Neodymium(III) Complexes with Bulky *ansa*-Bis(cyclopentadienyl) Ligands: Synthesis and Use in Olefin Oligomerization

Stéphane Bogaert,[†] Thomas Chenal,[†] André Mortreux,[†] Guy Nowogrocki,[‡]
Christian W. Lehmann,[§] and Jean-François Carpentier*,[†]

Laboratoire de Catalyse de Lille (CNRS UPRESA 8010), Ecole Nationale Supérieure de Chimie de Lille, B.P. 108, 59652 Villeneuve d'Ascq, France, Laboratoire de Cristallochimie et Physicochimie du Solide (CNRS UPRESA 8012), Ecole Nationale Supérieure de Chimie de Lille, B.P. 108, 59652 Villeneuve d'Ascq, France, and Max-Planck-Institut für Kohlenforschung, Strukturchemie, Postfach 101353, 45466 Mülheim/Ruhr, Germany

Received July 24, 2000

The trivalent neodymium complexes [*rac*-{$Me_2Si(\eta^5$-2-$SiMe_3$-4-*t*-Bu-$C_5H_2)_2$}$Nd(\mu$-$Cl)_2Li(THF)_2$] (*rac*-**3**), [*rac*-{$Me_2Si(\eta^5$-2,4-$(SiMe_3)_2C_5H_2)_2$}$Nd(\mu$-$Cl)_2Li(THF)_2$] (*rac*-**5**), and [{$Me_2Si(\eta^5$-2,4-$(SiMe_3)_2C_5H_2)(\eta^5$-3,4-$(SiMe_3)_2C_5H_2)$}$Nd(\mu$-$Cl)_2Li(THF)_2$] (C_1-**6**) have been prepared and their structures investigated by NMR and X-ray crystallography. These new chlorolanthanocenes, when combined in situ with a dialkylmagnesium cocatalyst, initiate the polymerization of ethylene and 1-octene to yield di(oligoalkyl)magnesium species, which can be finally hydrolyzed to oligomers. Bulky bridged complexes *rac*-**3**, *rac*-**5**, and C_1-**6** gave significantly more active catalysts for 1-octene oligomerization ($M_n = 400-1300$, $M_w/M_n = 1.11-1.65$) than systems based on nonbridged complexes [$(\eta^5$-$C_5Me_5)_2Nd(\mu$-$Cl)_2Li(Et_2O)_2$] (**1**) and [$(\eta^5$-1,3-$(SiMe_3)_2C_5H_3)_2Nd(\mu$-$Cl)_2Li(THF)_2$] (**7**). Ethylene oligomerization ($M_n = 400-5000$) was best achieved with complexes **1** and *rac*-**3**, as important catalyst decay occurred with bridged bis(trimethylsilyl) systems *rac*-**5** and C_1-**6**.

Introduction

Group 3/organolanthanide metal complexes[1] have recently attracted considerable attention as olefin polymerization catalysts.[2] The greatest advantage of d^0/f lanthanocenes lies in their intrinsic high polymerization activity, while group 4 metallocenes require an activator (MAO, $B(C_6F_5)_3$, ...) to generate active d^0 cationic species. Highly efficient lanthanocene initiators for ethylene polymerization include trivalent complexes [$\{Cp'_2LnR\}_n$] (Cp′ = substituted cyclopentadienyl ligand, typically C_5Me_5 = Cp*; Ln = La, Nd, Sm,...; R = H, Me, CH_2SiMe_3; n = 1, 2),[2] as well as divalent complexes such as [$Cp'_2Sm(THF)_n$] (n = 0, 2).[2c,3] These complexes, especially the hydride complexes [$\{Cp'_2LnH\}_2$], are, however, very sensitive, and their synthesis as their handling is arduous. An alternative to avoid this difficulty is the in situ alkylation of a readily available chloro precursor, e.g., [$Cp^*_2NdCl_2Li(OEt_2)_2$] (**1**), with a dialkylmagnesium compound (Scheme 1).[4] Such a combination provides an active, stable ethylene polymerization system in which a living ethylene growth chain transfer reaction between the MgR_2 derivatives and the catalytically active lanthanocene complexes takes place, yielding eventually long chain dialkylmagnesium compounds, $Mg(PE)_2$, with a narrow distribution.[4]

Neutral organolanthanocenes are also known to exhibit generally a much lower ability than cationic group 4 metal complexes to polymerize nonpolar α-olefins. Indeed, trivalent rare-earth-metal hydrides, [$\{Cp^*_2LnH\}_2$], and divalent [$Cp^*_2Sm(THF)_n$] complexes are completely inactive for the polymerization of higher α-olefins such as propene and 1-hexene, while *ansa*-bridged [$\{(Me_2Si(C_5Me_4)_2)LnH\}_2$] complexes are slightly active.[2d] Improved performances for this purpose have been reported recently using modified Cp-based com-

---

* Corresponding author. Fax: (+33) 320 436 585. E-mail: carpentier@ensc-lille.fr.

