# **ORGANOMETALLICS**

# Di- and Triphenylacetates of Lanthanum and Neodymium. Synthesis, Structural Diversity, and Application in Diene Polymerization

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**Supporting Information** 

**ABSTRACT:** A new family of lanthanide complexes with diand triphenylacetate ligands was prepared from LnCl<sub>3</sub>. Dimeric diphenylacetates were the only isolated products of the reaction between LnCl<sub>3</sub> (Ln = La, Nd) and Ph<sub>2</sub>CHCOONa. The exchange reaction between LnCl<sub>3</sub> and Ph<sub>3</sub>CCOONa led to the formation of three structurally different types of neodymium and lanthanum complexes under different reaction conditions. Various coordination modes of the carboxylate ligands were revealed, including  $\kappa^2$ - and  $\kappa^1$ -terminal coordination,  $\mu_2$ - $\kappa^1$ : $\kappa^1$ -bridging, and  $\mu_2$ - $\kappa^1$ : $\kappa^2$ -semibridging. The treatment of La and Nd tris-triphenylacetates with excess AlEt<sub>3</sub> produces the dimeric tetraethylaluminates [Ln<sub>2</sub>(( $\mu_2$ - $\kappa^1$ : $\kappa^1$ -



 $Ph_3CCOO)_4(AlEt_4)_2]$ . The structures of the key La and Nd triphenylacetates that were obtained from these reactions were verified by X-ray diffraction, and the complex  $[(THF)_4Nd_2(Ph_2CHCOO)_2(\mu_2 - \kappa^1 \cdot \kappa^2 - Ph_2CHCOO)_2(\mu_2 - \kappa^1 \cdot \kappa^1 - Ph_2CHCOO)_2]$  was studied by high-resolution X-ray diffraction. Neodymium di- and triphenylacetate complexes can serve as precursors of catalysts for butadiene and isoprene stereospecific 1,4-cis polymerization.

#### INTRODUCTION

The most important application of lanthanide compounds in homogeneous catalysis is the use of organic neodymium carboxylates and phosphates as precatalysts in the 1,4-cis polymerization of butadiene.<sup>1</sup> In the past decade, several types of rare-earth complexes with different types of ligands demonstrating high cis-1,4 selectivity (over 99%) for butadiene and isoprene polymerization have been described in the literature.<sup>1b-i</sup> However, as shown in Scheme 1, the precatalysts that are most frequently used for this process are saltlike neodymium carboxylates, such as neodymium versatate (NdV;<sup>2</sup> a mixture of isomers of different  $\alpha,\alpha$ -disubstituted ( $\alpha,\alpha$ dialkylated) decanoic acids that is also referred to as neodymium neodecanoate)<sup>1a</sup> (A), and neodymium tris[bis(2ethylhexyl) phosphate] (NdP) (B).<sup>3-5</sup>

Surprisingly, although neodymium catalysts have been extensively used in industry, both the polymerization mechanism and the nature of the catalytically active intermediates for these compounds remain uncharacterized. The main cause of this phenomenon is a dearth of information about the structures of both of the species that are directly involved in the catalytic cycle and the precursors to these species, including the starting tricarboxylate and triphosphate compounds. The use of low-symmetry lipophilic anions causes neodymium derivatives to be soluble in hydrocarbons, facilitating efficient polymerization processes.<sup>1a</sup> However, due to the high electronic and steric unsaturation of the neodymium ions in various compounds, such as NdV and NdP, these neodymium derivatives form oligomers of uncertain composition because of the coordination of these neodymium ions with the oxygen atoms of neighboring molecules.<sup>6,7</sup>

Little data are available from the literature regarding the structure of carboxylate precatalysts in solution. Kwag demonstrated that NdV typically exists in oligomers of variable composition; moreover, he successfully used an additional 1 equiv of carboxylic acid to prepare a monomeric neodymium tris-neodecanoate adduct. This monomeric complex demonstrated a productivity that was nearly 10 times higher than the productivity of the standard neodymium tris-neodecanoate for

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Scheme 2



butadiene polymerization.<sup>7</sup> Anwander synthesized certain individual lanthanide carboxylates by using bulky and structurally rigid anions that were based on ortho-disubstituted benzoic acids.<sup>8,9</sup> He isolated individual lanthanide carboxylates and was able to unambiguously characterize several products that were formed by the alkylation of these carboxylates with trimethylaluminium. This finding considerably contributed to our understanding of neodymium catalysis in diene polymerization. However, there is a considerable difference between substituted lanthanide benzoates and complexes that are based on  $\alpha$ -branched carboxylic acids; thus, it is difficult to compare these types of benzoates with neodymium versatates. Evans studied lanthanum and neodymium 2-phenyl- and 2,2dimethylbutyrates and their interactions with organoaluminum compounds.<sup>10,11</sup> Unfortunately, these compounds turned out to be too labile for isolation of heterometallic lanthanidealuminum complexes representing the active intermediates in the catalytic systems for diene polymerization.

In the present study, we suggested that the introduction of structurally rigid phenyl groups into the  $\alpha$ -position of the carboxylate ligand would be favorable for the isolation of various lanthanide carboxylates in crystalline form. With this in mind, we undertook the synthesis of **C**, lanthanide di- and triphenylacetates, which are close analogues of NdV. Surprisingly, we found that the synthesis of lanthanum and neodymium carboxylate complexes is accompanied by the formation of several types of compounds; we were able to isolate and characterize most of these compounds. This paper focuses on the synthesis of these compounds, the investigation of certain products formed from their reactions with triethylaluminum, and preliminary data addressing their applications for stereospecific butadiene and isoprene polymerization.

#### RESULTS AND DISCUSSION

Synthesis of Lanthanide Carboxylates. Lanthanide Diphenylacetates. Reactions of methanol solution of  $LnCl_3(THF)_x$  (Ln = La, Nd) with 3 equiv of sodium diphenylacetate, which was generated in situ from diphenylacetic acid and CH<sub>3</sub>ONa, resulted in white (for La) or light blue (for Nd) precipitates, which were extracted with dry THF.

The standard workup procedure produced corresponding carboxylates with the general formula of  $[Ln-(Ph_2CHCOO)_3(THF)_2]_2$  for Ln = La (1), Nd (2). Both of these compounds were isolated as powders that were soluble in THF and moderately soluble in chloroform and toluene (Scheme 2).



**Figure 1.** General view of the complexes 1 (Ln = La, Solv = THF), 2 (Ln = Nd, Solv = THF), and **2b** (Ln = Nd, Solv = dioxane) with atoms shown as thermal ellipsoids (p = 50%). Hydrogen atoms and carbon atoms of the phenyl groups and solvate molecules of these complexes are omitted for clarity.

The methanol adduct  $[Ln(Ph_2CHCOO)_3(CH_3OH)_n]$  is most likely formed as the primary product of the reaction of  $LnCl_3(THF)_x$  with sodium diphenylacetate in methanol. However, we were unable to isolate this compound and characterize it because it could not be separated from NaCl. This problem was circumvented through the use of diethylamine instead of CH<sub>3</sub>ONa as a base, allowing for the isolation of methanol adduct **2a**, which could easily be separated from the THF-soluble  $[Et_2NH_2]^+CI^-$ . According to the analytical data, complex **2a** corresponded to the formula

#### Scheme 3



Table 1. Selected Bond Distances (Å) in Compounds 1, 2, 2b, 7a, and 8a

	1 (La)	<b>2</b> (Nd)	<b>2b</b> (Nd)	7 <b>a</b> (La)	8a (Nd)
Ln–O (THF, dioxane, DME)	2.619(3), 2.647(3)	2.575(1), 2.606(1)	2.6064(9), 2.550(1)	2.620(1), 2.670(1)	2.567(3), 2.609(3)
Ln–O ( $\kappa^2$ -RCOO)	2.605(3)-2.537(3)	2.552(1) - 2.476(2)	2.5036(9)-2.504(1)	2.516(1), 2.544(1)	2.432(3) - 2.532(3)
Ln–O ( $\mu_2$ - $\kappa^1$ : $\kappa^2$ -RCOO)	2.717(3), 2.586(3), 2.470(3)	2.714(1), 2.398(1), 2.500(1)	2.6263(9), 2.4105(9), 2.4967(9)		
Ln–O ( $\mu_2$ - $\kappa^1$ : $\kappa^1$ -RCOO)	2.444(3), 2.468(3)	2.403(1), 2.390(1)	2.416(1), 2.4192(9)	2.431(1) - 2.475(1)	2.362(3) - 2.417(3)
LnLn	4.1434(8)	4.0796(3)	4.0546(1)	4.428(1)	4.379(1)

 $[Nd_2(Ph_2CHCOO)_6(CH_3OH)_5]_{x^*}$  The recrystallization of **2a** from THF produces compound **2** (Scheme 2).

The <sup>1</sup>H NMR spectra of compounds 1 and 2 consist of signals from methine protons of the  $Ph_2CH$  groups and from the phenyl protons, which are broadened in the case of 2. Because all of the spectra were nearly uninformative about the structures of these complexes, X-ray crystallography was used to determine these structures (Figure 1 and Table 1). Compounds 1 and 2 appeared to be isostructural binuclear complexes that possessed a "Chinese lantern" structure with both bridging and terminal carboxylate ligands (see Structural Studies for additional details).

Lanthanide Triphenylacetates. A similar synthetic approach was applied to obtain triphenylacetates of La and Nd from the starting material of LnCl<sub>3</sub>(THF)<sub>x</sub>. In contrast to **1** and **2**, triphenylacetates of La and Nd are moderately soluble in methanol. The solubility of these compounds was sufficient to isolate and characterize the primary products of this reaction, which were the methanol adducts of the mononuclear carboxylate complexes [Ln( $\kappa^2$ -Ph\_3CCOO)\_2( $\kappa^1$ -Ph\_3CCOO)-(CH<sub>3</sub>OH)\_4] for Ln = La (**3**), Nd (**4**) (Scheme 3). The structures of **3** and **4** were resolved by X-ray crystallography (Figure 2 and Table 2) (see Structural Studies for additional details).

