1.52(27H, s, tBu), 1.36(27H, s, tBu), 1.30(12H, m, THF); ^{13}C NMR δ 162.63(O-Ar), 137.34(tBu-Ar), 134.83(tBu-Ar), 133.70(C-Ar), 127.65(H-Ar), 122.01(H-Ar), 68.20(THF), 35.83(-*C*(CH3)3), 35.01(-*C*(CH3)3), 33.04(-C(CH_3)$_3$), 31.45(-C(CH_3)$_3$), 28.83(*C*-H), 25.96(THF).

Synthesis of $\mathbf{Nd_2(L)_2(THF)_4}$ (1). **L**Na_3 was added to the slurry of $NdCl_3$ (1 g, 4 mmol) in THF (40 mL) at room temperature. This mixture were sealed and stirred at 70°C for 3 days. NaCl was filtered off. The solution was concentrated and blue crystals were obtained at room temperature in two days. (3.00 g, 72%). Found: C, 67.20; H, 8.61; Nd, 13.24. C118H186Nd2O14 requires C, 66.94; H, 8.85; Nd, 13.63.

Synthesis of $\mathbf{Gd_2(L)_2(THF)_3}$ (2). The synthesis of complex **2** was carried out in the same way as that described for complex **1**, but $GdCl_3$ (1.11 g, 4.2 mmol) was used instead of $NdCl_3$. Colourless block crystals were isolated from the concentrated THF solution at room temperature. (3.1 g, 83%). Found: C, 65.72; H, 8.46; Gd, 18.04. C98H146Gd2O9 requires C, 66.03; H, 8.25; Gd, 17.64.

Synthesis of $\mathbf{Lu_2(L)_2(THF)_2}$(3). The synthesis of complex **3** was carried out in the same way as that described for complex **1**, but $LuCl_3$ (0.98 g, 3.5 mmol) was used instead of $NdCl_3$. Block crystals were isolated from the concentrated THF solution at room temperature. (2.4 g, 79%). ^1H NMR(600 MHz, toluene-d_8) δ 7.61(4H, s, Ar-H), 7.45(4H, s, Ar-H), 7.34(2H, s, Ar-H), 6.53(2H, s, Ar-H), 5.55(2H, s, C-H), 3.61(8H, t, THF), 1.61(36H, s, tBu), 1.53(18H, s, tBu), 1.40(36H, s, tBu), 1.30(8H, s, THF), 1.22(18H, s, tBu); ^{13}C NMR δ 151.92(O-Ar), 144.15(tBu-Ar), 138.21(tBu-Ar), 126.79(C-Ar), 124.72(H-Ar), 124.22(H-Ar), 69.80(THF), 43.00(*C*-H), 36.03(-*C*(CH3)3), 35.76(-*C*(CH3)3), 34.95(-*C*(CH3)3), 34.91(-*C*(CH3)3), 32.49(-C(CH_3)$_3$), 31.97(-C(CH_3)$_3$), 30.85(-C(CH_3)$_3$), 30.45(-C(CH_3)$_3$), 25.92(THF). Found: C, 64.76; H, 8.28; Lu, 19.46. C94H138Lu2O8 requires C, 64.66; H, 7.97; Lu, 20.04.

Typical Procedure for Isoprene Polymerization. A toluene solution (1 mL) of complex **1** (10 μmol, 0.021g) and Al^iBu_3 (300 μmol) were placed in a 20 mL flask, and then aged at 60 °C for 2 h. After aging, a toluene solution (1 mL) of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (20 μmol, 0.018g) and isoprene (5 mmol, 0.34 g) was added. The mixture was magnetically stirred at 25°C. The polymerization was quenched by addition of excess ethanol containing 5% 2,6-di-*tert*-butyl-4-methylphenol. The white-off precipitate was dried under vacuum and weighed.

X-Ray crystallography. Suitable crystals of **1**-**3** and **L**Na_3 were sealed in liquid paraffin oil. Data collections for the crystals of compound were performed on a CrysAlisPro, Oxford Diffraction Ltd. using graphite-monochromatic Mo-Kα radiation (λ= 0.71073 Å) at the temperature shown in Table 4. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. All structures were solved by direct methods, and refined by full-matrix least-square methods with the SHELX-97 programs. The contribution of the disordered THF in all these complexes was removed by PLATON/SQUEEZ program. All non-hydrogen atoms including solvent molecules were located successfully from Fourier maps and were refined anisotropically. Crystal and refinement data for complexes **1**-**3** and **L**Na_3 are given in Table 4.

Computational details. All geometries were optimized at the B3LYP level utilizing the Stuttgart/Dresden (SDD) pseudopotentials and basis set for Lu and Ta atoms and the 6-31G(d,p) for the other elements. The *tert*-butyl groups on the ligands were replaced by methyl groups to save the calculation cost without affecting the coordination environment of the metals. Vibrational frequency calculations confirmed the minima of all geometries without imaginary frequencies and gave all real frequency values. All calculations including the natural bonding orbital (NBO) analyses were carried out using Gaussian 03 package.[24]

Table 4 Crystallographic data for complexes **1**-**3** and **L**Na_3.

Compound reference	**1**	**2**	**3**	**LNa$_3$**
Chemical formula	$C_{102}H_{154}Nd_2O_{10}$•4(C4H8O)	$C_{98}H_{146}Gd_2O_9$	$C_{94}H_{138}Lu_2O_8$	$C_{110}H_{170}Na_6O_{12}$•2(C_4H_8O)
Formula Mass	2117.15	1782.65	1745.98	1966.61
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	14.0035(4)	50.4714(11)	14.4829(4)	14.2943(5)
b/ Å	19.2561(7)	17.9307(5)	18.0577(5)	18.2621(4)
c/ Å	24.5571(6)	29.1703(6)	21.7071(7)	21.6621(5)
α/°	90.00	90.00	90.00	90.00
β/°	122.730(2)	112.425(3)	89.676(3)	93.795(3)
γ/°	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	5570.5(3)	24402.6(10)	5676.9(3)	5642.4(3)
Temperature/K	406(2)	140(2)	170(2)	140(2)
Space group	*P*21/*c*	*C*2/*c*	*P*21/*n*	*P*21/*n*
No. of formula units per unit cell, *Z*	2	8	2	2
Absorption coefficient, μ/mm^{-1}	0.981	1.118	1.770	0.093
No. of reflections measured	22824	47029	23674	22519
R_{int}	0.0262	0.0248	0.0385	0.0308
Final R_1 values ($I > 2\sigma(I)$)	0.0339	0.0505	0.0434	0.0542
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0738	0.1492	0.1158	0.1351
Final R_1 values (all data)	0.0479	0.0646	0.0625	0.0784
Final $wR(F^2)$ values (all data)	0.0826	0.1582	0.1268	0.1519
Goodness of fit on F2	1.069	1.074	1.065	1.033
CCDC number	969246	969247	969248	969249

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Lanthanide complexes supported by carbon bridged triphenolate ligand were synthesized and theoretical calculations were carried out on Lu complex.