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Lanthanide Carboxylate Precursors for Diene Polymerization Catalysis: Syntheses, Structures, and Reactivity with Et₂AlCl

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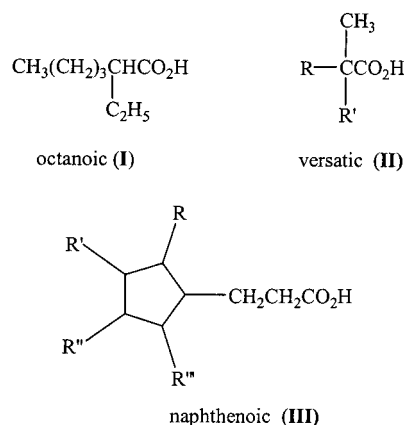
Synthetic, structural, and reactivity results are presented on neodymium and lanthanum carboxylates that can function as models for diene polymerization catalysts. The neodymium and lanthanum carboxylates {Nd[O₂CC(CH₃)₂CH₂CH₃]₃}_x (**1**) and {La[O₂CC(CH₃)₂CH₂CH₃]₃}_x (**2**) were synthesized from the lanthanide metal and 2,2-dimethylbutyric acid in the presence of a catalytic amount of HgCl₂ and Hg(OAc)₂. Nd₂[O₂CCH(C₆H₅)CH₂CH₃]₆[HO₂CCH(C₆H₅)CH₂CH₃]₄ (**3**) was prepared similarly from neodymium powder and 2-phenylbutyric acid. **1** and **2** crystallize from hot pyridine as the dimeric pyridine adducts Nd₂[O₂CC(CH₃)₂CH₂CH₃]₆[pyridine]₄ (**4**) and La₂[O₂CC(CH₃)₂CH₂CH₃]₆[pyridine]₄ (**5**). **3** crystallizes from hexanes as the carboxylic acid adduct. **1** and **2** react with Et₂AlCl to form the isolable solids **6** and **7**, which react with Al(ⁱBu)₃ to generate catalytically active systems which polymerize isoprene, ethylene, and styrene. Although crystallization of **6** from THF forms NdCl₃(THF)₄ (**8**) and crystallization of **7** from pyridine forms [LaCl₃(pyridine)₄]₂ (**9**), complexes **6** and **7** are not simply LnCl₃, since elemental analyses show that they contain aluminum.

Introduction

The development of high-quality elastomers via the polymerization of butadiene and substituted butadienes has grown in importance as demands for high-performance synthetic rubbers have increased.^{1–3} For example, the need for high-performance tires which match cost, safety, and optimum gasoline mileage presents ongoing challenges for a better understanding of how to generate elastomers. In addition, the limited supply of natural rubber contributes to the need for better synthetic polyisoprene.

Of the several types of diene polymerization catalysts which have been reported,^{4,5} neodymium-based catalysts are among the best systems for efficient formation of high-*cis* 1,4-polydienes. Neodymium catalysts can polymerize butadiene and isoprene to >98% *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene, respectively.^{6–11} Since the bulk of natural rubber is *cis*-1,4-polyisoprene, the neodymium-based catalysts are of particular interest in the development of better synthetic elastomers.

Although the neodymium systems provide high-*cis* 1,4-polydienes, relatively little is known about the mechanism of catalysis or even the composition of the catalyst precursors. Typical systems have three components: a neodymium carboxylate, an ethyl aluminum chloride reagent, and triisobutylaluminum or isobutylaluminum hydride.^{9–11} The literature indicates that the neodymium carboxylate starting materials are typically made from neodymium acetates or oxides and mixtures of isomers of carboxylic acids readily obtained from petrochemical plants.^{9,11–13} Octanoic (**I**), versatic (**II**), and naphthenoic (**III**) acids are commonly used without separation of the several isomers which are present.



(1) Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed.; Wiley: New York, 1965; Vol. 7.

(2) Terry, L. *Chem. Week* **1999**, 161, 18.

(3) Terry, L. *Chem. Week* **1989**, 144, 40.

(4) Porri, L.; Giarrusso, A. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 4, Part II, p 53.

(5) Boor, J. *Ziegler-Natta Catalysts and Polymerizations*; Academic Press: New York, 1979; Vol. 17, p 130.

(6) Porri, L.; Ricci, G.; Giarrusso, A.; Shubin, N.; Lu, Z. *ACS Symp. Ser.* **2000**, No. 749, 15.

(7) Marina, N. G.; Monakov, Y. B.; Sabirov, Z. M.; Tolstikov, G. A. *Polym. Sci.* **1991**, 33, 387.

(8) Porri, L.; Giarrusso, A. *Comprehensive Polymer Science*; Pergamon Press: Oxford, U.K., 1989.

(9) Wilson, D. J.; Jenkins, D. K. *Polym. Bull.* **1992**, 27, 40.

(10) Porri, L.; Ricci, G.; Shubin, N. *Macromol. Symp.* **1998**, 128, 53.

(11) Yunlu, K. et al. U.S. Patent 6,111,082, U.S. Class 534/16.

These neodymium carboxylates are treated with an ethylaluminum chloride reagent, e.g. EtAlCl₂ or Et₂AlCl, to form an intermediate which is subsequently

(12) Falbe, J. *Houben-Weyl Methoden der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, New York, 1985; Vol. E 5/1, p 471ff.

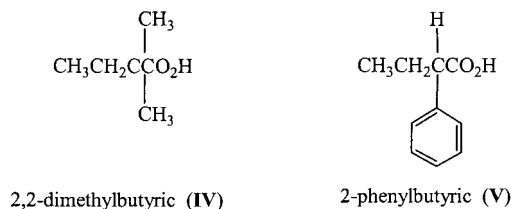
(13) Wilson, D. J.; Jenkins, D. K. *Polym. Bull.* **1995**, 34, 257.

treated with an isobutylaluminum-containing compound to generate the active catalysts. Some reports in the literature suggest that the ethylaluminum chloride reaction with the neodymium carboxylates forms NdCl_3 , in analogy to Ziegler–Natta formation of TiCl_3 . The NdCl_3 is subsequently alkylated by the isobutylaluminum reagent to make an active Nd–C bond which initiates catalysis.^{6,10}

Since this ternary neodymium catalyst is one of the most successful lanthanide-based catalytic systems and it has important commercial applications, it is desirable to study for both fundamental and applied reasons. Detailed knowledge of the mechanism of this reaction could provide insight into how the unique properties of the lanthanides can be used in organometallic and catalytic chemistry as well as how to make better diene polymerization systems.

Initially we sought to identify some well-characterized precursors and intermediates so that their reaction chemistry could be studied in detail. Each of the three steps of the catalyst preparation sequence deserves attention. To this end we have begun to synthesize a series of fully characterizable lanthanide carboxylates which can be converted to active catalysts. Our goal was to find convenient syntheses of carboxylates that could be fully defined by X-ray crystallography and converted to active catalysts.

