ORGANOMETALLICS

Volume 21, Number 22, October 28, 2002

Communications

Rare-Earth Ziegler−Natta Catalysts: Carboxylate−Alkyl Interchange

Andreas Fischbach, Franc Perdih, Peter Sirsch, Wolfgang Scherer, and
Reiner Anwander*

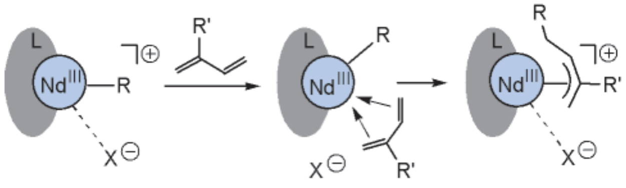
*Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4,
D-85747 München, Germany*

Received July 9, 2002

Summary: Alkylated rare-earth-metal centers are definitely formed in "Mischkatalysatoren": the homoleptic, tailor-made rare-earth carboxylate complexes $\{Ln(O_2CC_6H_2iPr_3\text{-}2,4,6)_3\}_n$ *(Ln = Y, La, Nd, Lu) react with trimethylaluminum to yield hexane-soluble monolanthanide complexes of the larger elements featuring a* η^2*-coordinating tetraalkylaluminate ligand and a novel ancillary* $AlMe_2$*-bridged bis(carboxylate) ligand. In the presence of* $AlMe_2Cl$*, such alkylated derivatives transform isoprene to a high-cis polymer (>99%).*

Ziegler−Natta multicomponent systems represent one of the few classes of homogeneous rare-earth catalysts which are applied commercially. Stereospecific polymerization of 1,3-dienes, e.g., butadiene, isoprene, and 2,3-dimethylbutadiene, is efficiently initiated by neodymium-based catalysts for the industrial-scale production of high-quality synthetic rubbers (cis 1,4-polymers).[1,2] Such empirically designed ternary catalytic systems comprise Nd(III) carboxylates (also alkoxides or halides), aluminum alkyl halides, and aluminum alkyls or aluminum alkyl hydrides.[3−7] Typically, the carboxylic acids, which are provided as mixtures of isomers from petrochemical plants (octanoic, versatic, naphthenoic acids), are carrying solubilizing aliphatic substituents. Although cationic alkyl or hydrido Nd(III) sites are proposed to promote 1,3-diene polymerization via an allyl insertion mechanism (Scheme 1), details of the polymerization mechanism and of the structure of the catalytically active center are elusive.[8−10]

Scheme 1. Proposed Intermediates of the Rare Earth (Neodymium) Catalyzed Polymerization of Conjugated Dienes[a]



[a] R = H, alkyl, R′ = H, Me, X = halide, L = carboxylate.

---

* To whom correspondence should be addressed. Fax: +49 89 289 13473. E-mail: reiner.anwander@ch.tum.de.

(1) Shen, Z.; Ouyang, J. In *Handbook on the Physics and Chemistry of Rare Earth*; Gschneidner, K. A., Jr., Fleming, L., Eds.; Elsevier Science Publishers: Amsterdam, 1987; Chapter 61.

(2) Taube, R.; Sylvester, G. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996; Vol. 1, pp 280−318.

(3) Porri, L.; Ricci, G.; Shubin, N. *Macromol. Symp.* **1998**, *128*, 53−61.

(4) Oehme, A.; Gebauer, U.; Gehrke, K.; Beyer, P.; Hartmann, B.; Lechner, M. D. *Macromol. Chem. Phys.* **1994**, *195*, 3773−3781.

(5) Wilson, D. J. *Macromol. Chem., Macromol. Symp.* **1993**, *66*, 273−288.