[†] Laboratoire de Catalyse de Lille (CNRS UPRESA 8010).

[‡] Laboratoire de Cristallochimie et Physicochimie du Solide (CNRS UPRESA 8012).

[§] Max-Planck-Institut für Kohlenforschung, Strukturchemie.

(1) For recent organolanthanide reviews, see: (a) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (b) Anwander, R.; Herrmann, W. A. *Top. Curr. Chem.* **1996**, *179*, 1. (c) Edelmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 247. (d) Molander, G. A. *Chemtracts: Org. Chem.* **1998**, *11*, 237. (e) Molander, G. A.; Dowdy, E. C. *Top. Organomet. Chem.* **1999**, *2*, 119.

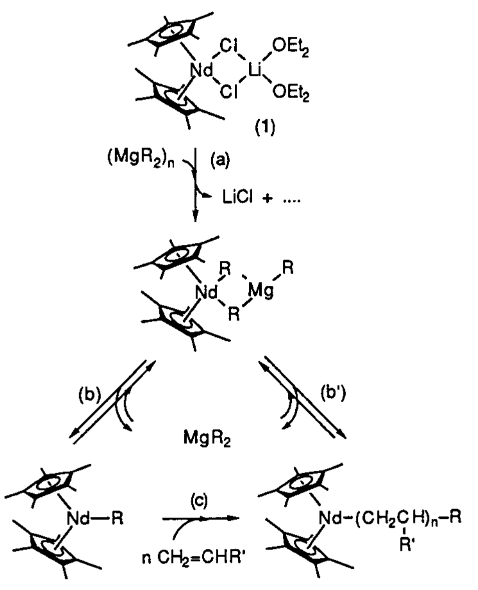
(2) (a) Ballard, D. G. H.; Courtis, A.; Holton, J.; McMeeking, J.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1978**, 994. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (c) Watson, P. L.; Herskovitz, T. *ACS Symp. Ser.* **1983**, *212*, 459. (d) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (e) Jeske, G.; Lauke, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (f) Burger, B. J.; Thompson, M. E.; Cotter, D. W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.

(3) (a) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314. (b) Ihara, E.; Nodono, M.; Yasuda, H.; Kanehisa, N.; Kai, Y. *Macromol. Chem. Phys.* **1996**, *197*, 1909. (c) Ihara, E.; Nodono, M.; Katsura, K.; Adachi, Y.; Yasuda, H.; Yamagashira, M.; Hashimoto, H.; Kanehisa, N.; Kai, Y. *Organometallics* **1998**, *17*, 3945. (d) Yasuda, H.; Ihara, E. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1745.

(4) (a) Olonde, X.; Mortreux, A.; Petit, F.; Bujadoux, K. *J. Mol. Catal.* **1993**, *82*, 75. (b) Patent WO 93/07180 A1 to ECP Enichem Polymeres France; *Chem. Abstr.* **1993**, *119*, 271958s. (c) Pelletier, J.-F.; Mortreux, A.; Olonde, X.; Bujadoux, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1854. (d) Bujadoux, K.; Chenal, T.; Fouga, C.; Olonde, X.; Pelletier, J.-F.; Mortreux, A. In *Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer-Verlag: Berlin, 1999; pp 590−600. (e) Bogaert, S.; Carpentier, J.-F.; Chenal, T.; Mortreux, A.; Ricart, G. *Macromol. Chem. Phys.* **2000**, *201*, 1813.

10.1021/om0006357 CCC: $20.00
Publication on Web 12/06/2000

Scheme 1



plexes, e.g., [{(η^5-C_5Me_4)$SiMe_2$(η-N^tBu)Sc(η-H)}$_2$][5] and [*rac*-{Me_2Si(η^5-2-Me_3Si-4-^tBu-C_5H_2)$_2$YH}$_2$][6] developed by Bercaw et al. and divalent samarocenes developed by Yasuda et al. such as [*rac*-{Me_2Si(η^5-2-Me_3Si-4-^tBu-C_5H_2)$_2$}Sm(THF)$_2$].[3b,c] Herein, we describe the preparation of some new trivalent chloroneodymium complexes based on similarly substituted *ansa*-bridged Cp ligands[7] and the results of ethylene and 1-octene polymerizations using in situ chloroneodymocene/MgR_2 systems.