The subsequent treatment of 3 and 4 with THF led to the formation of the THF adducts 5 and 6, respectively (Scheme 3). These compounds represent mononuclear complexes with three  $\kappa^2$ -coordinated carboxylate ligands [Ln( $\kappa^2$ -



**Figure 2.** General view of the complexes **3** (Ln = La) and **4** (Ln = Nd) with atoms shown as thermal ellipsoids (p = 50%). Hydrogen atoms have been omitted for clarity.

 $Ph_3CCOO_3(THF)_3$  for Ln = La (5), Nd (6) (Figure 3 and Table 2) (see Structural Studies for additional details).

Heating under vacuum caused complexes 5 and 6 to readily lose THF, producing compounds of composition [Ln-(Ph<sub>3</sub>CCOO)<sub>3</sub>(THF)<sub>2</sub>]<sub>x</sub> for Ln = La (7), Nd (8). Presumably, complexes 7 and 8 possess a dimeric or oligomeric nature. This perspective is somewhat supported by the fact that the recrystallization of either 5 and 6 or 7 and 8 from DME generated the binuclear DME adducts [Ln-(Ph<sub>3</sub>CCOO)<sub>3</sub>(DME)]<sub>2</sub> for Ln = La (7a), Nd (8a) (Scheme 3, Figure 4, and Table 1).

<sup>1</sup>H NMR spectra of **5** and **6** that were obtained in toluene- $d_8$  and chloroform-d were nearly uninformative, due to the broadening of the signals that were assigned to the phenyl group protons. This broadening was even observed in the case of **5**, a diamagnetic compound, and apparently reflected the loss of coordinated THF molecules and the formation of oligomeric species that were similar to 7 and **8** which had nonequivalent Ph<sub>3</sub>C- groups. A spectrum of **5** that was obtained in THF- $d_8$  displayed three well-resolved phenyl group signals, confirming this hypothesis.

We found that the byproducts that are formed in the reaction of La and Nd chlorides with sodium triphenylacetate are the unusual ate complexes **9** and **10** that contain five carboxylate moieties, including a free acid molecule, and a sodium cation (Scheme 3). Interestingly, from the starting materials of La chloride and Nd chloride, the appropriate stoichiometry can be used to generate compounds **9** and **10**, respectively, with yields of 61 and 81%, respectively. If La and Nd chlorides react with an excess of sodium triphenylacetate in the presence of DME,



**Figure 3.** General view of one of the independent molecules of the complex **6** with atoms shown as thermal ellipsoids (p = 50%). Hydrogen atoms and carbon atoms of the phenyl groups and THF solvate species have been omitted for clarity.



**Figure 4.** General view of the complexes 7a (Ln = La) and 8a (Ln = Nd) with atoms shown as thermal ellipsoids (p = 50%). Hydrogen atoms and carbon atoms of the phenyl groups are omitted for clarity. Although the complex 8a corresponds to a  $C_1$  point group in the crystal, the distribution of bond lengths is rather similar to those in a centrosymmetric arrangement, as in 7a.

another ate complex containing four carboxylate moieties (11) is formed. The molecular structures of compounds 9-11 were determined by X-ray diffraction studies (Figures 5 and 6 and Table 3; see Structural Studies for additional details).

Table 2. Selected Bond Distances	s (Å) ir	n Complexes	3, 4,	and	6
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3 (La)	4 (Nd)	<b>6</b> (Nd) <sup><i>a</i></sup>
2.514(2) (O(1C))	2.4501(14) (O(1C))	2.541(3)-2.569(3)
2.568(2) (O(2C))	2.5207(14) (O(2C))	
2.5650(2) (O(3C))	2.5016(14) (O(3C))	
2.619(2) (O(4C))	2.5558(15) (O(4C))	
2.438(2)	2.388(1)	
2.546(2) - 2.613(2)	2.490(1) - 2.556(1)	2.441(3) - 2.484(3)
	$\begin{array}{c} 3 (La) \\ 2.514(2) (O(1C)) \\ 2.568(2) (O(2C)) \\ 2.5650(2) (O(3C)) \\ 2.619(2) (O(4C)) \\ 2.438(2) \\ 2.546(2) - 2.613(2) \end{array}$	3 (La)         4 (Nd)           2.514(2) (O(1C))         2.4501(14) (O(1C))           2.568(2) (O(2C))         2.5207(14) (O(2C))           2.5650(2) (O(3C))         2.5016(14) (O(3C))           2.619(2) (O(4C))         2.5558(15) (O(4C))           2.438(2)         2.388(1)           2.546(2)-2.613(2)         2.490(1)-2.556(1)

<sup>*a*</sup>The bond lengths are given for only one of the three independent molecules in 6.



**Figure 5.** General view of the complexes **9** (Ln = La) and **10** (Ln = Nd) with atoms shown as thermal ellipsoids (p = 50%). Hydrogen atoms, carbon atoms of the phenyl groups, and solvate molecules are omitted for clarity.



Figure 6. General view of the complex 11 with atoms shown as thermal ellipsoids (p = 50%). Hydrogen atoms and atoms of the phenyl groups are omitted for clarity.

Thus, we demonstrated that the reaction of  $LnCl_3(THF)_x$ and sodium triphenylacetate generates a series of products, including mononuclear, binuclear homobimetallic, and various ate complexes; the product ratio is controlled by the solvent and the reactant ratio that are utilized. In this series of transformations, the mononuclear lanthanide complex is the primary product, and it is subsequently converted to a binuclear or ate complex. Because we used the bulky and structurally rigid triphenylacetate ligand, we were able to isolate and reliably characterize the broad range of carboxylates that were formed. Presumably, similar processes may also occur for other carboxylates, including the well-known neodymium versatates. However, the impossibility of isolating these compounds in a pure state precludes their characterization.

**Reactions with Organoaluminum Compounds.** The reaction of neodymium carboxylates with trialkylaluminum followed by reaction with alkylaluminum chlorides is the most frequently used approach for obtaining a ternary catalyst system for stereospecific diene polymerization.<sup>1a</sup> In this work, we studied the first stage of this process: namely, the reaction of

Table 3. Selected Bond Distances (Å) for Complexes 9-11 and 11a

	9 (La)	10 (Nd)	11 (La)	<b>11a</b> (La)
Ln–O (THF, DME)	2.654(2), 2.584(2)	2.604(2), 2.543(2)	2.625(2), 2.656(2)	2.638(2), 2.632(2)
Ln–O (terminal Ph <sub>3</sub> CCOO <sup>–</sup> )	2.522(2), 2.557(2)	2.465(2), 2.497(2)	2.564(2), 2.526(2)	2.540(2), 2.574(2)
Ln-O ( $\mu_2$ - $\kappa^1$ - $\kappa^2$ - Ph <sub>3</sub> CCOO <sup>-</sup> )				
Ln-O	2.516(2), 2.545(2)	2.461(2), 2.490(2)	2.468(2), 2.580(2)	2.542(2), 2.538(2)
Ln–O (Na)	2.580(2), 2.598(2)	2.540(2), 2.564(2)	2.708(2), 2.597(2)	2.628(2), 2.598(2)
Ln-O $(\mu_2 - \kappa^1 - \kappa^1 - Ph_3CCOO^-)$	2.519(2)	2.445(2)	2.397(2)	2.425(2)
Na−O (THF, DME)	2.278(3)	2.273(2)	2.398(3), 2.310(3)	2.316(2), 2.392(2)
Na-O ( $\mu_2$ - $\kappa^1$ - $\kappa^1$ -Ph <sub>3</sub> CCOO <sup>-</sup> )	2.296(2)	2.293(2)	2.280(3)	2.272(2)
Na-O ( $\mu_2$ - $\kappa^1$ - $\kappa^2$ - Ph <sub>3</sub> CCOO <sup>-</sup> )	2.298(2), 2.344(2)	2.274(2,) 2.332(2)	2.279(3), 2.336(3)	2.282(2), 2.303(2)
Na-O (Ph <sub>3</sub> CCOOH)	2.354(2)	2.341(2)		
LnNa	3.810(2)	3.792(2)	3.782(2)	3.803(2)

Nd triphenylacetates with triethylaluminum. We revealed that the treatment of **6** with excess of AlEt<sub>3</sub> at a 1:5 reactant ratio in toluene generated a pale greenish yellow solution from which extremely moisture- and air-sensitive pale blue crystals of  $[Nd_2(Ph_3CCOO)_4(AlEt_4)_2]$  (13) were isolated after the addition of hexanes. Similar reactions of AlEt<sub>3</sub> with the oligomeric compound **8** and the ate complex **10** also produced compound **13** (Scheme 4).

It would be particularly interesting to isolate the product of the reaction of the complex **6** with  $Al(i-Bu)_3$ , because this reaction takes place at the first phase of the catalyst system preparation. Nevertheless, reactions of **5** and **6** with excess  $Al(i-Bu)_3$  gave mixtures of compounds. All of the attempts to separate these mixtures or to crystallize at least one individual compound failed, probably due to the low stability of the heterometallic lanthanide—aluminum complexes with a bridging isobutyl ligand or the high solubility of these complexes.

The structure of **13** was resolved by X-ray diffraction (Figure 7 and Table 4; see Structural Studies for additional details).

Complex 13 is composed of a dineodymium core and contains four bridging carboxylate ligands that bear two  $[AlEt_4]^-$  moieties; *i.e.*, it is the product of the formal substitution of two  $[AlEt_4]^-$  anions for two terminal carboxylate ligands in the dimeric complex 8. In this instance, two tetraethylaluminate anions are  $\eta^3$ -coordinated to the neodymium, causing the ethyl groups of  $[AlEt_4]^-$  to be nonequivalent.