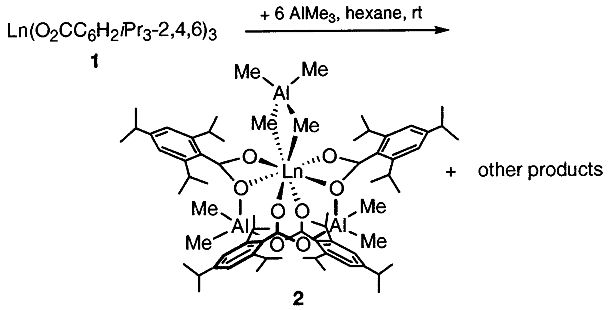
(6) Yunlu, K.; He, M.; Cuif, J.-P.; Alas, M. U.S. Patent 6,111,082, 2000.

(7) Porri, L.; Giarrusso, A. In *Comprehensive Polymer Sciene*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 4, Part II, pp 53−108.

(8) Taube, R.; Maiwald, S.; Sieler, J. *J. Organomet. Chem.* **2001**, *621*, 327−336 and references therein.

10.1021/om0205389 CCC: $22.00 © 2002 American Chemical Society
Publication on Web 09/24/2002

Scheme 2. Synthesis of Mixed Aluminate Carboxylate Complexes 2



Herein, we describe the synthesis and characterization of a new class of structurally well-defined heterobimetallic carboxylates. Tailor-made, well-defined rare-earth carboxylates were employed in order to investigate their reactivity toward aluminum alkyl reagents. Trimethylaluminum not only disrupts the oligomeric structure of $\{Ln(O_2CC_6H_2iPr_3\text{-}2,4,6)_3\}_n$ but also alkylates the rare-earth-metal center by formation of a tetramethylaluminate ligand. To our knowledge this is the first structural evidence for a carboxylate−alkyl interchange. Moreover, dimethylaluminum-bridged carboxylate moieties, which are probably formed in situ via a rare-earth-cation templating effect, constitute a new type of ancillary ligand.

The new homoleptic lanthanide carboxylates $\{Ln(O_2CC_6H_2iPr_3\text{-}2,4,6)_3\}_n$ (**1**; Ln = Y (**a**), La (**b**), Nd (**c**), Lu (**d**)) were obtained quantitatively by the reaction of $[Ln\{N(SiMe_3)_2\}_3]$ with 3 equiv of triisopropylbenzoic acid.[11] Addition of an excess of trimethylaluminum to a suspension of complexes **1** in hexane gave heterobimetallic complexes of net composition $[LnAl_3Me_8(O_2CC_6H_2iPr_3\text{-}2,4,6)_4]$ (Scheme 2).[12] The lanthanum (**2b**) and neodymium (**2c**) complexes are readily soluble in hexane and were obtained in ca. 45% yield after recrystallization. The smaller yttrium (**2a**) and lutetium (**2d**) derivatives dissolve in toluene (yield ca. 35%).

^1H NMR spectroscopic investigations at 25 °C clearly revealed two signals in the alkyl region. For example, the corresponding resonances of complex **2a** (**2b**) appeared at −0.08 (0.13) and −0.41 (−0.62) ppm in a 1:1 ratio. At lower temperatures, the higher field shifted aluminate resonance separates into two well-resolved signals at −0.17 (−0.24) and −0.80 (−1.05) ppm (−80 °C), attributable to bridging (broad signal, no ^{89}Y coupling) and terminal alkyl groups. The relatively lower coalescence temperature of −60 °C for **2b** compared to that for **2a** (−10 °C) is consistent with increased steric unsaturation and more rapid alkyl exchange at the larger metal center.