Results and Discussion

Preparation of Bulky Chloroneodymocenes(III). To investigate the relationship between the structure of the catalyst precursor and the polymerization activity, some ligands having bulky substituents were selected. In light of literature results,[3b,c,6] we focused our attention on *ansa*-bridged Cp ligands having either one $SiMe_3$ and one *t*-Bu group per Cp ring or two $SiMe_3$ groups. The trivalent chloroneodymium complexes were synthesized by the reaction of the dilithium salt of the corresponding ligand with $NdCl_3$ (Scheme 2). As earlier reported,[3c] NMR analysis revealed that both types of ligands in their Cp-H form exist as a mixture of isomers which differ in the position of the C=C double bonds and likely also in the position of the $SiMe_3$ groups, in the Cp ring. Nonetheless, the NMR spectra of the corresponding dilithium salts show only one set of resonances, consistent with the existence of a single product (Scheme 2).

The reaction of the dilithium salt **2** with $NdCl_3$ afforded [*rac*-{Me_2Si(η^5-2-$SiMe_3$-4-^tBu-C_5H_2)$_2$}Nd(μ-Cl)$_2$Li(THF)$_2$] (*rac*-**3**). The ^1H and ^{13}C NMR spectra of the crude reaction product and of the isolated complex (50% yield) display only one set of resonances (>98%), consistent with a C_2-symmetric structure. The racemic structure was confirmed by X-ray analysis (Figure 1, Table 1) (vide infra).

In a similar manner, the dilithium salt **4** was reacted with $NdCl_3$ (Scheme 2). In this case, the ^1H NMR analysis of the crude reaction product displayed two sets of resonances in a ca. 65:35 ratio, respectively attributable to a C_1-symmetric species (four $SiMe_3$, four CpH, two bridging $SiMe_2$ signals) and a C_2-symmetric species (two $SiMe_3$, two CpH, one bridging $SiMe_2$ signals). Repeated syntheses afforded reproducibly such mixtures of complexes. The C_2-symmetric species proved much more soluble in hexane than the C_1-symmetric species. Extraction of the crude reaction mixture with this solvent and fractional crystallization afforded first a crop of analytically pure [{Me_2Si(η^5-2,4-($SiMe_3$)$_2C_5H_2$)(η^5-3,4-($SiMe_3$)$_2C_5H_2$)}Nd(μ-Cl)$_2$Li(THF)$_2$] (C_1-**6**, 20% yield based on Nd) and then [*rac*-{Me_2Si(η^5-2,4-($SiMe_3$)$_2$-C_5H_2)$_2$}Nd(μ-Cl)$_2$Li(THF)$_2$] (*rac*-**5**, 25% yield). Symmetry features for the isolated complexes *rac*-**5** and C_1-**6** were established from their ^1H and ^{13}C NMR spectra and confirmed by X-ray analysis (Figures 2 and 3, Table 1). Complex C_1-**6** has two $SiMe_3$ groups at 2,4-positions in one Cp ring and at 3,4-positions in the other Cp, while complex *rac*-**5** has the $SiMe_3$ groups at 2,4-positions in both Cp rings. Similar rearrangement of the $SiMe_3$ groups during coordination of the bridged ligand **4** onto a metal center has been observed during the preparation of divalent samarocenes, leading in this case to the exclusive formation of the C_1-symmetric complex.[3c,8]

Selected bond distances and bond angles for *rac*-**3**, *rac*-**5**, and C_1-**6** are given in Table 2. Two independent molecules were found in the unit-cell of *rac*-**3**, but the two molecules are quite similar so that only the distances and the angles for one of them are listed in Table 2. In the three complexes *rac*-**3**, *rac*-**5**, and C_1-**6**, there is steric crowding between the $-SiMe_3$ group at the 2-position (and the one at the 3-position in C_1-**6**) and the rest of the molecule. This strain is evidenced by two