We report here synthetic and structural studies on neodymium carboxylate salts using 2,2-dimethylbutyric acid (**IV**) and 2-phenylbutyric acid (**V**), as well as



preliminary data on their reactivity with diethylaluminum chlorides. We have examined lanthanum as well as neodymium salts, since the diamagnetic lanthanum complexes are more amenable to NMR spectroscopy and could have similar reactivity due to the similar radial size of these metals.^{14,15} Even this initial study seems to indicate that the sequence of reactions assumed in the literature is not followed in all cases.

Experimental Section

General Procedures. Complexes **1–3** were synthesized and handled in air. All other procedures were conducted under nitrogen using glovebox and Schlenk techniques in an environment free of coordinating solvents. ¹H and ¹³C NMR spectra were obtained using Omega 500 MHz and GN 500 MHz NMR spectrometers at 23 °C. ²⁷Al NMR spectra were obtained using a GN 500 MHz NMR spectrometer at variable temperatures. The external standard used for ²⁷Al NMR was 1.0 M aqueous $\text{Al}(\text{NO}_3)_3$ at pH 1. IR spectra were obtained using a Perkin-Elmer Series 1600 FTIR and an ASI ReactIR 1000 spectrometer. Elemental analyses were performed by Desert Analytics,

Tucson, AZ, and Analytische Laboratorien, Lindlar, Germany. Molecular weights were determined by the isopiestic Signer method.¹⁶

Reagents. Nd and La powders in oil (Strem) were washed with hexanes and dried under vacuum. HgCl_2 , $\text{Hg}(\text{OAc})_2$, Et_2AlCl (1.0 M solution in hexane), $\text{Al}(\text{iBu})_3$ (1.0 M solution in hexane), 2,2-dimethylbutyric acid, 2-phenylbutyric acid, toluene, anhydrous pyridine, D_2O , methanol, and hydrochloric acid were all purchased from Aldrich and used without further purification. Hexane, tetrahydrofuran, deuterated pyridine, and deuterated tetrahydrofuran used in the nitrogen-containing gloveboxes were heated to reflux over potassium metal and then distilled under nitrogen. Isoprene was dried over molecular sieves and vacuum-transferred.

Synthesis of $\{\text{Nd}[\text{O}_2\text{CC}(\text{Me})_2\text{Et}]_3\}_x$ (1**).** In a 100 mL Schlenk flask equipped with a reflux condenser, neodymium powder (2.00 g, 13.87 mmol) was suspended in toluene (50 mL). 2,2-Dimethylbutyric acid (4.99 g, 42.96 mmol) was added to the suspension via syringe. The solution was heated at reflux for 30 min, and then HgCl_2 (50 mg, 0.184 mmol) and $\text{Hg}(\text{OAc})_2$ (50 mg, 0.158 mmol) were added as catalysts. The solution was heated to reflux and stirred for 3 h. The solution was then decanted and filtered hot through a medium-porosity filter frit. The solid on the frit was washed three times with hexanes, placed in a 50 mL beaker, and put in an oven for 30 min at 175 °C. The solid was then dried at 5×10^{-4} Torr with heating at 120 °C to give **1** as a light blue powder (5.98 g, 88%). The solid was transferred to a nitrogen-filled glovebox. Anal. Calcd for $\text{Nd}_2\text{C}_{36}\text{H}_{66}\text{O}_{12}$: Nd, 29.5; C, 44.2; H, 6.8. Found: Nd, 29.9; C, 44.4; H, 7.0. ¹H NMR ($\text{C}_5\text{D}_5\text{N}$, 23 °C): δ 6.08 (b, s, 12H, CH_2 , Et, $\Delta\nu_{1/2}$ = 360 Hz), 3.70 (b, s, 36H, C– CH_3 , $\Delta\nu_{1/2}$ = 270 Hz), 2.05 (b, s, 18H, CH_3 , Et, $\Delta\nu_{1/2}$ = 315 Hz). IR (thin film): 2968 m, 2926 m, 2884 m, 1598 s, 1567 s, 1532 s, 1478 s, 1417 s, 1359 m, 1332 m, 1293 m, 1224 s, 1038 s, 1007 s, 988 m, 930 m, 880 s, 803 s, 749 s, 699 s cm^{-1} .

Synthesis of $\{\text{La}[\text{O}_2\text{CC}(\text{Me})_2\text{Et}]_3\}_x$ (2**).** **2** was prepared as described for **1** using lanthanum powder (1.65 g, 8.3 mmol), 2,2-dimethylbutyric acid (3.08 g, 26.5 mmol), 50 mg of HgCl_2 , and 50 mg of $\text{Hg}(\text{OAc})_2$. The reaction yielded a white powder (8.9 g, 94%). Anal. Calcd for $\text{La}_2\text{C}_{36}\text{H}_{66}\text{O}_{12}$: La, 28.7; C, 44.6; H, 6.9. Found: La, 28.5; C, 44.4; H, 6.7. ¹H NMR ($\text{C}_5\text{D}_5\text{N}$, 23 °C): δ 1.62 (q, 12H, CH_2 , Et), 1.21 (s, 36H, C– CH_3), 0.89 (t, 18H, CH_3 , Et). ¹³C NMR ($\text{C}_5\text{D}_5\text{N}$, 23 °C): δ 189.3 (C– CO_2), 43.5 (C– CO_2), 33.6 (CH_3 – CH_2), 25.2 (C– CH_3), 9.8 (CH_2 – CH_3). IR (thin film): 2964 m, 2922 m, 2880 m, 1594 s, 1567 s, 1532 s, 1478 s, 1417 s, 1359 m, 1332 m, 1293 m, 1224 s, 1038 s, 1007 s, 988 m, 930 m, 883 s, 803 s, 714 m cm^{-1} .

Synthesis of $\{\text{Nd}[\text{O}_2\text{CCH}(\text{Ph})\text{Et}]_3[\text{HO}_2\text{CCH}(\text{Ph})\text{Et}]_2\}_2$ (3**).** In a 100 mL Schlenk flask equipped with a reflux condenser, neodymium powder (1.10 g, 7.63 mmol) was suspended in toluene (30 mL). 2-Phenylbutyric acid (15.00 g, 91.6 mmol) was added to the suspension via syringe. The solution was heated at reflux for 30 min, and then 50 mg of HgCl_2 and 50 mg of $\text{Hg}(\text{OAc})_2$ were added. The solution was heated to reflux and stirred for 16 h. The solution was filtered hot through a medium-porosity filter frit, the solid was washed three times with hot toluene, and the solvent was removed from the filtrate under vacuum. The purple viscous liquid product was dried at 5×10^{-4} Torr with heating at 150 °C (6.60 g, 90%). The viscous liquid was dissolved in 50 mL of hexane and kept at –31 °C overnight. The solvent was decanted from the insoluble materials, and purple crystals were obtained during rotary evaporation of the hexane. Anal. Calcd for $\text{Nd}_2\text{C}_{100}\text{H}_{120}\text{O}_{20}$: Nd, 15.0. Found: Nd, 14.7. IR (thin film): 3065 m, 3030 m, 2964 s, 2934 s, 2876 m, 2563 m, 1949 m, 1876 m, 1806 m, 1728 m, 1706 s, 1679 s, 1594 s, 1573 m, 1547 m, 1494 m, 1451 m, 1413 s, 1390 m, 1289 s, 1243 m, 1224 s, 1085 m, 1031 m, 946 m, 842 m, 803 m, 699 s cm^{-1} .