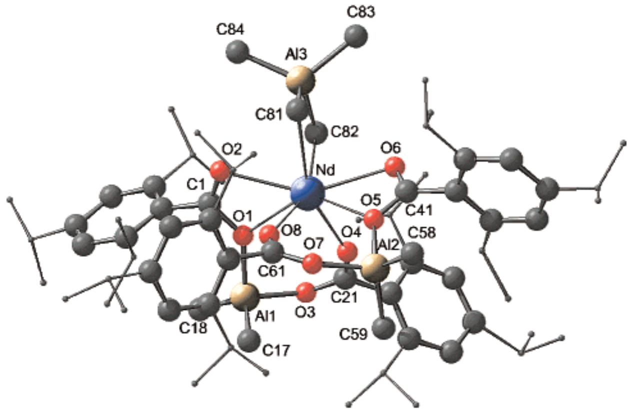


Figure 1. SCHAKAL drawing of the complex $[\{AlMe_2(O_2CC_6H_2iPr_3\text{-}2,4,6)_2\}_2NdAlMe_4]$ (**2c**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Nd−C(81) = 2.650(2), Nd−C(82) = 2.659(2), Nd−O(1) = 2.555(2), Nd−O(2) = 2.523(2), Nd−O(4) = 2.359(2), Nd−O(5) = 2.577(2), Nd−O(6) = 2.523(2), Nd−O(8) = 2.350(2), Al(3)−C(81) = 2.065(3), Al(3)−C(82) = 2.068(3), Al(3)−C(83) = 1.969(3), Al(3)−C(84) = 1.956(3), Al(1)−C(17) = 1.934(3), Al(1)−C(18) = 1.936(3), Al(2)−C(58) = 1.937(3), Al(2)−C(59) = 1.935(3), Al(1)−O(1) = 1.860(2), Al(1)−O(3) = 1.828(2), Al(2)−O(5) = 1.851(2), Al(2)−O(7) = 1.813(2), C(1)−O(1) = 1.314(3), C(1)−O(2) = 1.222(3), C(21)−O(3) = 1.271(3), C(21)−O(4) = 1.255(3), C(41)−O(5) = 1.315(3), C(41)−O(6) = 1.232(3), C(61)−O(7) = 1.270(3), C(61)−O(8) = 1.250(3); C(81)−Nd−C(82) = 79.83(8), O(1)−Nd−O(2) = 50.61(5), O(1)−Nd−O(4) = 72.87(5), O(5)−Nd−O(6) = 50.52(5), O(5)−Nd−O(8) = 72.81(5), C(81)−Al(3)−C(82) = 111.0(1), O(1)−Al(1)−O(3) = 96.72(8), O(5)−Al(2)−O(7) = 96.88(8).

The molecular structure of complex **2c** was unequivocally revealed by an X-ray structural determination (Figure 1).[13] The neodymium atom is eight-coordinated by one η^2-coordinating tetramethylaluminate ligand and six oxygen atoms of four carboxylate ligands, resulting in an inner coordination sphere of local C_2 symmetry. The average Nd−C(μ-Me) distance of 2.655 Å is elongated compared to those in homoleptic six-coordinated $Nd(AlMe_4)_3$ (average 2.590 Å).[14] Each of the two $AlMe_2$-bridged bis(carboxylate) ligands coordinates the neody-

---

(9) (a) Kaita, S.; Hou, Z.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 9078−9079. (b) Kaita, S.; Hou, Z.; Wakatsuki, Y. *Macromolecules* **2001**, *34*, 1539−1541.

(10) (a) Kwag, G.; Lee, H.; Kim, S. *Macromolecules* **2001**, *34*, 5367−5369. (b) Sabirov, Z. M.; Minchenkova, N. K.; Monakov, Y. B. *Vysokomol. Soedin., Ser. B* **1990**, *11*, 803−804. (c) Porri, L.; Ricci, G.; Giarrusso, A.; Shubin, N.; Lu, Z. *ACS Symp. Ser.* **2000**, *No. 749*, 15−30.

(11) (a) Compounds **1** crystallize from DMSO to give mononuclear (Y) and carboxylate-bridged dinuclear (La) complexes: Unpublished results. (b) For the use of the silylamide route to prepare rare-earth carboxylate complexes, see: Spino, C.; Clouston, L. L.; Berg, D. J. *Can. J. Chem.* **1997**, *75*, 1047−1054.