To assess whether this type of coordination environment remains unchanged in a toluene solution, the diamagnetic lanthanum analogue 12 was synthesized. This compound appeared to be isostructural with 13 (see Structural Studies for additional details). NMR studies of 12 in toluene solution demonstrated that all of the ethyl groups of this compound are equivalent on an NMR time scale; this equivalence likely reflects a fast exchange process or solvation effects.

Two notable points exist with respect to the formation of 8. First, this compound is formed not only from binuclear precursors but also from mononuclear compounds 6 and 12, indicating that this binuclear structure is rather stable. Therefore, a compound of type 13 can indeed be a prototype

#### Scheme 4





Figure 7. General view of the complexes 12 (La) and 13 (Nd) with atoms shown as thermal ellipsoids (p = 50%). Hydrogen atoms and atoms of the phenyl groups are omitted for clarity.

of the intermediate formed during the reaction of neodymium versatate with certain trialkylaluminum derivatives. The yield of the product that is formed upon the monosubstitution of carboxylate for aluminate appears to be surprisingly high (greater than 50%), assuming that an excess of AlEt<sub>3</sub> is used. It appears that the structure of type **13** is kinetically stable due to the presence of bulky triphenylacetate bridging ligands, causing the further replacement of carboxylate ligands by aluminate groups to be a complicated process. This characteristic may produce adverse effects on the formation of catalytically active species in diene polymerization, given that these species are believed to result from the double replacement of carboxylate by aluminate.<sup>1a,6</sup>

The reaction of **6** with  $Et_3Al$  followed by treatment with  $Et_2AlCl$  produced a mixture of compounds that gave a viscous oil after the evaporation of the solvent. All of the attempts to separate any of the Nd-containing products failed; instead, the only compound that was isolated by crystallization from a hexane/toluene mixture and subsequently characterized by X-ray diffraction studies was compound **14**, diethylaluminum triphenylacetate (Figure 8).

Application of Neodymium Di- snd Triphenylacetates for Butadiene Polymerization in Ternary Catalyst Systems. We tested several of the compounds that were obtained in this work as potential precatalysts of butadiene and

Table 4. Selected Bond Distances (Å) in Compounds 12 and 13

	<b>12</b> (La)	13 (Nd)
Ln–O ( $\mu_2$ - $\kappa^1$ - $\kappa^1$ -Ph <sub>3</sub> CCOO <sup>-</sup> )	2.363(1)-2.419(1)	2.310(2)-2.379(2)
$Ln-C(C_2H_5)$	2.823(2) - 3.044(2)	2.768(4)-3.044(3)
Ln…Al	2.9960(7)-3.0172(6)	2.975(1)-2.944(1)
Al–C $(C_2H_5)$	1.971(2)-1.979(2) (noncoordinated), 2.027(2)-2.069(2) (coordinated)	1.972(4)-1.984(3) (noncoordinated), 2.023(3)-2.066(4) (coordinated)



**Figure 8.** General view of 14 with atoms shown as thermal ellipsoids (p = 50%). Hydrogen atoms are omitted for clarity.

isoprene polymerization (Table 5). Neodymium complexes 2, 6, and 13 demonstrated good performance for both butadiene and isoprene polymerization. Complex 1 appeared to be virtually inactive in this role; this result was unsurprising, because La derivatives are typically less active than Nd complexes.<sup>1</sup> Compound 2 appeared to be active for both 1,3-butadiene and isoprene polymerization (as evidenced by runs 3, 4, 9, and 10). The low activity of 2a was apparently caused by its coordinated methanol, which could destroy organo-aluminum cocatalysts and lead to the formation of oligomeric Nd alkoxides.

In comparison with compound **6**, which bears bulky triphenylacetate ligands, compound **2**, which is less sterically hindered, consistently demonstrated higher activity (as evidenced by the comparison of runs 2 and 3 to runs 4 and 5). The polydispersity index of polybutadiene that was obtained with a diphenylacetate-based catalyst system was lower than the polydispersity index of polybutadiene that was produced by triphenylacetate derivatives. It appears that, in the sterically crowded neodymium triphenylacetate complex, the exchange rate between carboxylate and alkylaluminate ligands is low, favoring the simultaneous formation of several structurally different catalytically active species.

As the heterometallic Ln–Al complexes were isolated only in the reaction of La and Nd triphenylacetates with AlEt<sub>3</sub>, not in the case of Al(i-Bu)<sub>3</sub>, it was necessary to make sure that the catalytic system formed using AlEt<sub>3</sub> instead of Al(i-Bu)<sub>3</sub> would be active in the diene polymerization. The complex **6** with AlEt<sub>3</sub> cocatalyst (runs 7 and 11) demonstrated relatively low activity in the polymerization of butadiene and isoprene. Polymers that were obtained in these experiments had high polydispersity indexes (runs 7 and 11) and low cis-1,4 selectivity for butadiene polymerization (run 7).

It was also interesting to compare the catalytic performances of compounds **6** and **13** as precatalysts. **13** demonstrated slightly higher activity than **6** (run 8 versus run 6; Table 5), and the polybutadiene that was obtained with **13** had a significantly higher  $M_w$  and lower polydispersity index than the polybutadiene that was obtained with **6**. Presumably, complexes similar to **13** might be responsible for the formation of the high-molecular-weight fraction in the polymerization of butadiene that occurs through ternary catalyst systems. The detailed results from a thorough investigation of this phenomenon will be described and discussed in a separate contribution.

**Structural Studies.** Diphenylacetate complexes 1, 2, and 2b are similar (1 and 2 are isomorphous) in that all of these complexes contain centrosymmetric  $Ln_2(RCOO)_4$  dimer units with four bridging carboxylates (two  $\mu_2$ - $\kappa^1$ - $\kappa^2$  and two  $\mu_2$ - $\kappa^1$ - $\kappa^1$  Ph<sub>2</sub>CHCOO- ligands), two terminal carboxylates, and terminal O-donor ligands (THF for 1 and 2 but dioxane for 2b); thus, the metal of these complexes has a coordination number of 9 (Figure 1 and Table 1).

The triphenylacetate complexes **7a** and **8a** are somewhat similar to the aforementioned diphenylacetate complexes; however, the chemical bonding pattern for the bridging carboxylates differs between the examined triphenylacetate complexes and the diphenylacetate complexes. In particular, all of the bridging Ph<sub>3</sub>CCOO- ligands in **7a** and **8a** are  $\mu_2 \kappa^1 \kappa^1$  coordinated, whereas in **1**, **2**, and **2b**,  $\mu_2 \kappa^1 \kappa^1$  and  $\mu_2 \kappa^1 \kappa^2$  coordinated Ph<sub>2</sub>CHCOO- ligands are found. Each Ln atom in **7a** and **8a** is also coordinated by two terminal  $\kappa^2$ -triphenylacetate ligands and by DME; thus, the Ln atoms in these two compounds have coordination numbers of 8 (Figure 4 and Table 1).

In all five of the aforementioned structures, the Ln–O distances (for terminal carboxylates, bridging carboxylates, and O-donor ligands) (Table 1) are in good agreement with the distances that have been found in the literature for binuclear carboxylate complexes of rare-earth metals.<sup>12</sup> This structural motif, featuring either four  $\mu_2$ - $\kappa^1$ : $\kappa^1$  RCOO– ligands or a

Table 5. Polymerization of Butadiene and Isoprene in Combination with Ethylaluminum Sesquichloride and Different Quantities of  $Al(i-Bu)_3$ ,  $AlEt_3$ , and  $HAl(i-Bu)_2^a$ 

run	precat.	cocat.	Al <sup>b</sup> :Nd	monomer	%, yield	cis-1,4, %	trans-1,4, %	1,2 (3,4), %	$M_{\rm w} (\times 10^{-3})$	$M_{\rm n}~( imes~10^{-3})$	$M_{\rm w}/M_{\rm n}$
1	1	Al(i-Bu)3	30	butadiene	<10						
2	2a	Al(i-Bu)3	30	butadiene	38	95.0	0.5				
3	2	Al(i-Bu)33	30	butadiene	89	99.1	0.8	0.1	1059	421	2.53
4	2	HAl(i-Bu) <sub>2</sub>	15	butadiene	>95	98.9	0.8	0.3	580	96	6.05
5	6	Al(i-Bu)3	30	butadiene	74	98.4	1.2	0.4	395	98	4.03
6	6	$HAl(i-Bu)_2$	15	butadiene	48	99.2	0.7	0.1	514	68	7.59
7	6	$Al(Et)_3$	30	butadiene	31	82.2	16.7	1.1	1120	105	11.29
8	13	$HAl(i-Bu)_2$	15	butadiene	83	98.6	1.1	0.3	1000	304	3.29
9	2	Al(i-Bu)33	30	isoprene	64	94.0	6.0		1307	621	2.10
10	2	$HAl(i-Bu)_2$	15	isoprene	95	96.5	3.5		645	147	4.37
11	6	$Al(Et)_3$	30	isoprene	22	95		5	551	57.5	9.58

<sup>*a*</sup>General conditions: [monomer]<sub>0</sub>/[Nd]<sub>0</sub> = 10000 (5000 for runs 7 and 11), [Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>]/[Nd] = 0.83, reaction time 3 h;  $T = 50 \degree C$ . <sup>*b*</sup>Al = Al(i-Bu)<sub>3</sub>, HAl(i-Bu)<sub>2</sub>, Al(Et)<sub>3</sub>. <sup>*c*</sup>Isolated polymer.

combination of two  $\mu_2$ - $\kappa^1$ : $\kappa^2$ - and two  $\mu_2$ - $\kappa^1$ : $\kappa^1$  RCOO- ligands, is quite common for lanthanide carboxylates. However, few examples of discrete homodinuclear complexes have been described for lanthanum and neodymium. Most of these complexes correspond to the general formula of [L(RCOO)-Ln( $\mu_2$ -RCOO)\_4Ln(RCOO)L], where RCOO- is an alkyl or aryl carboxylate and L is a chelating ligand, such as 1,10phenanthroline or 2,2'-bipyidine.<sup>13</sup>

As expected, the differences in the Ln–O bond lengths between La and Nd complexes is governed by the lanthanide contraction, with the only exception being the Ln–O bonds for the  $\mu_2$ - $\kappa^1$ : $\kappa^2$  type of coordination. The majority of the Ln–O bonds in **2** and **8a** are shortened by ca. 0.06–0.08 Å in comparison with the corresponding bonds in **1** and **7a**. The Ln(1)–O(5A) bond length in the  $\mu_2$ - $\kappa^1$ : $\kappa^2$ -coordinated RCOO– ligand is, however, the same in **1** and **2** but is shortened by 0.09 Å in **2b**. This finding can be an indication of the forced character of this type of additional coordination.