(14) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, 32, 751.

(15) Evans, W. J. *Polyhedron* **1987**, 6, 803.

(16) Signer, R. *Justus Liebigs Ann. Chem.* **1930**, 478, 246.

Table 1. X-ray Data Collection Parameters^a for Nd₂(O₂CR')₆(HO₂CR')₄ (3), Nd₂(O₂CR)₆(pyridine)₄ (4), La₂(O₂CR)₆(pyridine)₄ (5), and [LaCl₃(pyridine)₄]₂ (9)

	3·2C ₁₀ H ₁₂ O ₂	4·C ₅ H ₅ N	5·C ₅ H ₅ N	9
empirical formula	C ₁₀₀ H ₁₂₀ O ₂₀ Nd ₂ ·2C ₁₀ H ₁₂ O ₂	C ₅₆ H ₈₆ O ₁₂ N ₄ Nd ₂ ·C ₅ H ₅ N	C ₅₆ H ₈₆ O ₁₂ N ₄ La ₂ ·C ₅ H ₅ N	C ₄₀ H ₄₀ N ₈ Cl ₆ La ₂
fw	2252.78	1374.87	1364.21	1123.32
temp (K)	163(2)	158(2)	158(2)	188(2)
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	15.8618(7)	11.4336(8)	13.5796(9)	11.9859(4)
<i>b</i> (Å)	18.1180(8)	16.1820(12)	14.2645(10)	17.0473(6)
<i>c</i> (Å)	22.1074(10)	18.0028(13)	19.5501(13)	12.6734(5)
α (deg)	100.1440(10)	90	72.9060(10)	90
β (deg)	91.9180(10)	101.5970(10)	85.7260(10)	118.1050(10)
γ (deg)	114.9850(10)	90	62.5420(10)	90
<i>V</i> (Å ³)	5627.2(4)	3262.9(4)	3203.6(4)	2284.18(14)
<i>Z</i>	2	2	2	2
ρ_{calcd} (Mg/m ³)	1.330	1.399	1.414	1.633
μ (mm ⁻¹)	0.983	1.633	1.376	2.234
R1 ^b (<i>I</i> > 2.0 σ (<i>I</i>))	0.0323	0.0344	0.0356	0.0188
wR2 ^c (all data)	0.0822	0.0792	0.0888	0.0467

^a Conditions: radiation, Mo K α (λ = 0.710 73 Å); monochromator, highly oriented graphite. ^b R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^c wR2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

{Nd[O₂CC(Me)₂Et]₃(pyridine)₂]₂ (4). **1** (0.251 g, 0.511 mmol) was dissolved in hot pyridine and crystallized at -30 °C to form **4** as light blue cubes (0.315 g, 95%). Molecular weight (pyridine): calcd for monomeric NdC₂₈H₄₃N₂O₆, 647.9; found, 580.

{La[O₂CC(Me)₂Et]₃(pyridine)₂]₂ (5). **2** (0.410 g, 0.846 mmol) was dissolved in hot pyridine and crystallized at -30 °C to form **5** as colorless cubes (0.495 g, 91%). Molecular weight (pyridine): calcd for monomeric LaC₂₈H₄₃N₂O₆, 642.6; found, 580.

"Nd₂AlCl₅C₁₃H₂₂O_x" (6). **1** (3.2 g, 3.30 mmol) was suspended in 5 mL of hexane, and 16.3 mL of a 1.0 M solution of Et₂AlCl in hexane (1.97 g, 16.3 mmol) was added via syringe. The solution was stirred for 1 h at room temperature and filtered through a coarse filter frit. The solid was washed three times with 20 mL of hexane and dried by rotary evaporation to yield **6** as a light blue powder (2.0 g, 78%). Anal. Calcd for Nd₂AlCl₅C₁₃H₂₂O₂: Nd, 43.0; Al, 4.0; Cl, 26.4; C, 23.3; H, 3.3. Found: Nd, 42.7; Al, 3.9; Cl, 26.5; C, 23.1; H, 3.3. IR (KBr): 3003 s, 2895 s, 1640 m, 1482 s, 1444 s, 1413 s cm⁻¹.

"La₂AlCl₅C₁₂H₂₁O_x" (7). **7** was synthesized as described for **6** by using **2** (6.20 g, 5.43 mmol) and 27.1 mL of a 1.0 M solution of diethylaluminum chloride (3.27 g, 27.1 mmol) in hexane. **7** was isolated as a white powder (3.10 g, 74%). Anal. Calcd for La₂AlCl₅C₁₂H₂₁O₂: La, 40.9; Al, 4.0; Cl, 26.1; C, 21.2; H, 3.1. Found: La, 41.3; Al, 3.9; Cl, 25.9; C, 21.0; H, 3.1. IR (KBr): 3001 s, 2893 s, 1637 m, 1478 s, 1441 s, 1410 s cm⁻¹.

NdCl₃(THF)₄ (8). Crystallization of **6** (0.210 g, 0.269 mmol) from THF (2 mL) at -30 °C in the glovebox overnight formed crystals of NdCl₃(THF)₄ (0.096 g, 66%), which were identified by X-ray crystallography.

[LaCl₃(pyridine)₄]₂ (9). Crystallization of **7** (0.185 g, 0.165 mmol) from pyridine (3 mL) at -30 °C in the glovebox overnight formed crystals of [LaCl₃(pyridine)₄]₂ (0.082 g, 61%), which were identified by X-ray crystallography.