(12) Representative synthesis and characterization of **2b**: in an argon-filled glovebox, $AlMe_3$ (216 mg, 3.00 mmol) was added to tricarboxylate **1b** (439 mg, 0.50 mmol) suspended in *n*-hexane. Within several minutes a clear solution formed. After additional stirring for 16 h, the reaction mixture was filtered and the solvent removed in vacuo. After it was dried for several hours to remove excess trimethylaluminum, the solid was dissolved in *n*-hexane and crystallized at −45 °C to yield **2b** (298 mg, 45%) as a colorless solid. IR (Nujol, cm^{-1}): 1618 m, 1527 s, 1425 s, 1365 s, 1350 m, 1331 m, 1316 m, 1196 w, 1150 w, 1108 w, 1086 w, 940 w, 877 m, 779 w, 698 s, 632 w, 592 w, 489 w, 459 w, 406 w. Anal. Calcd for $C_{72}H_{116}Al_3LaO_8$: C, 65.04; H, 8.79. Found: C, 64.76; H, 9.50. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 7.06 (s, 8 H, Ar *H*), 3.27 (septet, $^3J_{HH} = 7.0$ Hz, 8 H, *o*-*i*Pr), 2.72 (septet, $^3J_{HH} = 6.6$ Hz, 4 H, *p*-*i*Pr), 1.28 (d, $^3J_{HH} = 7.0$ Hz, 48 H, *o*-*i*Pr), 1.17 (d, $^3J_{HH} = 6.6$ Hz, 24 H, *p*-*i*Pr), 0.13 (s, 12 H, $AlMe_2$), −0.62 (s, 12 H, $AlMe_4$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 183.3/151.4/144.8/131.8/121.3/34.8/32.2/24.6/24.0/3.9/−10.8.

(13) Crystal data for **2c**: $C_{72}H_{116}Al_3NdO_8$, $M_r = 1334.74$, triclinic, space group $P\bar{1}$, $a = 14.7684(1)$ Å, $b = 14.8321(1)$ Å, $c = 21.9615(2)$ Å, $\alpha = 77.5941(3)°$, $\beta = 71.9592(4)°$, $\gamma = 76.2673(4)°$, $V = 4391.01(6)$ Å^3, $Z = 2$, $D_c = 1.0095(1)$ g cm^{-3}, $F(000) = 1422$, KappaCCD (Nonius) Mo-rotating anode ($\lambda = 0.71073$ Å), $T = -160$ °C, $R = 0.0325$, $R_w = 0.0821$, GOF = 0.970. The disorder of one phenyl ring and its isopropyl substituents is described in the Supporting Information. A potentially accessible area of 870 Å^3 has been calculated for **2c**. Due to severe disorder no solvent molecule, which was identified as hexane by NMR, could be located. Thus, the BYPASS method was applied to account for the disordered solvent contribution to the structure factor in the final refinement.

(14) Evans, W. J.; Anwander, R.; Ziller, J. W. *Organometallics* **1995**, *14*, 1107−1109.

mium center asymmetrically in a new η^3 fashion by forming fused four- and six-membered (heterobi)metallacycles (coordination modes are referred to the neodymium center). The η^2-coordinating carboxylate moiety exhibits two similar Ln−O bond lengths in the range of 2.522(2)−2.577(2) Å, which are comparable to the Nd−O distances of the chelating bidentate carboxylate ligands in nine-coordinated neodymium(III) butyrate, $Nd(C_3H_7CO_2)_3 \cdot H_2O$ (2.490(10), 2.582(8) Å).[15] The average Nd−O bond length of 2.354 Å of the η^1-coordinating carboxylate moiety is significantly shorter than that of the μ,η^1: η^1-coordinating carboxylate ligand in $Nd(C_3H_7CO_2)_3 \cdot H_2O$ (2.421(9), 2.470(9) Å).[15,16] In comparison, the dinuclear complexes $\{(CF_3CO_2)_3NdAlHR_2(THF)_2\}_2$ (R = Et, *i*Bu), prepared from $\{(CF_3CO_2)_2NdCl\}$ and R_2AlH, feature nine-coordinated neodymium centers and two types of bridging carboxylate ligands: μ,η^1: η^1-(O_2CCF_3) and μ,η^3: η^1-$\{(O_2CCF_3)_2AlMe_2\}$.[17]