---

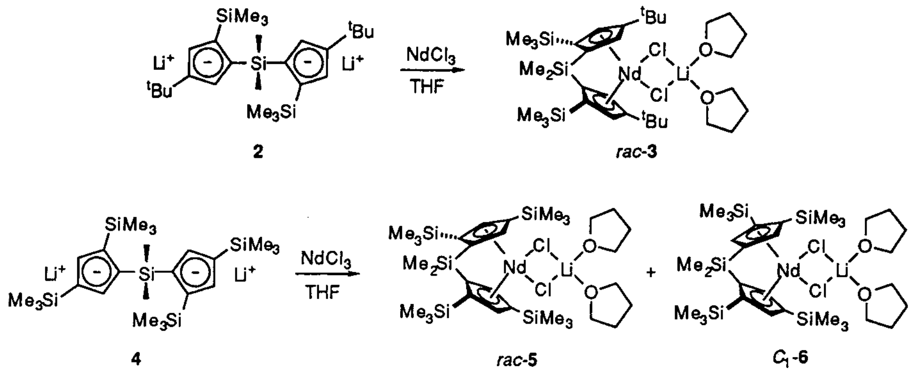
(5) (a) Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74. (c) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623.

(6) (a) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606. (b) Coughlin, E. B.; Shapiro, P. J.; Bercaw, J. E. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1992**, *33*, 1226. (c) Marsh, R. E.; Schaefer, W. P.; Coughlin, E. B.; Bercaw, J. E. *Acta Crystallogr., Sect. C* **1992**, *C48*, 1773. (d) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045.

(7) For leading references and recent developments in *ansa*-lanthanidocene chemistry, see: (a) Stern D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558. (b) Giardello, M.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212. (c) Roesky, P. M.; Denninger, U.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 4486. (d) Roesky, P. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 4705. (e) Evans, W. J.; Cano, D. A.; Greci, M. A.; Ziller, J. W. *Organometallics* **1999**, *18*, 1381. (f) Gilbert, A. T.; Davis, B. L.; Emge, T. J.; Broene, R. D. *Organometallics* **1999**, *18*, 2125. (g) Lee, M. H.; Hwang, J.-W.; Kim, Y.; Kim, J.; Han, Y.; Do, Y. *Organometallics* **1999**, *18*, 5124. (h) Hitchcock, P. B.; Lappert, M. F.; Tian, S. *Organometallics* **2000**, *19*, 3420. (i) Qian, C.; Zou, G.; Sun, J. *J. Chem. Soc., Dalton Trans.* **1998**, 1607. (j) Qian, C.; Zou, G.; Sun, J. *J. Chem. Soc., Dalton Trans.* **1999**, 519. (k) Qian, C.; Nie, W.; Sun, J. *J. Chem. Soc., Dalton Trans.* **1999**, 3283. (l) Qian, C.; Nie, W.; Sun, J. *Organometallics* **2000**, *19*, 4134. (m) Eppinger, J.; Spiegler, M.; Hieringer, W.; Herrmmann, W. A.; Anwander, R. *J. Am. Chem. Soc.* **2000**, *122*, 3080. (n) Schumann, H.; Zietzke, K.; Weimann, R.; Demtschuk, J.; Kaminsky, W.; Schauwienold, A.-M. *J. Organomet. Chem.* **1999**, *574*, 228. (o) Halterman, R. L.; Schumann, H.; Dübner, F. *J. Organomet. Chem.* **2000**, *604*, 12. (p) Khvostov, A. V.; Belsky, V. K.; Sizov, A. I.; Bulychev, B. M.; Ivchenko, N. B. *J. Organomet. Chem.* **1998**, *564*, 5. (q) Khvostov, A. V.; Belsky, V. K.; Sizov, A. I.; Bulychev, B. M.; Ustinov, B. B. *J. Organomet. Chem.* **1998**, *571*, 243. (r) Khvostov, A. V.; Bulychev, B. M.; Belsky, V. K.; Sizov, A. I. *J. Organomet. Chem.* **1999**, *584*, 164. (s) Khvostov, A. V.; Bulychev, B. M.; Belsky, V. K.; Sizov, A. I.; Antipin, M. Y. *J. Organomet. Chem.* **1999**, *589*, 222.

(8) The preparation of the trivalent samarium complexes has been reported, without detailed description of the synthesis and structural features, to give also a mixture of the racemic and the C_1-symmetric complexes: Yasuda, H.; Ihara, E. *Macromol. Chem. Phys.* **1995**, *196*, 2417.