{Et₂Al[O₂CC(Me)₂Et]₃}_n (10). **10** was isolated as a byproduct in the syntheses of **6** and **7**. After compound **6** was washed three times with 10 mL of hexane, the solvent was removed from the solution by rotary evaporation to yield **10** as a colorless liquid (1.54 g, 58%). In the same manner compound **7** was washed three times with 10 mL of hexane and the solvent removed by rotary evaporation to also yield **10** as a colorless liquid (4.20 g, 57%). ¹H NMR (C₅D₆, 23 °C): δ 1.38 (q, 2H, CH₂), 1.30 (t, 3H, Al-C-CH₃), 0.99 (s, 6H, C-CH₃), 0.73 (t, 3H, CH₂-CH₃), 0.20 (q, 2H, Al-CH₂). ¹³C NMR (C₅D₆, 23 °C): δ 188.1 (s), 45.0 (s), 33.7 (s), 9.3 (s), 9.2 (s), 1.2 (s). ²⁷Al NMR (toluene, 23 °C): δ 124 (b, s, $\Delta\nu_{1/2}$ = 2500 Hz). IR (neat): 2976 s, 2941 s, 2903 s, 2864 s, 2795 m, 1602 s, 1559 s, 1490 s,

1459 m, 1406 m, 1386 m, 1366 m, 1297 s, 1208 s, 1065 m, 1011 m, 988 s, 950 m, 845 m, 803 m, 699 s, 672 s cm⁻¹.

Polymerization Procedures. In a typical polymerization, 0.003 mmol of the catalyst precursor was weighed in a glovebox and suspended in 5 mL of dry hexane. Al(^{*i*}Bu)₃ (0.042 mL, 0.003 mmol) was added as a 1.0 M solution in hexane. The resulting suspension was continuously stirred at room temperature for 1 h. Isoprene (2.5 mL, 25.0 mmol) in 5 mL of hexane was added via syringe, and the reaction mixture was stirred at room temperature. The polymerization reaction was terminated with methanol and 5% hydrochloric acid. The precipitated polymer was repeatedly washed with methanol and then dried under vacuum at room temperature. All polymers were characterized by ¹H and ¹³C NMR spectroscopy. Compounds **6** and **7** quantitatively generated a plug of polymer in 5–10 min at room temperature. NdCl₃(THF)₄ (**8**) and LaCl₃(pyridine)₄ (**9**) required an overnight reaction period to generate a plug of polymer. In all cases ¹³C NMR spectroscopy indicated high-cis 1,4-polyisoprene content. Compounds **6** and **7** also both polymerized ethylene and styrene. The styrene was run using the same methods as the isoprene reaction with a 21.8 mmol to 0.003 mmol monomer-to-catalyst ratio. Ethylene was polymerized on a vacuum line at atmospheric pressure using the same hexane solutions described above.

X-ray Data Collection, Structure Solution, and Refinement. X-ray crystallographic data were obtained by mounting a crystal on a glass fiber and transferring it to a Bruker CCD platform diffractometer. The SMART¹⁷ program package was used to determine the unit-cell parameters and for data collection (30 s/frame scan time for a sphere of diffraction data for **4** and **5**, 20 s/frame scan time for a sphere of diffraction data for **3** and **9**). The raw frame data were processed using SAINT¹⁸ and SADABS¹⁹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL²⁰ program. The structures were solved by direct methods and refined on *F*² by full-matrix least-squares techniques. The analytical scattering factors²¹ for neutral atoms were used throughout the analysis. Hydrogen atoms were either included using a riding model or located from a

(17) SMART Software Users Guide, Version 5.1; Bruker Analytical X-ray Systems: Madison, WI, 1999.

(18) SAINT Software Users Guide, Version 6.0; Bruker Analytical X-ray Systems: Madison, WI, 1999.

(19) Sheldrick, G. M. SADABS; Bruker Analytical X-ray Systems, Madison, WI, 1999.

(20) Sheldrick, G. M. SHELXTL, Version 5.10; Bruker Analytical X-ray Systems, Madison, WI, 1999.

(21) International Tables for X-ray Crystallography; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C.

difference Fourier map and refined (x , y , z , and U_{iso}). X-ray data collection parameters for **3**–**5** and **9** are given in Table I.

{Nd[O₂CCH(Ph)Et]₃[HO₂CCH(Ph)Et]₂]₂ (3). A pale blue crystal of approximate dimensions 0.21 × 0.30 × 0.32 mm showed no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. There were two uncoordinated acid molecules present per dimeric formula unit. One of the free acid molecules was disordered and included using multiple components with partial site occupancy factors. At convergence, $wR2 = 0.0822$ and $GOF = 1.049$ for 1303 variables refined against 26 472 data. As a comparison for refinement on F , $R1 = 0.0323$ for those 21 485 data with $I > 2.0\sigma(I)$.

{Nd[O₂CC(Me)₂Et]₃(pyridine)₂]₂ (4). A pale purple crystal of approximate dimensions 0.21 × 0.22 × 0.26 mm showed that the diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$, which was later determined to be correct. The molecule was a dimer and was located on an inversion center. Carbon atoms C(15)–C(18) were disordered and included using multiple components with partial site occupancy factors (0.75/0.25; major/minor components). There was one molecule of pyridine present per formula unit. The pyridine was also located about an inversion center and was therefore disordered. It was not possible to distinguish between carbon and nitrogen atoms. Hydrogen atoms associated with the solvent were not included. At convergence, $wR2 = 0.0792$ and $GOF = 1.026$ for 357 variables refined against 4675 data. As a comparison for refinement on F , $R1 = 0.0344$ for those 3771 data with $I > 2.0\sigma(I)$.

{La[O₂CC(Me)₂Et]₃(pyridine)₂]₂ (5). A colorless crystal of approximate dimensions 0.14 × 0.21 × 0.28 mm showed no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. There were two independent molecules of the formula unit present. Each molecule was located on an inversion center. Carbon atoms C(2)–C(6) were disordered and included using multiple components with partial site occupancy factors. There was one molecule of pyridine solvent present per formula unit. At convergence, $wR2 = 0.0888$ and $GOF = 1.031$ for 716 variables refined against 15 118 data. As a comparison for refinement on F , $R1 = 0.0356$ for those 12145 data with $I > 2.0\sigma(I)$.

{LaCl₃(pyridine)₄]₂ (9). A colorless crystal of approximate dimensions 0.17 × 0.23 × 0.30 mm showed that the diffraction symmetry was $2/m$, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$, which was later determined to be correct. The molecule was a dimer and was located on an inversion center. Hydrogen atoms were located from a difference Fourier map and refined (x , y , z , and U_{iso}). At convergence, $wR2 = 0.0467$ and $GOF = 1.057$ for 334 variables refined against 5508 data. As a comparison for refinement on F , $R1 = 0.0188$ for those 5032 data with $I > 2.0\sigma(I)$.

Results

Synthesis of Carboxylate Salts. The preparation of fully characterizable neodymium and lanthanum carboxylates was attempted with a variety of acids, including octanoic acid, versatic acid, 2,2-dimethylbutyric acid, and 2-phenylbutyric acid. Since the last two acids were the only ones which in our hands gave crystallographically characterizable acid salts, initial efforts have focused on these systems. Both systems function as precursors to successful polymerization catalysts, as described later.