Changes in the coordination mode of the RCOO- group from the combination of  $\mu_2$ - $\kappa^1$ : $\kappa^1$  and  $\mu_2$ - $\kappa^1$ : $\kappa^2$  modes that are observed in compounds **1**, **2**, and **2b** to the  $\mu_2$ - $\kappa^1$ : $\kappa^1$  mode that is observed in compounds **7a** and **8a** causes the elongation of Ln---Ln distances (Table 1).

The use of triphenylacetates allows for a number of complexes with different coordination environments to be obtained. In particular, in the case of triphenylacetates of La and Nd, the mononuclear complexes 3-6 that were formed by the reaction of  $LnCl_3(THF)_x$  and  $Ph_3CCOONa$  (Scheme 3) were isolated, and the crystal structures of these complexes were analyzed (Figures 2 and 3).

Complexes 3 and 4 are isostructural and crystallize with two solvate methanol molecules. An interesting feature of their structures is the coexistence of  $\kappa^1$ - and  $\kappa^2$ -coordinated carboxylate ligands, which maintains the coordination number of the lanthanide cations at 9. In both complexes, the lanthanide cation is surrounded by two  $\kappa^2$ -coordinated Ph<sub>3</sub>CCOO- ligands, one  $\kappa^1$ -coordinated Ph<sub>3</sub>CCOO- ligand, and four CH<sub>3</sub>OH molecules. The Ln-O bond for the  $\kappa^1$ coordinated Ph<sub>3</sub>CCOO is consistently shorter than the Ln-O bonds for the  $\kappa^2$ -coordinated Ph<sub>3</sub>CCOO by more than 0.1 Å. Surprisingly, nearly equal average Ln-O bond lengths are found between compounds 3 and 7a and between compounds 4 and 8a, despite the fact that the two compounds in each of these pairs involve different lanthanide coordination numbers (Table 2). It is likely that this effect reflects both the intrinsic characteristics of the solvate molecules (i.e., steric volume and donating ability) and crystal-packing effects. In fact, the recrystallization of complex 4 from THF led to the formation of the new complex 6, which is characterized by  $C_3$  symmetry. In complex 6, the Nd atom is coordinated with three  $\kappa^2$ -Ph<sub>3</sub>CCOO- ligands and three THF molecules (Figure 3 and Table 2). The Nd–O bonds in complex 6 are slightly shortened (2.441-2.484(3) Å) in comparison to those in complex 4.

The role of crystal packing and H bonds can be illustrated within the analysis of Ln–O(H)Me bond lengths in 3 and 4. The Ln–O(H)Me bond lengths vary across a wide range (2.514(2)-2.619(2) and 2.450(1)-2.556(1) Å in compounds 3 and 4, respectively) and are governed by the peculiarities of inter-/intramolecular hydrogen bonding. In fact, the shortest Ln–O(1C) bond involves a methanol molecule that participates in the intramolecular O–H···O hydrogen bond (O···O = 2.586(1), 2.595(1) Å) with an  $\kappa^1$ -coordinated Ph<sub>3</sub>CCOO–ligand, whereas the longest bond of this type, Ln–O(4C),

involves a molecule that is involved in the weakest  $O-H\cdots\pi$ interaction ( $O\cdots C = 3.665(2)$  Å) with one of the Ph rings. Finally, intermediate values of the Ln–O(H)Me bonds are observed for the molecules that participate in H bonds of moderate strength with solvate methanol species. The observed variation in the Ln–O(H)Me bond lengths is clearly related to the degree of charge transfer that occurs as a result of H-bond formation, which should have a maximum value for the interactions with anionic ligands.<sup>14</sup> Clearly, this charge transfer will influence not only the lengths of the Ln–O bonds involving solvate molecules but also the lengths of the Ln–O bonds involving Ph<sub>3</sub>CCOO– ligands.

It should be noted that the compounds **3–6** represent relatively rare examples of mononuclear rare-earth-metal carboxylate complexes. A few examples of these types of complexes have been structurally characterized; these examples primarily consist of complexes with substituted benzoate, pyridinecarboxylato, acetylglycinato, acetate, and trimethyl- and trichloroacetato ligands.<sup>9,15–18</sup>

Another structural type which was obtained in the same reaction (Scheme 3) as for the complexes 5-8 is ate complexes 9-11 (Figures 5 and 6, Table 3). Two species of this type were isolated: namely, one containing a coordinated molecule of the Ph<sub>3</sub>CCOOH acid (9 and 10) as well as the "regular" ate complexes 11 and 11a.

The coordination environment of La and Nd cations in the isostructural complexes 9 and 10, respectively, is composed of the oxygen atoms of two THF molecules and of seven oxygen atoms of four Ph<sub>3</sub>CCOO ligands having different types of Ln-O coordination: terminal, bridging, and two semibridging. The coordination number of Ln is equal to 9, and the lanthanide polyhedron is a distorted capped tetragonal antiprism. The environment of the sodium cation is a distorted trigonal bipyramid in which two equatorial positions are occupied by the oxygen atoms of semibridging  $\mu_2$ - $\kappa^1$ : $\kappa^2$  Ph<sub>3</sub>CCOO ligands and the third one by an oxygen atom of the Ph<sub>3</sub>CCOOH molecule. In the apical positions, oxygen atoms of the bridging  $\mu_2$ - $\kappa^1$ : $\kappa^1$  Ph<sub>3</sub>CCOO ligand and THF are located. The OH group of the acid molecule is involved in a hydrogen bond with the O(7) atom of the bridging Ph<sub>3</sub>CCOO ligand with an O···O separation equal to  $\sim 2.62$  Å.

The lanthanum ate complex with coordinated DME molecules was isolated in two crystalline modifications, as monoclinic (11) and triclinic forms (11a) (see Table 7). Despite the exchange of THF molecules by one DME molecule in 11 and 11a, the general features of chemical bonding are rather close to those observed in 9 except for a less distorted character of the capped tetragonal prism and significant shortening of the La–O bond for the  $\mu_2$ - $\kappa^1$ : $\kappa^1$  Ph<sub>3</sub>CCOO ligand in 11 and 11a (Table 3). The same is true for the sodium atom, for which the positions of THF and Ph<sub>3</sub>CCOOH ligands in 9 are replaced by a DME molecule. Furthermore, in one of the modifications (11) there is a weak coordination between the sodium atom and one of the phenyl rings of the Ph<sub>3</sub>CCOO ligand; the shortest Na…C distance is equal to 3.048(2) Å (Figure 6).

Analysis of the geometry in the above two types of ate complexes revealed a significant difference between  $\mu_2 - \kappa^1 : \kappa^2$  coordination of Ph<sub>3</sub>CCOO- ligands in 9-11 and those observed in 1 and 2 (see above). Indeed, in all the ate complexes shortening of the Ln-O bond with a  $\mu_2 - \kappa^1 : \kappa^2$  Ph<sub>3</sub>CCOO<sup>-</sup> ligand is observed for the semibridging oxygen atom (compare Table 3 and Table 1). This shortening,

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Figure 9. Two Newman type projections illustrating the mutual disposition of the  $[Al(Et)_4]^-$  anion with respect to the LaO<sub>4</sub> fragment in 12. In each case, only half of the molecule is shown. The carbon atoms of triphenylacetate ligands are omitted for clarity.



Figure 10. Deformation electron density (DED) maps illustrating the pecularities of chemical bonding in the case of bridging (A) and semibridging (B) carboxylate groups. The DED contours are drawn with 0.05 e Å<sup>-3</sup> steps; negative values of DED are shown as dashed lines.

apparently, results from the lower value of the Na ionic radius in comparison with that of Ln. The latter point is also reflected in the decrease of  $Ln\cdots Na$  separation in comparison to  $Ln\cdots Ln$  in 1 and 2.

In the molecules of isostructural heterometallic complexes 12 and 13, the central fragment is composed of two Ln cations connected by four bridging  $\mu_2$ - $\kappa^1$ : $\kappa^1$  Ph<sub>3</sub>CCOO ligands and two Al(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> anions that are coordinated to the Ln cations in a  $\eta^3$ manner from both sides of the central fragment (Figure 7). The structure of the central fragments in 12 and 13 is similar to that observed in 7a and 8a except for some shortening of Ln-O bond lengths (the average Ln–O lengths in pairs 7a, 12 and 8a, 13 are equal to 2.454, 2.387 Å and 2.388, 2.338 Å, respectively). This shortening is likely to be the result of the coordination number decreasing from 9 in 7a and 8a to 7 in 12 and 13. The average bond lengths between Ln and CH<sub>2</sub> groups of the  $\eta^3$ coordinated Al( $C_2H_5$ )<sub>4</sub> anions are 2.93 Å (La- $C_{av}$ ) and 2.89 Å  $(Nd-C_{av})$ . It should be noted that this coordination causes significant elongation of the Al-C bonds by up to 0.1 Å in comparison with the noncoordinated Et groups, providing an inverse relation between the Al–C and Ln–C bonds (Table 4).