$AlMe_3$-mediated formation of lanthanide carbon bonds has been reported previously for amide → alkyl and silylamide → alkyl transformations,[14,18] while the displacement of alkoxide ligands in the presence of organoaluminum compounds has been discussed contrarily.[19,20] Given the higher coordination ability of chelating carboxylate moieties relative to alkoxide ligands, a carboxylate → alkyl transformation is remarkable. Complexes **2** form in constant yields when the precursor carboxylates **1** are reacted with >6 equiv of $AlMe_3$. The more soluble coproducts have not yet been fully identified; however, ^{1}H NMR spectroscopic examinations indicated the formation of at least two additional metal alkyl species. Note that complexes **2** do not form according to a simple ligand redistribution process, because the η^3-coordinating monoanionic ligand $[AlMe_2(O_2CC_6H_2iPr_3\text{-}2,4,6)_2]$ seems to be generated only by a rare-earth-cation-templated reaction.[21,22] This is reinforced by the absence of any $[AlMe_2(O_2CC_6H_2iPr_3\text{-}2,4,6)]$ coproduct.[23] Moreover, if complexes **2** are real intermediates of the formation of the active species, their peculiar solubility behavior might significantly contribute to their catalytic performance in "homogeneous" diene polymerization. Note that the "large" neodymium—in the present examination the more soluble system—supposedly displays the most efficient rare-earth-metal center.

Preliminary catalytic investigations show that hexane-soluble neodymium complex **2c** polymerizes isoprene when combined with Et_2AlCl as a cocatalyst. Polymer yield and cis content (by ^{13}C NMR spectroscopy) depend, as expected,[24] on the lanthanide-to-halide ratio (**2c**:Et_2AlCl = 1:1, 62% conversion, 94% *cis*-1,4-polyisoprene; **2c**:Et_2AlCl = 1:5, 35% conversion, >99% *cis*-1,4-polyisoprene; monomer-to-neodymium ratio of 1000; a coactivating third component such as $AlHiBu_2$ is not necessary).

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and Prof. W. A. Herrmann for financial support.

Supporting Information Available: Tables giving crystallographic data for **2c** and text giving experimental details for **1a**−**d** and **2a**−**d**. This information is available free of charge via the Internet at http://pubs.acs.org.

OM0205389

---

(15) Binnemanns, K.; Jongen, L.; Bromant, C.; Hinz, D.; Meyer, G. *Inorg. Chem.* **2000**, *39*, 5938−5945.

(16) For the structural characterization of rare-earth carboxylates in dimeric and polymeric forms, see: Ouchi, A.; Suzuki, Y.; Ohki, Y.; Koizumi, Y. *Coord. Chem. Rev.* **1988**, *92*, 29−43. (b) The μ,η^2:η^1-carbonate ligands in $[Co(NH_3)_6]_6[K_2(H_2O)_{10}][Nd_2(CO_3)_8]_2 \cdot 20H_2O$ exhibit bond lengths of 2.475(5)−2.547(5) and 2.398(5)−2.438(5) Å, respectively.

(17) Shen, Q.; Chen, W.; Jin, Y.; Shan, C. *Pure Appl. Chem.* **1998**, *60*, 1251−1256.

(18) Klimpel, M. G.; Anwander, R.; Tafipolsky, M.; Scherer, W. *Organometallics* **2001**, *20*, 3983−3992.

(19) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5084−5092.

(20) Shan, C.; Lin, Y.; Quyang, J.; Fan, Y.; Yang, G. *Macromol. Chem.* **1987**, *188*, 629−635.

(21) Fenton, D. E.; Kitchen, S. J.; Spencer, C. M.; Tamburini, S.; Vigato, P. A. *J. Chem. Soc., Dalton Trans.* **1988**, 685−690.

(22) Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A. Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 11, Chapter 6.

(23) Bethley, C. E.; Aitken, C. L.; Harlan, C. J.; Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1997**, *16*, 329−341.

(24) Oehme, A.; Gebauer, U.; Gehrke, K.; Beyer, P.; Hartmann, B.; Lechner, M. D. *Macromol. Chem. Phys.* **1994**, *195*, 3773−3781.