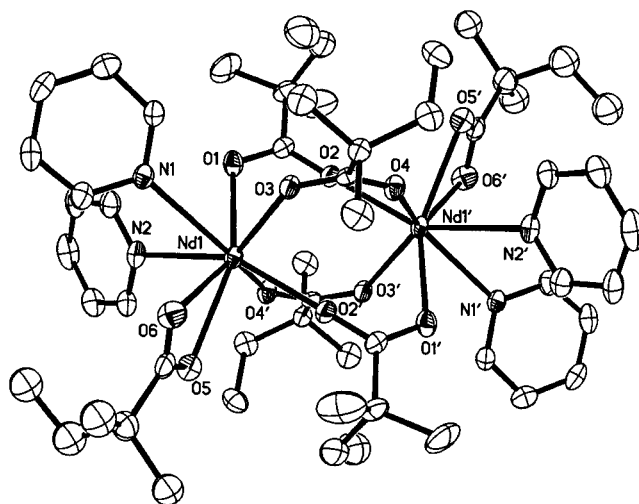
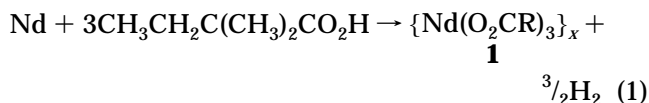


Figure 1. Thermal ellipsoid plot for Nd₂[O₂CC(CH₃)₂CH₂CH₃]₆(pyridine)₄ (**4**), with ellipsoids drawn at the 50% probability level (the hydrogen atoms and pyridine molecule were omitted for clarity).

Reaction of neodymium powder and 2,2-dimethylbutyric acid in toluene in the presence of the 1/1 HgCl₂/Hg(OAc)₂ catalyst frequently used to activate lanthanide metals²² generates {Nd(O₂CR)₃]_x (**1**; R = C(CH₃)₂CH₂CH₃), as a light blue powder in >85% yield in under 4 h according to eq 1. A slight excess of 2,2-dimethylbu-



tyric acid was used to favor the isolation of the product, since the acid can be easily removed with a hexane wash. Elemental analysis on **1** was consistent with a 3/1 carboxylate to Nd composition with no additional carboxylic acid present. Consistent with the assignment of **1** as an acid-free complex, infrared spectroscopy revealed no absorptions attributable to O–H stretching vibrations.

1 could be crystallized from pyridine to generate the pyridine adduct Nd₂(μ-O₂CR)₄(O₂CR)₂(pyridine)₄ (**4**) (Figure 1). Although **4** crystallizes as a dimer in the solid state, isopiestic molecular weight studies indicates that it exists as a monomer in pyridine solution.

To work with a diamagnetic system that would be more amenable to analysis by NMR spectroscopy, the lanthanum analogues of **1** and **4** were prepared. {La(O₂CR)₃]_x (**2**) was obtained in a similarly high yield following the method of eq 1 and crystallized from pyridine as dimeric La₂(μ-O₂CR)₄(O₂CR)₂(pyridine)₄ (**5**) (Figure 2). As found for **4**, isopiestic molecular weight studies on **5** indicated that it exists as a monomer in pyridine solution, rather than a dimer as found in the solid state.

To determine if a crystallographically characterizable neodymium carboxylate complex could be isolated without the presence of coordinating solvents, the bulkier 2-phenylbutyric acid was used. Nd₂(O₂CR')₆(HO₂CR') (**2**; R' = CH(C₆H₅)CH₂CH₃) was synthesized in the same manner as **1** from neodymium powder and 2-phenylbu-

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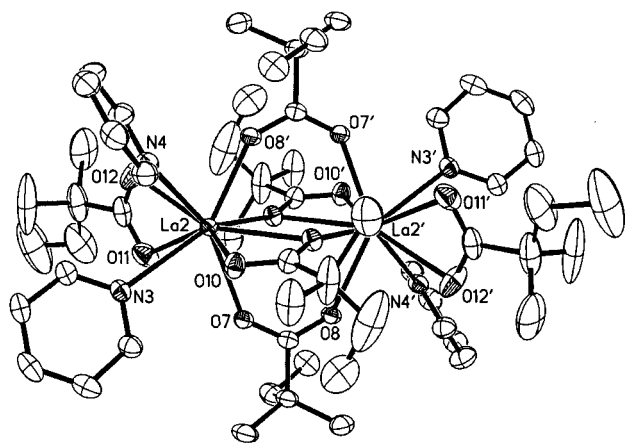
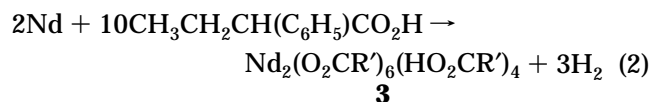


Figure 2. Thermal ellipsoid plot for $\text{La}_2[\text{O}_2\text{CC}(\text{CH}_3)_2\text{CH}_2\text{CH}_3]_6(\text{pyridine})_4$ (**5**), with ellipsoids drawn at the 50% probability level (the hydrogen atoms and pyridine molecule were omitted for clarity).

tyric acid (eq 2). However, this required a large excess

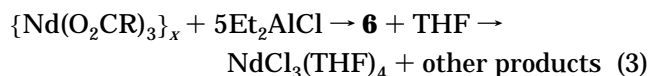


of 2-phenylbutyric acid to favor isolation of the complex. The product of the reaction was initially isolated as a viscous purple oil, but crystallization from hexane gave **3** as purple cubic crystals. X-ray crystallographic analysis revealed another dimeric structure, $\text{Nd}_2(\mu\text{-O}_2\text{CR}')_4(\text{O}_2\text{CR}')_2(\text{HO}_2\text{CR}')_4$ (Figure 3), which in this case contains coordinated carboxylic acids. Consistent with this, the IR spectrum of **3** contained additional absorptions compared to the spectra of **1** and **2** in the OH stretching region.

Structural Aspects of 3–5. Figure 4 diagrammatically compares the structures of **3–5**, and Tables 2 and 3 show selected bond distances. All three complexes are similar in that they are dimeric with four bridging carboxylates, two terminal carboxylates, and four terminal base adduct ligands. Complexes **4** and **5** have pyridine molecules as the base adducts, whereas **3** has a monodentate carboxylic acid in this position. Subtle differences exist between the complexes in terms of how the carboxylates bridge. Hence, in **4** all of the bridging carboxylates are $\eta^1:\eta^1$ -carboxylates, which gives a coordination number of 8 to the metal. In **3** and **5**, two of the four bridging carboxylates are $\eta^1:\eta^2$, giving the metal a coordination number of 9. Both bridging carboxylate modes are common for lanthanide carboxylates, but it is interesting that the La/pyridine adduct combination **5** matches the Nd/carboxylic acid adduct combination **3** rather than the Nd/pyridine adduct combination **4**. One might expect that the La/pyridine adduct would prefer a higher coordination number than the Nd/pyridine complex, since lanthanum is larger. However, it is not as easy to rationalize why the carboxylic acid adduct **3** would prefer a higher coordination number than the pyridine adduct. The Nd–O(terminal carboxylic acid) distances are in the 2.50–2.55 Å range, compared to 2.72–2.73 Å for Nd–N(pyridine) distances. Hence, the carboxylic acid approaches closer to the metal and one might think this would cause the complex to be more crowded and generate the eight-coordinate structure.