An interesting feature of the above complexes is a clear interplay between the  $\eta^3$ -coordinated Al(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and Ph<sub>3</sub>CCOO ligands. Indeed, in the La complex the oxygen atoms of bridging ligands, which are located in a staggered conformation with respect to the CH<sub>2</sub> groups of the aluminate anion (Figure 9), are characterized by the longest La–O bonds (2.419(1), 2.417(1) Å); these CH<sub>2</sub> groups (C(45), C(55) atoms) also form the shortest La–C bonds (2.823(2), 2.908(2) Å). The observed relation between the bond lengths in the central fragment and Al(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> anions makes possible to propose the important covalent contribution to the La···Al-(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> interactions, which is in line with the rather high stability of **12** and **13** in both the solid state and solution.

Diethylaluminum triphenylacetate (14), which was isolated in the reaction of **6** with organoaluminum compounds, crystallizes as a centrosymmetric dimer with an almost planar eight-membered cycle (Figure 8) in which the metal atoms are coordinated by two ethyl groups and two oxygen atoms of the carboxylate moiety in a tetrahedral fashion. The corresponding Al–O and Al–C bonds are 1.816(1), 1.826(1) Å and 1.952(2), 1.953(2) Å, respectively, which is in good agreement with the

Table 6.	Topological	Parameters in	the CPs	(3, -1)	) for the	Nd–O	Bonds in 2
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bond	d, Å	$ ho({f r})/{f e}$ Å $^{-3}$	$ abla^2 ho({f r})/{f e}~{ m \AA}^{-5}$	V( <b>r</b> )/au	$h_{ m e}({f r})/{ m au}$	$E_{\rm cont}/{\rm kcal}~{\rm mol}^{-1}$
Nd(1) - O(3)	2.4025(7)	0.36	5.7	-0.06298	-0.00171	19.8
Nd(1) - O(5)	2.3961(7)	0.36	5.8	-0.06234	-0.00121	19.6
Nd(1) - O(2)	2.4761(9)	0.32	5.2	-0.05324	0.000186	16.7
Nd(1) - O(1)	2.5542(8)	0.26	4.2	-0.03937	0.002041	12.3
Nd(1)-O(1S)	2.5751(7)	0.24	3.8	-0.03491	0.002457	11.0
Nd(1)-O(2S)	2.6083(8)	0.22	3.5	-0.03104	0.002548	9.7
Nd(1)-O(4A)	3.3908(7)	0.36	6.0	-0.06463	-0.0011	20.3
Nd(1)-O(6A)	2.4985(8)	0.29	4.8	-0.04721	0.001404	14.8
Nd(1)-O(5A)	2.7136(8)	0.19	2.9	-0.02444	0.002564	7.7

metric parameters reported for the similar dialkylaluminum carboxylate  $[Me_2Al(\mu-OOCC_6H_2(i-Pr)_3]_2$ .

**Charge Density Analysis.** To estimate the relative energy of the Ln-ligand bonds in the complexes studied, we have performed a charge density analysis within Bader's "Atoms in Molecules" (QTAIM) theory for complex 2, which gave a crystal of excellent diffraction quality.<sup>19</sup>

This approach involves the detailed analysis of the electron density distribution function  $\rho(\mathbf{r})$  in a crystal obtained directly from the X-ray diffraction data. The most important is that the topological analysis of  $\rho(\mathbf{r})$  within QTAIM gives a unique opportunity to estimate the energy of numerous interatomic interactions: from weak H…H contacts to H bonds<sup>20</sup> and even to coordinate bonds<sup>21</sup> using the correlation scheme suggested by Espinosa, Mollins, and Lecomte (EML).<sup>22</sup> The latter was successfully applied in many cases, having proved to be suitable for detailed analysis of chemical bonding patterns in, among other systems, coordination compounds of lanthanides.<sup>14a</sup>

The main features of the electron density distribution around the Nd ion in **2** are similar to those found in  $[GdClPhen_2(H_2O)_3]Cl_2(H_2O)$ .<sup>14a</sup> In particular, deformation electron density maps show four maxima formally assigned to its 4f electrons (Figure 10), and oxygen lone pairs of carboxylate groups are directed toward the above maxima around the metal ion. This is somewhat different from the chemical bond pattern observed in transition-metal complexes with the so-called "peak–hole" types of interactions.<sup>23</sup>

Critical points (CP) (3,-1) of the electron density distribution in the crystal 2 were located for all the expected Nd–O bonds (Figure 1) as well as for the C–C, C–H, and C– O bonds within the ligands. According to the topological parameters of  $\rho(\mathbf{r})$  in these CPs (3,-1), the latter bonds correspond to the shared type of interatomic interactions (electron energy density  $h_e(\mathbf{r})$  and Laplacian of  $\rho(\mathbf{r})$  ( $\nabla^2 \rho(\mathbf{r})$ ) values are negative), while the type of Nd-O bond depends on the Nd-O bond lengths. Thus, Nd-O bonds with the lengths less than ~2.40 Å correspond to the intermediate type of interactions  $(h_{\rm e}(\mathbf{r}) < 0, \nabla^2 \rho(\mathbf{r}) > 0)$  and cannot be considered as fully ionic (Table 6). The covalent contribution in these short Nd-O bonds in 2 exceeds at least the corresponding contribution for closed-shell types of bonds involving alkaline and alkaline-earth metals;<sup>24</sup> thus, they are close to intermediate bonds formed by transition metals in their complexes.<sup>23</sup> In contrast, the Nd-O bonds with lengths higher than the above threshold value are characterized by positive values of both  $\nabla^2 \rho(\mathbf{r})$  and  $h_{\rm e}(\mathbf{r})$ , which is indicative of a "closed-shell interaction".

The difference in the type of interatomic interaction the Nd–O bonds belong to is illustrated by their energy. The interaction energies  $E_{int}$  were estimated as  $-0.5[V(\mathbf{r})]$ 

according to Espinosa's correlation scheme (EML) and are summarized in Table 6. A summation of Nd–O bond energies for different types of ligands in 2 (bridging and semibridging) gave 40.0 and 42.0 kcal/mol, respectively. The similarity between the latter values explains the variation in the type of coordination involving tri- and diphenylacetate ligands. Given that these energies are close, an increase in the steric volume of a substituent can cause a variation in the coordination mode observed in tri- and diphenylacetates 1, 2 and 7, 8.

It should be noted that the longest Nd(1)–O(5A) bond for the  $\mu_2$ - $\kappa^1$ : $\kappa^2$  RCOO<sup>-</sup> type of coordination has the lowest energy equal to 7.7 kcal/mol; this explains its unexpected variation upon the exchange of Ln atom in 1 and 2 or solvate molecule in 2 and 2b (see above). The total interaction energy for the terminal ligands (29.1 kcal/mol) is significantly lower than for bridging and semibridging ligands. For comparison, the energy of interaction for the THF solvate molecules in a crystal is only 9.7–11.0 kcal/mol.

Charges of atoms in 2 were estimated by integration of the  $\rho(\mathbf{r})$  function over atomic basins ( $\Omega$ ) surrounded by zero-flux surface. The atomic charge for the Nd(1) atom in 2 (+1.2 e) is very far from its formal value but rather close to one obtained for a gadolinium complex.<sup>14a</sup> All the oxygen atoms are characterized by negative charges varying in the range from -0.95 to -1.31 e. The minimum negative charge (by the absolute value) is observed for the oxygen atoms of the THF molecules and the maximum for the atom O(5) involved in three coordinated bonds (see Figure 1); thus, the obtained atomic charges and the estimated energies of the Nd-O bond are in line with each other. At the same time, the Nd-O bond energies from high-resolution X-ray diffraction data are in good agreement with the reactivity of lanthanide di- and triphenylacetate. Thus, complex 2 easily transforms to 2b, and the reactions of  $6_1$ -8 and 10 with AlEt<sub>3</sub> are accompanied by the exchange of terminal carboxylate ligands, while bridging carboxylate ligands forming Nd-O bonds of higher energy are more inert.

#### CONCLUSION

We have studied the synthesis of La and Nd diand triphenylacetates and isolated a series of mono- and bimetallic products, including mononuclear complexes, binuclear homobimetallic complexes, and various ate complexes; the product ratio is controlled by the solvent and reagent stoichiometry that are selected. We determined that mononuclear carboxylates that were stabilized with a donor ligand (MeOH or THF) are the primary reaction products. These products can lose several of their stabilizing donor ligands and either dimerize or oligomerize. Dimerization also occurs within the reaction of La and Nd carboxylates with Et<sub>3</sub>Al. For La and Nd tris-triphenylacetates, we demonstrated that the dimeric aluminate in which the  $[AlEt_4]^-$  anions are  $\eta^3$ -coordinated to the metal and occupy terminal positions in the dimer is the major product that is formed from the alkylation of both monometallic and bimetallic carboxylate complexes.

In our opinion, similar processes can also occur during the synthesis and interconversion of other saltlike lanthanide derivatives, including well-known versatates and organic neodymium phosphates.