Reactivity of 1 and 2 with Et_2AlCl . Reaction of $\{\text{Nd}(\text{O}_2\text{CR})_3\}_x$ (**1**) with 2.5 equiv of Et_2AlCl in hexane in a glovebox free of coordinating solvents yields the solid product **6** and a solution from which $\text{Et}_2\text{Al}(\text{O}_2\text{CR})$ (**10**) can be isolated as a colorless liquid. **10** was characterized by IR and ^1H , ^{13}C , and ^{27}Al NMR spectroscopy.

Crystallization of **6** from THF at room temperature formed $\text{NdCl}_3(\text{THF})_4$ (eq 3), which was identified by X-ray crystallography as being identical with the structure previously reported in the literature.²³ The isolation

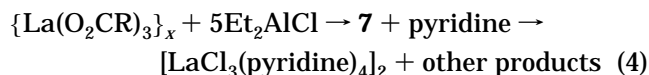


of $\text{NdCl}_3(\text{THF})_4$ from **6** is consistent with the literature view that the purpose of Et_2AlCl is to prepare NdCl_3 .^{6,10}

However, elemental analysis of **6** revealed that it was not simply NdCl_3 : the elemental composition was found to be $\text{Nd}_2\text{AlCl}_5\text{C}_{13}\text{H}_{22}$. The ^1H NMR spectrum of the solution of **6** in THF from which $\text{NdCl}_3(\text{THF})_4$ crystallized revealed several peaks that could be attributed to ethyl groups on aluminum and the methyl and ethyl groups of the carboxylate O_2CR . Attempts to crystallize **6** in the absence of coordinating solvents, to determine how the chloride, ethyl, and carboxylate ligands are arranged around the Nd and Al atoms, have not been successful.

To check for the presence of ethyl groups in **6**, a sample was treated with D_2O in a Toepler pump system and the evolved gas was identified by GC-MS as $\text{CH}_3\text{-CH}_2\text{D}$. Further evidence for the presence of ethyl groups was obtained from a reaction of **6** with CO_2 in toluene. A reaction occurred, and the alkyl region of the soluble component was shifted compared to that described above. Unfortunately, the goal to obtain crystallographically characterizable material from this derivatization was not achieved.

Parallel treatment of the diamagnetic lanthanum analogue $\{\text{La}(\text{O}_2\text{CR})_3\}_x$ (**2**) with 2.5 equiv of Et_2AlCl per La in hexane in a glovebox free of coordinating solvents gave the solid product **7** and a solution from which $\text{Et}_2\text{-Al}(\text{O}_2\text{CR})$ (**10**) was again isolated. Unlike **6**, complex **7** did not dissolve in THF. Instead, pyridine was necessary to form a solution and from this pyridine solution were isolated crystals of $[\text{LaCl}_3(\text{pyridine})_4]_2$ (**9**; eq 4, Figure



5). However, as in the case of **6**, elemental analysis revealed that **7** was more than just LaCl_3 . The analysis on **7** revealed the following composition: $\text{La}_2\text{AlCl}_5\text{C}_{12}\text{H}_{21}$. The ^1H NMR spectrum of the solution of **7** in pyridine from which $[\text{LaCl}_3(\text{pyridine})_4]_2$ crystallized contained several sets of resonances attributable to carboxylate methyl and ethyl groups, but it contained too many other peaks in the alkyl region to allow definitive identification of a single compound. Compound **7** also reacts with D_2O to form $\text{CH}_3\text{CH}_2\text{D}$.

Structure of $[\text{LaCl}_3(\text{pyridine})_4]_2$ (9**).** Complex **9** differs from most $\text{LaCl}_3(\text{donor ligand})_x$ complexes in the

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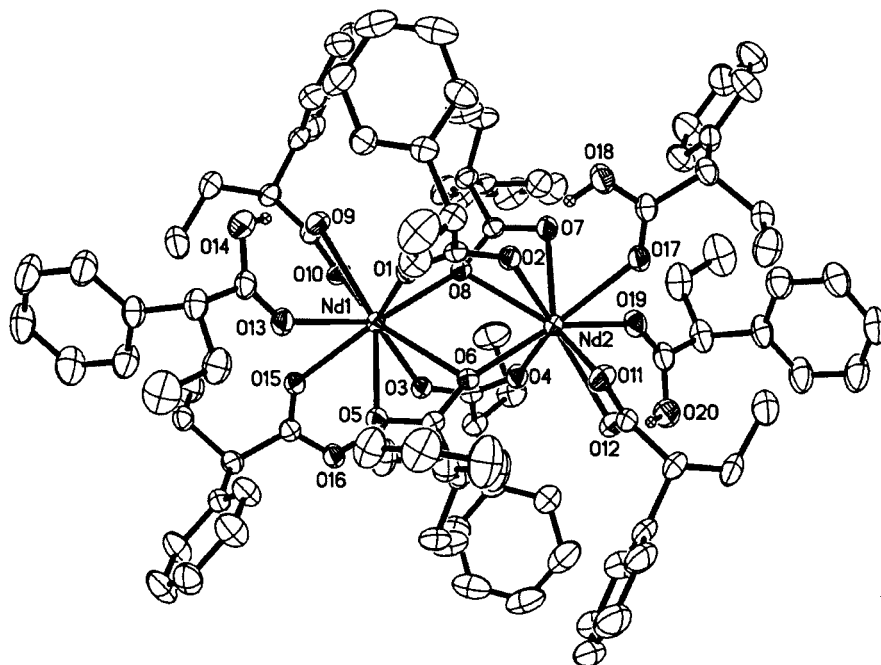


Figure 3. Thermal ellipsoid plot for $\text{Nd}_2[\text{O}_2\text{CCH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_3]_6[\text{HO}_2\text{CCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_3]_4$ (**3**), with ellipsoids drawn at the 50% probability level (the hydrogen atoms and free acid molecules were omitted for clarity).