#### EXPERIMENTAL SECTION

General Considerations. All of the described manipulations were conducted under argon, using standard Schlenk and vacuum line techniques. Argon was purified by passage through the columns of a molecular sieve (4 Å) that was impregnated with a Na/K alloy and vermiculite that was impregnated with Mn(II) oxide.<sup>25</sup> Lanthanide tetrahydrofuranates were synthesized according to the published procedure.<sup>26</sup> Diphenylacetic and triphenylacetic acids were recrystallized from dry toluene and dried under vacuum prior to their use. AlEt<sub>3</sub> was purchased from Aldrich and was used as received. Methanol was distilled from Mg/I2.27 Tetrahydrofuran, dioxane, and DME were predried over NaOH and distilled from potassium/benzophenone ketyl under argon. Hexane was distilled from an Na/K alloy (benzophenone ketyl) under argon. Toluene was distilled from sodium/benzophenone ketyl under argon. Toluene-d<sub>8</sub> and THF-d<sub>8</sub> (Deutero GmbH) were degassed and dried over an Na/K alloy. CDCl<sub>3</sub> (Deutero GmbH) was distilled over calcium hydride and than degassed and stored in a Schlenk flask over activated molecular sieves (4 Å). NMR spectra were recorded on Bruker AM-300, Bruker Avance 400, and Bruker DRX500 instruments. <sup>1</sup>H shifts are referenced to internal solvent resonances and reported in parts per million relative to TMS. Infrared spectra were recorded on an IFS-66v/s Bruker instrument. Elemental analyses were performed on a PerkinElmer 2400 Series II elemental analyzer. The lanthanide content was determined by direct complexometric titration using xylenol orange as an indicator. Hexane used in the catalyst synthesis and polymerization was dried by reflux over sodium wire. The microstructures of polybutadiene and isoprene were measured by IR spectroscopy according to the literature.<sup>28</sup> Gel permeation chromatography was performed on a high-pressure chromatograph equipped with a Styrogel HR 5E, HR 4E system of columns, a Rheodyne injector with a 200-µL loop, and a Waters 2410 refractometer; THF was used as the eluent.

**Synthesis of**  $[La(Ph_2CHCOO)_3(THF)_2]_2$  (1). A solution of LaCl<sub>3</sub>(THF) (892 mg, 2.81 mmol) in 20 mL of dry methanol was added to 60 mL of a stirred solution of Ph<sub>2</sub>CHCOONa (8.46 mmol) in dry methanol, which was obtained from Ph<sub>2</sub>CHCOOH (1.793 g, 8.46 mmol) and a solution of CH<sub>3</sub>ONa in dry methanol (7.0 mL, 1.21 M). The resulting white suspension was stirred for 4 h at room temperature. The precipitate was filtered away and dried in vacuo, and 50 mL of THF was then added. The precipitate was removed by decantation. The solution was concentrated to 10 mL, and 60 mL of hexane was added slowly, leading to the precipitation of 1 in the form of colorless crystals (2.143 g, 83%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.10–6.25 (m, 60H, *-Ph*), 4.85–4.44 (br s, 6H, *-Ph*), 3.82–3.62 (m, 16H, *THF*), 1.91–1.78 (m, 16H, *THF*). Anal. Calcd for La<sub>2</sub>C<sub>100</sub>H<sub>98</sub>O<sub>16</sub>: C, 65.50; H, 5.39; La, 15.15. Found: C, 65.55; H, 5.48; La, 15.19.

**Synthesis of [Nd(Ph<sub>2</sub>CHCOO)<sub>3</sub>(THF)<sub>2</sub>]<sub>2</sub> (2).** This compound was prepared by the method that was described for **1**. NdCl<sub>3</sub>(THF)<sub>1.8</sub> (1.357 g, 3.57 mmol), Ph<sub>2</sub>CHCOOH (2.240 g, 10.56 mmol), and a solution of CH<sub>3</sub>ONa in dry methanol (14.1 mL, 0.75 M) were used to produce **2** (1.940 g, 59%). Anal. Calcd for Nd<sub>2</sub>C<sub>100</sub>H<sub>98</sub>O<sub>16</sub>: C, 65.12; H, 5.36; Nd, 15.64. Found: C, 64.79; H, 5.61; Nd, 15.70. IR  $\nu_{max}$  (cm<sup>-1</sup>): 1545 (s, COO<sup>-</sup><sub>terminal</sub>), 1600 (s, COO<sup>-</sup><sub>bridge</sub>). X-ray-quality

crystals of 2 were grown by the slow diffusion of hexane into a tetrahydrofuran solution.

Synthesis of  $[Nd(Ph_2CHCOO)_3(CH_3OH)_{2.5}]_x$  (2a). Et<sub>2</sub>NH (1.4 mL, 13.5 mmol) was added to a stirred solution of Ph<sub>2</sub>CHCOOH (2.860 g, 13.5 mmol) in 30 mL of dry methanol. The resulting solution was added to a stirred solution of NdCl<sub>3</sub>(THF)<sub>1.8</sub> (1.717 g, 4.57 mmol) in 15 mL of dry methanol. The suspension that was produced was stirred for 6 h at room temperature, and the liquid was filtered away. The solid was washed twice with 15 mL of dry methanol and dried in vacuo to yield 2a as a blue powder (3.2 g, 84%). Anal. Calcd for Nd<sub>2</sub>C<sub>89</sub>H<sub>86</sub>O<sub>17</sub>: C, 62.29; H, 5.05; Nd, 16.80. Found: C, 62.35; H, 4.88; Nd 16.82.

Synthesis of  $[La(Ph_3CCOO)_3(CH_3OH)_4]$ -CH\_3OH (3). A solution of Ph<sub>3</sub>CCOONa (4.30 mmol) in 20 mL of dry methanol, which was obtained from Ph<sub>3</sub>CCOOH (1.238 g, 4.30 mmol) and a solution of CH<sub>3</sub>ONa in dry methanol (5.05 mL, 0.85 M), was added to a stirred solution of LaCl<sub>3</sub> (0.352 g, 1.43 mmol) in 25 mL of dry methanol. The resulting white suspension was stirred for 2 h at room temperature, and the precipitate was removed by decantation. The solution was cooled to 0 °C, leading to the precipitation of 3 as colorless crystals (1.3 g, 78%). Anal. Calcd for LaC<sub>65</sub>H<sub>65</sub>O<sub>11</sub>: C, 67.24; H, 5.64; La, 11.96. Found: C, 67.26; H, 5.57; La, 11.99. IR  $\nu_{max}$  (cm<sup>-1</sup>): 1550 (s, COO<sup>-</sup><sub>terminal</sub>). Single-crystal X-ray analysis revealed that the unit cell of complex 3 contains two free methanol molecules; one of these solvent molecules is lost after the compound is dried under vacuum.

Synthesis of [Nd(Ph<sub>3</sub>CCOO)<sub>3</sub>(CH<sub>3</sub>OH)<sub>4</sub>](CH<sub>3</sub>OH) (4). Crystals of 4 were prepared by the method that was described for 3, without the removal of NaCl. NdCl<sub>3</sub>THF<sub>1.8</sub> (0.671 g, 1.76 mmol), Ph<sub>3</sub>CCOOH (1.525 g, 5.30 mmol), and a solution of CH<sub>3</sub>ONa in dry methanol (4.33 mL, 1.22 M) were used in this preparation. A few crystals were extracted for analysis. Anal. Calcd for Nd<sub>2</sub>C<sub>65</sub>H<sub>65</sub>O<sub>11</sub>: C, 66.93; H, 5.62. Found: C, 66.91; H, 5.34. IR  $\nu_{max}$  (cm<sup>-1</sup>): 1545 (s, COO<sup>-</sup><sub>terminal</sub>). Single-crystal X-ray analysis revealed that the unit cell of complex 4 contains two free methanol molecules; one of these solvent molecules is lost after the compound is dried under vacuum.

**Synthesis of [La(Ph<sub>3</sub>CCOO)<sub>3</sub>(THF)<sub>3</sub>] (5).** Crystals of 5 were prepared from a THF solution of 3 by the addition of hexane. <sup>1</sup>H NMR (300 MHz, THF- $d_8$ ):  $\delta$  7.31–7.21 (m, 18H, *Ph*–), 7.05–6.98 (m, 27H, *Ph*–), 3.67–3.58. Anal. Calcd for La<sub>2</sub>C<sub>72</sub>H<sub>69</sub>O<sub>9</sub>: C, 71.04; H, 5.71; La, 11.41. Found: C, 71,11; H, 5,66; La, 11.48.

**Synthesis of [Nd(Ph<sub>3</sub>CCOO)<sub>3</sub>(THF)<sub>3</sub>] (6).** A solution of Ph<sub>3</sub>CCOONa (10.33 mmol) in 30 mL of dry methanol was obtained from Ph<sub>3</sub>CCOOH (2.973 g, 10.33 mmol) and a solution of CH<sub>3</sub>ONa in dry methanol (8.32 mL, 1.24 M) and was then slowly added to a stirred solution of NdCl<sub>3</sub>(THF)<sub>1.8</sub> (1.308 g, 3.44 mmol) in 60 mL of dry methanol. The resulting solution was stirred for 5 h at room temperature, and the solvent was removed in vacuo. After the removal of this solvent, 50 mL of THF was added, and the resulting precipitate was removed by decantation. The solution was evaporated to a volume of 5 mL, and 80 mL of hexane was added. The suspension was cooled to 0 °C, leading to the precipitation of 6 as a blue powder (3.496 g, 83%). Anal. Calcd for NdC<sub>72</sub>H<sub>69</sub>O<sub>9</sub>: C, 70.73; H, 5.69; Nd, 11.80. Found: C, 70.68; H, 5.76; Nd, 11.88. IR  $\nu_{max}$  (cm<sup>-1</sup>): 1545 (*s*, COO<sup>-</sup> terminal). X-ray-quality crystals of 6 were grown by the slow diffusion of hexane to a tetrahydrofuran solution.

**Synthesis of [La(Ph<sub>3</sub>CCOO)<sub>3</sub>(THF)<sub>2</sub>]<sub>***x***</sub> (7). A sample of 5 (0,160 g, 0.131 mmol), was evacuated under dynamic vacuum at 100 °C for 10 h and cooled to room temperature to yield 7 (0.143 g, 95%). Anal. Calcd for La<sub>2</sub>C<sub>68</sub>H<sub>61</sub>O<sub>8</sub>: C, 71.32; H, 5.37; La, 12.13. Found: C, 71.20; H, 5.54; La, 12.09. IR \nu\_{max} (cm<sup>-1</sup>): 1548 (m, COO<sup>-</sup><sub>terminal</sub>), 1622 (m, COO<sup>-</sup><sub>bridee</sub>).** 

Synthesis of  $[La(Ph_3CCOO)_3(DME)]_2(THF)$  (7a). Crystals of 7a were prepared from a DME-THF solution of 5 or 7 by the slow addition of hexane. Anal. Calcd for  $La_2C_{132}H_{118}O_{17}$ : C 70.33; H, 5.28; La, 12.32. Found: C, 69.92; H, 5.17; La, 12.14.