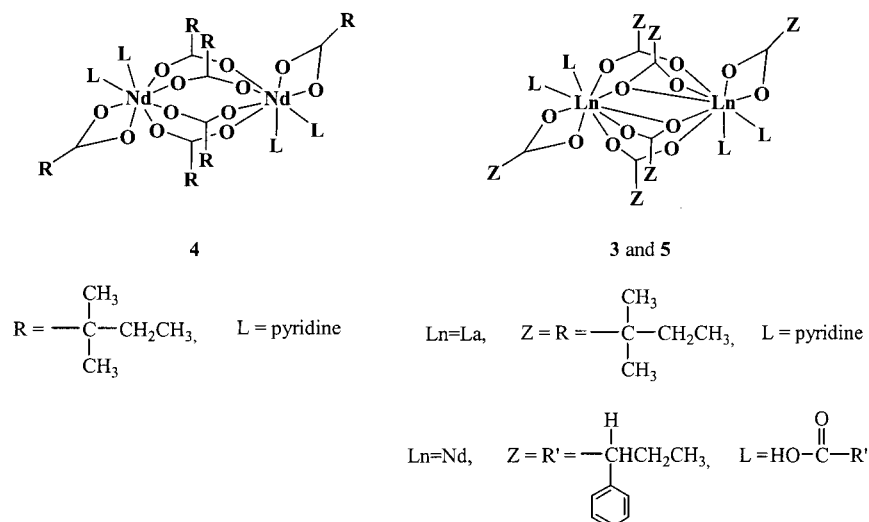


Figure 4. Schematic drawings of $\text{Nd}_2(\text{O}_2\text{CR})_6(\text{HO}_2\text{CR}')_4$ (**3**), $\text{Nd}_2(\text{O}_2\text{CR})_6(\text{pyridine})_4$ (**4**), and $\text{La}_2(\text{O}_2\text{CR})_6(\text{pyridine})_4$ (**5**).

Table 2. Bond Distances (Å) in $\text{Nd}_2(\text{O}_2\text{CR})_6(\text{pyridine})_4$ (4**) and $\text{La}_2(\text{O}_2\text{CR})_6(\text{pyridine})_4$ (**5**)**

	4	5		4	5
$\text{Ln}(1)\text{---O}(1)$	2.434(3)	2.473(2)	$\text{Ln}(1)\text{---O}(5)$	2.545(3)	2.625(2)
$\text{Ln}(1)\text{---O}(2)'$	2.360(3)	2.468(2)	$\text{Ln}(1)\text{---O}(6)$	2.494(3)	2.517(2)
$\text{Ln}(1)\text{---O}(3)$	2.384(3)	2.725(2)	$\text{Ln}(1)'\text{---O}(3)$	<i>a</i>	2.488(2)
$\text{Ln}(1)\text{---O}(3)'$	<i>a</i>	2.488(2)	$\text{Ln}(1)\text{---N}(1)$	2.727(4)	2.809(3)
$\text{Ln}(1)\text{---O}(4)'$	2.381(3)	2.537(2)	$\text{Ln}(1)\text{---N}(2)$	2.729(4)	2.777(3)

^a Not bonded.

literature^{24,25} in that it contains a formally eight-coordinate lanthanum rather than the usual seven-coordinate metal. However, examination of the coordination geometry around the metal shows that it is so

Table 3. Bond Distances (Å) in $\text{Nd}_2(\text{O}_2\text{CR})_6(\text{HO}_2\text{CR}')_4$ (3**)**

$\text{Nd}(1)\text{---O}(1)$	2.4065(16)	$\text{Nd}(2)\text{---O}(2)$	2.4646(16)
$\text{Nd}(1)\text{---O}(3)$	2.4836(16)	$\text{Nd}(2)\text{---O}(4)$	2.4176(17)
$\text{Nd}(1)\text{---O}(5)$	2.4493(16)	$\text{Nd}(2)\text{---O}(6)$	2.3594(16)
$\text{Nd}(1)\text{---O}(6)$	2.6253(16)	$\text{Nd}(2)\text{---O}(7)$	2.4590(17)
$\text{Nd}(1)\text{---O}(8)$	2.3612(16)	$\text{Nd}(2)\text{---O}(8)$	2.6151(16)
$\text{Nd}(1)\text{---O}(9)$	2.5485(17)	$\text{Nd}(2)\text{---O}(11)$	2.5435(17)
$\text{Nd}(1)\text{---O}(10)$	2.5432(17)	$\text{Nd}(2)\text{---O}(12)$	2.5375(17)
$\text{Nd}(1)\text{---O}(13)$	2.5384(17)	$\text{Nd}(2)\text{---O}(17)$	2.5046(16)
$\text{Nd}(1)\text{---O}(15)$	2.4999(16)	$\text{Nd}(2)\text{---O}(1)$	2.5190(17)

distorted from typical eight-coordinate geometries that it is, in fact, quite close to the seven-coordinate systems. Conventional eight-coordinate geometries are ruled out by the fact that chlorides Cl(1), Cl(3), and Cl(3') are nearly coplanar and define an isosceles triangle. However, complex **9** can be viewed as a distorted pentagonal bipyramid if the two bridging chlorides are considered to occupy a single axial coordination site, as is sometimes done with small-bite chelating ligands.^{26–29} Cl(1)

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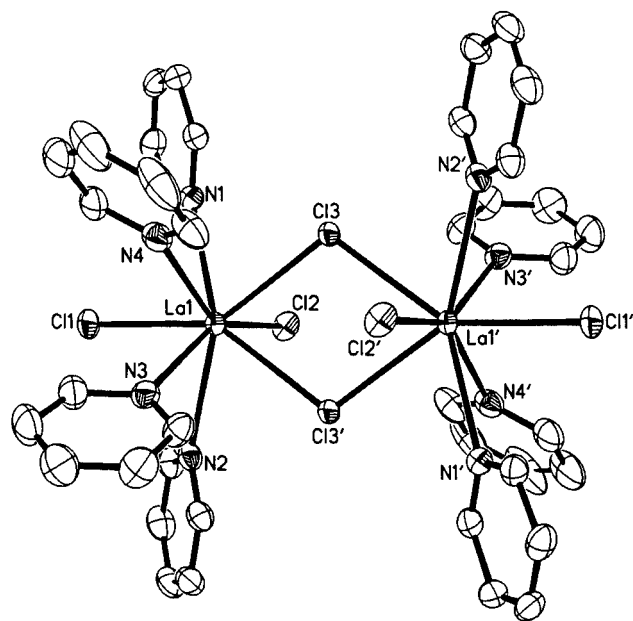


Figure 5. Thermal ellipsoid plot for $[\text{LaCl}_3(\text{pyridine})_4]_2$ (**9**), with ellipsoids drawn at the 50% probability level (the hydrogen atoms were omitted for clarity).

Table 4. Bond Distances (Å) in $[\text{LaCl}_3(\text{pyridine})_4]_2$ (**9**)

La(1)–Cl(1)	2.7778(4)	La(1)–N(1)	2.7577(15)
La(1)–Cl(2)	2.7859(5)	La(1)–N(2)	2.7798(16)
La(1)–Cl(3)	2.9287(4)	La(1)–N(3)	2.7886(16)
La(1')–Cl(3')	2.9169(4)	La(1)–N(4)	2.7221(17)

would be in one axial site, and the chelating Cl(3)–La–Cl(3') unit in the other axial site. The remaining five ligands are not coplanar, but they are located in a roughly pentagonal arrangement around the Cl(1)–La–[Cl(3)–La–Cl(3')] axis previously described. Consistent with this, the La–Cl bond distances are very similar to those in dimeric $[\text{LaCl}_3(\text{PrOH})_3]_2$, the seven-coordinate pentagonal-bipyramidal lanthanum chloride complex most closely related to **9** in the literature.²⁴ Table 4 lists the bond distances for **9**.