Synthesis of  $[Nd(Ph_3CCOO)_3(THF)_2]_x$  (8). The compound was prepared by the method that was described for 7. 6 (0.274 g, 0.224 mmol) was used to produce 8 (0.250 g, 97%). Anal. Calcd for  $NdC_{68}H_{61}O_8$ : C, 70.99; H, 5.34; Nd, 12.54. Found: C, 70.61; H, 5.15;

	1	2	a	2b	3	4	6	7 <b>a</b>	ano
formula	$C_{100}H_{98}La_2O_{16}$	5 C100H98N	Vd <sub>2</sub> O <sub>16</sub> C	$^{100}H_{98}Nd_2O_{20}$	C <sub>66</sub> H <sub>69</sub> LaO <sub>12</sub>	C <sub>66</sub> H <sub>69</sub> NdO <sub>12</sub>	$C_{72}H_{69}NdO_9$	$C_{144}H_{142}La_2O_{20}$	ne
$M_{ m r^{ m ;}}~F(000)$	1833.60; 1880	1844.26;	1892 1	908.26; 978	1193.12; 1236	1198.45; 1242	1222.51; 3798	2470.40; 5120	la
cryst syst; space group	monoclinic; P2	$2_1/c$ monoclir	iic; $P2_1/c$ ti	iclinic; PI	triclinic; $P\overline{I}$	triclinic; $P\overline{I}$	trigonal; P3c1	monoclinic; $C2/c$	
Z (Z')	2 (0.5)	2 (0.5)	1	(0.5)	1 (1)	1(1)	6(3/3)	4 (0.5)	3
<i>a</i> , Å	12.185(2)	11.8097(	6) 1	3.0275(2)	13.4191(13)	13.3666(6)	20.3827(6)	30.134(2)	
$b,  m \AA$	21.789(4)	21.5927(	12) 1	3.0747(2)	13.6351(13)	13.5856(6)	20.3827(6)	14.7826(11)	
c, Å	16.478(3)	16.8574(	9) 1	4.7602(2)	17.706(3)	17.6743(13)	24.4901(10)	26.9229(19)	
$\alpha$ , deg	90	06	1	13.0584(6)	92.596(2)	92.8410(10)	06	06	
$\beta$ , deg	104.55(3)	103.977(	2) 9	5.0251(7)	93.621(2)	93.2730(10)	06	92.8400(10)	
$\gamma$ , deg	90	06	1	06.0341(7)	118.519(2)	118.4690(10)	120	06	
<i>V</i> , Å <sup>3</sup>	4234.5(15)	4171.4(4	) 2	168.09(6)	2830.4(6)	2806.0(3)	8811.4(5)	11978.3(15)	
$d_{ m calcdv}$ g cm <sup>-3</sup> ; $\mu$ , cm <sup>-1</sup>	1.438; 10.64	1.468; 13	1.01	.462; 12.57	1.400; 8.19	1.418; 9.90	1.382; 9.44	1.370; 7.75	
$2\theta_{\rm max}$ deg	56	58	~	3	58	58	56	58	
no. of rflns measd	26548	31956	1	00101	33913	24120	94652	54430	
no. of indep rflns $(R_{ m int})$	10208 (0.0776	) 11080 (0	0.0309) 2	1119 (0.0293)	15010(0.0420)	14559 (0.0211)	14191 (0.0848)	15895 (0.0437)	
no. of obsd rflns $(I > 2\sigma(I))$	6793	9200	1	9172	12610	12968	8639	11847	
R1	0.0461	0.0270	0	.0258	0.0393	0.0292	0.0359	0.0309	
wR2	0.1085	0.0667	0	.0677	0.0837	0.0695	0.0761	0.0630	
GOF	0.945	0.964	1	600	1.017	1.032	0.948	0.922	
$\Delta ho_{ m max}~\Delta ho_{ m min}$ e $ m \AA^{-3})$	1.077, -0.941	1.117,	0.569 1	.679, -1.333	0.919,-0.854	1.018, -1.260	1.755, -1.030	0.928, -0.833	
	8a	6	10	11	11a	12	13	14	
formula	C <sub>138</sub> H <sub>135</sub> Nd <sub>2</sub> O <sub>21</sub>	C <sub>120</sub> H <sub>116</sub> LaNaO <sub>15</sub>	C <sub>120</sub> H <sub>116</sub> NaNdO	15 C <sub>92</sub> H <sub>88</sub> LaNaO <sub>13</sub>	C <sub>94</sub> H <sub>95</sub> LaNaO <sub>15</sub>	$C_{96}H_{100}Al_2La_2O_8$	C <sub>96</sub> H <sub>100</sub> Al <sub>2</sub> Nd <sub>2</sub> O <sub>8</sub>	$C_{48}H_{50}Al_2O_4$	
$M_{ij} F(000)$	2417.94, 6.96	1960.03, 2048	1965.36, 2054	1563.52, 3248	1626.60, 1694	1713.54, 1760	1713.54, 1760	744.84, 1584	
cryst syst; space group	triclinic, PI	triclinic, $P\overline{1}$	triclinic, $P\overline{1}$	monoclinic, P2 <sub>1</sub> /	n triclinic, PI	triclinic, PI	triclinic, $P\overline{1}$	orthorhombic, Pbca	
Z (Z')	2 (1)	2 (1)	2(1)	4 (1)	2 (1)	2(1)	2 (1)	4 (0.5)	
<i>a</i> , Å	14.330(4)	14.4284(6)	14.382(3)	14.9186(8)	15.6966(6)	13.4822(6)	13.472(3)	15.3405(7)	
b, Å	19.169(5)	18.4950(7)	18.590(4)	35.9032(19)	16.1619(6)	14.6498(6)	14.630(3)	14.8579(7)	
c, Å	22.304(6)	18.5519(7)	18.617(4)	15.4383(8)	18.5589(7)	20.8819(9)	20.893(4)	17.7921(8)	
$\alpha$ , deg	90.700(7)	99.4050(10)	100.38(3)	90.00	108.5160(10)	89.8740(10)	89.93(3)	90	
$\beta$ , deg	105.847(5)	94.5820(10)	93.86(3)	110.8700(10)	98.6550(10)	87.1020(10)	87.36(3)	90	
γ, deg	97.538(5)	91.4680(10)	91.82(3)	90.00	106.8200(10)	83.4590(10)	83.60(3)	90	
$V, Å^3$	5835(3)	4864.7(3)	4880.2(17)	7726.6(7)	4118.3(3)	4092.3(3)	4087.7(14)	4055.3(3)	
$d_{\text{calcd}}$ g cm <sup>-3</sup> ; $\mu$ , cm <sup>-1</sup>	1.376; 9.51	1.338; 5.12	1.337; 6.05	1.344; 6.24	1.312; 5.90	1.391; 11.09	1.401; 13.35	1.220; 1.16	
$2\theta_{\max}$ deg	54	58	58	56	58	58	58	58	
no. of rflns measd	60444	58531	59877	86098	44689	49299	32796	40456	
no. of indep rflns $(R_{\rm int})$	25484 (0.0793)	25790 (0.0667)	25908 (0.0423)	$18680 \ (0.0877)$	21669 (0.0446)	21720(0.0320)	21207 (0.0230)	5395 (0.0657)	
no. of obsd rflns $(I > 2\sigma(I))$	13009	17645	21915	12235	16514	17830	16547	3908	
RI	0.0427	0.0522	0.0387	0.0477	0.0427	0.0295	0.0349	0.0439	
wR2	0.0762	0.1194	0.0988	0.1036	0.0931	0.0708	0.0898	0.1056	
GOF	0.859	0.949	0.989	0.979	0.928	1.024	0.988	1.010	
$\Delta ho_{ m max}~\Delta ho_{ m min}$ e $ m \AA^{-3})$	0.809, -1.320	1.002, -0.889	1.034, -0.816	0.712,; -0.861	1.038, -0.724	0.878, -0.814	1.812, -1.013	0.469, -0.305	
<sup>a</sup> For multipole refinement of <b>2</b>	the high-resolution of	lata (393808 measur	ed reflections with	$2\theta_{\rm max} < 100^{\circ}; 43733$	independent reflection	$S, R_{\text{int}} = 0.0458, \text{ wR2}$ =	= 0.0863, GOF = 1.04	5, R1 = 0.0295 (35181	icie
observed reflections with $1 > 20$	((I))) was used.								

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 $COO_{bridge}^{-}$ ). **Synthesis of [Nd(Ph<sub>3</sub>CCOO)<sub>3</sub>(DME)]<sub>2</sub>(DME) (8a).** Crystals of 8a were prepared from a DME-THF solution of 6 or 8 by the slow addition of hexane. IR  $\nu_{max}$  (cm<sup>-1</sup>): 1545 (m, COO<sub>terminal</sub>), 1630 (s,  $COO_{bridge}^{-}$ ). Anal. Calcd for Nd<sub>2</sub>C<sub>132</sub>H<sub>120</sub>O<sub>18</sub>: C, 69.45; H, 5.30; Nd, 12.64. Found: C, 69.27; H, 5.23; Nd, 12.59.

Synthesis of [La(Ph<sub>3</sub>CCOO)<sub>3</sub>][NaPh<sub>3</sub>CCOO][Ph<sub>3</sub>CCOOH](THF)<sub>5</sub> (9). A solution of LaCl<sub>3</sub>(THF) (350 mg, 1.42 mmol) in 20 mL of dry methanol was slowly added to 20 mL of a stirred solution of Ph<sub>3</sub>CCOONa (5.68 mmol) and Ph<sub>3</sub>CCOOH (1.45 mmol), which was obtained from Ph<sub>3</sub>CCOOH (2.053 g, 7.13 mmol) and a solution of CH<sub>3</sub>ONa in dry methanol (4.66 mL 1.22 M). After 4 h of stirring, a white precipitate was formed. The mixture was stirred for 3 h at room temperature, the solvent was removed in vacuo, and 40 mL of dry tetrahydrofuran was added. This solution was separated from the precipitate and evaporated to a volume of 5 mL; subsequently, 80 mL of hexane was added. The resulting suspension was cooled to 0 °C, leading to the precipitation of 9 in the form of colorless crystals (1.792 g, 61%). IR  $\nu_{max}$  (cm<sup>-1</sup>): 1706 (w, -COOH), 2584 (w, OH), 1550-1570 (s, COO-bridge Na-Nd), 1550 (s, COO-terminal). Anal. Calcd for LaNaC120H116O15: C, 73.53; H, 5.97; La, 7.09. Found: C, 73.66; H, 5.94; La, 6.98. X-ray-quality crystals of 9 were grown by the slow diffusion of hexane into a tetrahydrofuran solution.

Synthesis of  $[Nd(Ph_3CCOO)_3][NaPh_3CCOO][Ph_3CCOOH]-(THF)_5$  (10). The compound was prepared by the method that was described for 9. NdCl<sub>3</sub>(THF)<sub>2.14</sub> (435 mg, 1.07 mmol), Ph<sub>3</sub>CCOOH (1.548 g, 5.37 mmol), and a solution of CH<sub>3</sub>ONa in dry methanol (3.5 mL, 1.22 M) were used to produce 10 (1.71 g, 81%). IR  $\nu_{max}$  (cm<sup>-1</sup>): 1706 (w, -C(O)OH), 2584 (w, OH), 1550–1570 (s, COO<sup>-</sup><sub>bridge Na-Nd</sub>), 1550 (s, COO<sup>-</sup><sub>terminal</sub>). Anal. Calcd for NdNa-C<sub>120</sub>H<sub>116</sub>O<sub>15</sub>: C, 73.33; H, 5.95; Nd, 7.34. Found: C, 73.28; H, 5.88; Nd, 7.57. X-ray-quality crystals of 10 were grown by the slow diffusion of hexane into a tetrahydrofuran solution.

Synthesis of  $[La(Ph_3CCOO)_2]_2[Al(C_2H_5)_4]_2$  (12). A solution of Et<sub>3</sub>Al in toluene (1 mL, 1.03 M) was added to 10 mL of a stirred solution of  $[La(Ph_3CCOO)_3(THF)_2]_x$  (7; 225 mg, 0.101 mmol) in dry toluene. The mixture was stirred overnight at room temperature. The slow addition of hexane to the solution resulted in the precipitation of 12 in the form of colorless crystals (98 mg, 57%). <sup>1</sup>H NMR (500 MHz, toluene- $d_8$ ,  $\delta$ ): 7.04–6.87 (m, 60H, –*Ph*), 0.96 (t, 24H, –CH<sub>2</sub>CH<sub>3</sub>), 0.14–0.05 (m, 16H, –*CH*<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for La<sub>3</sub>Al<sub>2</sub>C<sub>96</sub>H<sub>100</sub>O<sub>8</sub>: C, 67.29; H, 5.88. Found: C, 67.98; H, 5.69.

Synthesis of  $[Nd(Ph_3CCOO)_2]_2[Al(C_2H_5)_4]_2$  (13). Method a. The compound was prepared by the method that was described for 12.  $[Nd(Ph_3CCOO)_3(THF)_2]_x$  (8; 965 mg, 0.839 mmol) and a solution of Et<sub>3</sub>Al in toluene (4.18 mL, 1.07 M) were used to produce 13 in the form of blue crystals (440 mg, 61%). Anal. Calcd for for  $Nd_2Al_2C_{96}H_{100}O_8$ : C, 66.87; H, 5.68. Found: C, 66.80; H, 5.99. X-ray-quality crystals of 13 were grown by the slow diffusion of hexane into a toluene solution.

Method b. A solution of  $Et_3Al$  in toluene (2.7 mL 1.07 M) was added to 10 mL of a stirred solution of **10** (568 mg, 0,289 mmol) in dry toluene. The mixture was stirred overnight at room temperature. The slow addition of hexane to the solution resulted in the precipitation of **11** as blue crystals (102 mg, 41%). The results from the elemental analysis of this compound were consistent with its identification as **13**.

Method c. A solution of  $Et_3Al$  in toluene (2.47 mL 1.47 M) was added to 10 mL of a stirred solution of 6 (0.633 mg, 0.518 mmol) in dry toluene. The mixture was stirred overnight at ambient temperature. The slow addition of hexane to the solution resulted in the precipitation of 13 in the form of blue crystals (200 mg, 45%). The results from the elemental analysis of this compound were consistent with its identification as 13.

Preparation of the Polymerization Catalyst from Carboxylates 1, 2, 2a, 6, and 13. A glass reactor was charged under argon with 0.1 mmol of a carboxylate and hexane (7.5 mL); butadiene (0.15 mL, 2 mmol) was recondensed (-78 °C). The mixture was cooled to -78 °C, and a 1 M solution of DIBAL-H (1.5 mL) in hexane was added with stirring. After 1 h, a 0.83 M solution of  $Me_3Al_2Cl_3$  (1 mL) in hexane was added to the reaction mixture. The mixture was stirred for 20 h at 20 °C and was then considered ready for use.

**Butadiene Polymerization.** The catalyst (0.3 mL, 0.003 mmol; see the protocol above) was placed into an ampule under an argon flow. Hexane (17 mL) was added, and butadiene (2.2 mL, 30 mmol) was condensed (-78 °C). The ampule was sealed and heated to 50 °C. After 3 h, the ampule was opened and the reaction mixture was poured into methanol (50 mL). The precipitated polymer was collected, washed twice with methanol, and dried *in vacuo*.

X-ray Crystallography. Crystalline samples of 1, 2, 5, 6, 9, and 10 were grown from THF/hexane solution. X-ray-quality crystals of 7a and 8a were obtained by the recrystallization of 7 and 8, respectively, from a 1/1 mixture of THF and DME. Appropriate crystals for 2b were obtained by the recrystallization of 2 from dioxane. Single-crystal samples of 4 and 5 were obtained from methanol at 0 °C, whereas crystalline samples of 12-14 were obtained by the slow diffusion of hexane into a toluene solution. Single-crystal samples of 11 and 11a were isolated as DME adducts from the THF/DME mixture during the course of attempts to isolate 7a.

All diffraction data were collected on a Bruker SMART APEX II CCD diffractometer ( $\lambda$ (Mo K $\alpha$ ) = 0.71072 Å,  $\omega$  scans) at 100 K. The substantial redundancy in data allows an empirical absorption correction to be performed with SADABS, using multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by full-matrix least-squares techniques against  $F^2$ in the anisotropic-isotropic approximation. For disordered Ph groups and THF molecules in some of the crystals the refinement was performed with additional constraints of C-C bond lengths and anisotropic displacement parameters of corresponding atoms. The positions of hydrogen atoms were calculated from a geometrical point of view and refined with the riding model. In crystals of 7a, 8a, and 11a the analysis of the Fourier electron density synthesis has revealed that some of the solvate THF (in 7a, 8a) and DME molecules (in 11a) are strongly disordered. We could not establishe an appropriate model for refinement of the above residual electron density corresponding to these molecules. Thus, we had to exclude unresolved solvent by means of the SQUEEZE procedure.<sup>29</sup> All calculations were performed with the SHELXTL software package.<sup>30</sup> Crystal data and structure refinement parameters are given in Table 7. CCDC 907196-907206 and 907208-907211 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data via www.ccdc.cam.ac.uk/data\_ request/cif.

The multipole refinement of 2 was carried out within the Hansen-Coppens formalism<sup>31</sup> using the XD program package.<sup>32</sup> Scattering factors obtained from STO atomic relativistic wave functions were obtained at PBE/QZ4P level of theory. The refinement was carried out against F and converged to R = 0.0204,  $R_w = 0.0207$  and GOF = 0.9269 for 28725 merged reflections with  $I > 3\sigma(I)$  and  $(\sin \theta)/\lambda > 1.0$ Å<sup>-1</sup>. All C-C, O-C, and Nd-O bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria (the maximum difference of the mean square displacement amplitudes was  $11 \times 10^{-4} \text{ Å}^2$ ). The only exceptions are the C-C bonds of one of the disordered THF cycles. The residual electron density for reflections with  $2\theta_{\rm max}$  < 75° was not more than 0.31 e Å<sup>-3</sup>. Topological analysis of the experimental  $\rho(\mathbf{r})$ function was carried out using the WinXPRO program package.<sup>33</sup> The estimation of the kinetic energy  $(g(\mathbf{r}))$  was based on Kirzhnits's approximation,<sup>34</sup> relating it with values of the  $\rho(\mathbf{r})$  and its derivatives:  $g(\mathbf{r}) = (3/10)(3\pi^2)^{2/3} [\rho(\mathbf{r})]^{5/3} + (1/72) |\nabla \rho(\mathbf{r})|^2 / \rho(\mathbf{r}) + (1/6) \nabla^2 \rho(\mathbf{r}).$ The usage of this relationship in conjunction with the virial theorem  $(2g(\mathbf{r}) + v(\mathbf{r}) = 1/4\nabla^2 \rho(\mathbf{r}))$  provided the value of potential energy density  $(v(\mathbf{r}))$  in the critical points from experimental diffraction data. The accuracy of this approach for closed-shell and intermediate types of interatomic interactions was shown for various complexes.<sup>35</sup>

#### ASSOCIATED CONTENT

#### **S** Supporting Information

CIF files giving X-ray crystallographic ata for compounds 1, 2, 2b, 3, 4, 6, 7a, 8a, 9–11, 11a, and 12–14. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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