Polymerization Reactivity. To ensure that these carboxylates were relevant to diene polymerization, polymerization reactions were examined with several samples. Treatment of **6** and **7** with 1 equiv of triisobutylaluminum in hexane generates catalyst precursors which consume a 7500-fold excess of isoprene in 5–10 min to make a plug of polymer which shows only resonances for *cis*-1,4-polyisoprene by ¹³C NMR spectroscopy. Compounds **6** and **7**, activated by 1 equiv of isobutylaluminum, also polymerize ethylene and styrene. $\text{NdCl}_3(\text{THF})_4$ and $[\text{LaCl}_3(\text{pyridine})_4]_2$ react with triisobutylaluminum to make systems which polymerize isoprene, but an excess of triisobutylaluminum is needed and reactions require at least 12 h. The reduced activity is, as expected, due to the presence of the coordinating bases.

Discussion

Pure samples of neodymium and lanthanum carboxylate salts can be conveniently prepared from the metal powder and the acid in air. 2,2-Dimethylbutyric acid gives salts which can be fully characterized by X-ray crystallography as pyridine adducts. These crystallographic data are valuable for complete identification of these catalytic precursors, but they did not reveal any unusual bonding. The complexes crystallize from pyridine as dimeric pyridine adducts. Dimers are commonly observed for lanthanide carboxylates.^{30–35} Solution molecular weight studies indicated that in pyridine the complexes exist as monomers, which again is not unusual for lanthanide carboxylates.³⁶

In contrast to the 2,2-dimethylbutyric acid system, 2-phenylbutyric acid gives a complex which crystallizes without any additional base, as a carboxylic acid adduct. The fact that the carboxylate precursors to the diene polymerization catalysts can form as carboxylic acid adducts could explain why excess alkylaluminum reagents are frequently used in subsequent steps to prepare diene polymerization catalysts. Some of the extra equivalents of alkylaluminum may simply react with the excess carboxylic acid to make alkane and aluminum carboxylate salts. This suggests that the amount of alkylaluminum reagent used in these catalyst preparations could be reduced if acid-free carboxylate salts were used as precursors.

The subtle structural differences between the neodymium and lanthanum analogues, **4** and **5**, are worth noting, since neodymium is normally the metal of choice for diene polymerizations. Generally trivalent lanthanide ions of similar size have similar properties, and one might have expected that these ions, which differ in size by only 0.066 Å,¹² would give structurally similar products. On the other hand, it is also well-known for the lanthanides that, for a given chemical property, there is often a change along the series as a function of size. Hence, the larger trivalent ions from La–Sm are nine-coordinate in aqueous solutions, while the smaller ions Eu–Lu are eight-coordinate. Hydrogenolysis of $\text{Cp}_2\text{Er}(\text{CMe}_3)(\text{THF})$ and $\text{Cp}_2\text{Y}(\text{CMe}_3)(\text{THF})$ works well in THF, but the identical reaction with the smaller metals Yb and Lu gives almost no product at all.³⁷ There are many examples of this in the literature, and the point of discontinuity can be anywhere in the series.

The reaction of Et_2AlCl with the carboxylates proceeds in part as predicted in the literature; i.e., it functions to substitute some carboxylate ligands with chloride ligands. However, detailed analysis of the {Nd-

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(O₂CR)₃}/Et₂AlCl reaction product, **6**, shows that this reaction does not simply make NdCl₃ as suggested in some reports. The formation of NdCl₃(THF)₄ by crystallization of **6** from THF suggests that **6** is NdCl₃, but elemental analysis shows that **6** contains Al in a 2:1 Nd:Al ratio and the Nd:Cl ratio is only 2:5, not 2:6. This exemplifies the well-known, but sometimes overlooked, fact that the species that crystallizes from solution may not be totally representative of the sample crystallized. Similar results are obtained for the lanthanum analogue, except in the case of lanthanum, the {La(O₂CR)₃}/Et₂AlCl reaction product, **7**, is not soluble in THF and pyridine must be used to achieve solubility.

The differing solubilities of the La and Nd products of the {Ln(O₂CR)₃}/Et₂AlCl reaction is another point of difference between these similarly sized metals. One might expect similar solubility from these two products. Apparently, in the {Ln(O₂CR)₃}/Et₂AlCl reaction systems, there is a discontinuity between La and Nd. The lower solubility of lanthanum could be rationalized by the fact that this larger metal may be coordinatively unsaturated compared to neodymium and may form additional bridging interactions with the ligands present, which could lower the solubility. Preliminary results on a samarium analogue of **6** and **7** show that it is also THF soluble, which is consistent with this trend.

The detailed composition of **6** and **7** cannot be inferred from the data available. However, it seems well-established that the reaction of these lanthanide carboxylates with ethylaluminum chloride does not simply make the metal trichlorides. The product contains aluminum, as well as ethyl groups. The presence of carboxylate groups is also indicated by the elemental analysis and NMR data. It is tempting to use the analytical data to propose a Ln₂AlCl₅(Et)₂(O₂CR) type of composition for this intermediate to the active catalyst. However, it is better not to overinterpret the data and conclude only that these intermediates are complicated and have the component parts mentioned above. It will be most interesting to see how these

compositions affect the polymerization reactivity following the isobutylaluminum activation.

Conclusions

It is possible to fully characterize neodymium and lanthanum carboxylate salts that successfully function as precursors to active diene polymerization catalysts. These carboxylates can be conveniently made from the elemental metals and carboxylic acids and generally form adducts with available Lewis bases. In some cases, the Lewis base can be the parent carboxylic acid, such that the metal carboxylate may contain reactive proton sources. This may explain why excess aluminum reagents are often needed to form an active catalyst.

The carboxylates react with Et₂AlCl to make mixed metal ligand compounds which contain minimally the lanthanide and aluminum as well as halide and ethyl ligands. These species give simple LnCl₃ compounds upon crystallization with coordinating solvents, but they are evidently more complicated than LnCl₃ alone. Hence, the role of the Et₂AlCl reagent in the diene polymerization catalyst preparation is to deliver chloride ligands to replace carboxylate ligands, but it is not necessarily there solely to make LnCl₃.

The lanthanum analogues in this study display chemistry very similar to that for the neodymium systems. However, subtle differences in structure and solubility are apparent between the lanthanum and neodymium analogues, which may provide clues as to why neodymium is often the favored metal for diene polymerizations.

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