Scheme 2



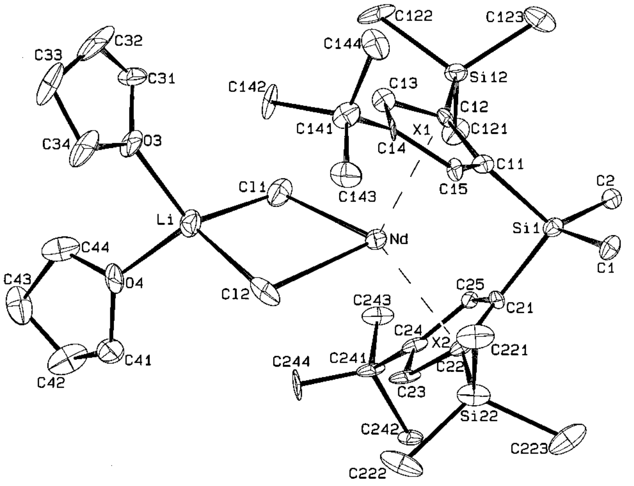


Figure 1. Molecular structure of [*rac*-{$Me_2Si(\eta^5$-2-$SiMe_3$-4-*t*-Bu-$C_5H_2)_2$}$Nd(\mu$-$Cl)_2Li(THF)_2$] (*rac*-**3**) (hydrogen atoms omitted for clarity). Only one of the two independent molecules is presented.

normal C(Cp)−Si−CH_3 angles (mean angles = 106.5 ± 1.1° and 109.8 ± 1.4°) and a third larger angle (mean angle = 115.7 ± 0.5°) to the methyl C atom near the other Cp ring. The Cp′(centroid)−Nd−Cp′(centroid) bite angles in the two racemic structures are nearly identical, and the one in C_1-**6** is ca. 2.5° smaller. The bite angle in *rac*-**3** is ca. 3° smaller than that in the equivalent Y(III) complex (122.3°)[6c] and ca. 3° larger than that in the analogous Sm(II) complex (115.8°).[3c] This trend agrees with the order of effective ionic radii, Sm^{2+} (1.36 Å) > Nd^{3+} (1.11 Å) > Y^{3+} (1.04 Å).[9] The bite angle in *rac*-**5** is ca. 8° smaller than that in its nonlinked analogue, i.e., [{$(\eta^5$-1,3-$(SiMe_3)_2C_5H_3)_2$}$Nd(\mu$-$Cl)_2Li(THF)_2$] (**7**) (126.2°).[10] For comparison, other related nonbridged lanthanocenes also display large bite angles, e.g., [$(\eta^5$-$C_5Me_5)_2Yb(\mu$-$Cl)_2Li(Et_2O)_2$], 136.6°;[11] [$(\eta^5$-$C_5Me_5)_2NdCH(SiMe_3)_2$], 134.4°.[2e]

The decrease of the bite angle in bridged complexes (with respect to equivalently substituted nonbridged complexes) corresponds to the increase of the vacant space around Nd, from which an increased olefin polymerization activity is expected considering the coordination of incoming olefin for chain propagation (c in Scheme 1) as the rate-determining step.[2d] This variation of space may, however, affect other steps of the catalytic process, e.g., (a) the in situ alkylation of the chloro precursor by MgR_2 and (b) the dissociation equilibrium between bimetallic species [Cp_2NdR−MgR_2] (assumed to be inactive) and the active [Cp_2NdR] species.

Ethylene Oligomerization. The performances of the new trivalent neodymocenes in combination with *n*-BuEtMg as a cocatalyst[12] were first explored in ethylene polymerization. Representative results are summarized in Table 3, and ethylene flow rates are depicted in Figure 4. Although less active than the reference system based on **1**, the *rac*-**3** system showed a similar polymerization behavior, typical of these systems,[4] i.e., a concomitant increase in activity with gradual precipitation of high molecular weight Mg products to reach a maximum after ca. 50−70 min, followed by deactivation. Systems based on complexes **1** and *rac*-**3** yielded oligomers with comparable molecular weights and molecular weight distributions (entries 1 and 2). On the other hand, both complexes *rac*-**5** and C_1-**6** led reproducibly to systems quite active in the first stage of the reaction, the former system reaching then a level of activity comparable with that of *rac*-**3**, while the second one deactivated rapidly (entries 3, 4). The nonbridged complex [{$(\eta^5$-1,3-$(SiMe_3)_2C_5H_3)_2$}$Nd(\mu$-$Cl)_2Li(THF)_2$] (**7**) did not show any activity at all upon activation with *n*-BuEtMg (entry 5).

The rapid catalyst decay observed with complex C_1-**6** and, to a lesser extent, with complex *rac*-**5** reinforces the idea aforementioned in the preparation of these chloro precursors that such $SiMe_2$-bridged systems bearing two $SiMe_3$ substituents are unstable.[3c] Although this deactivation phenomenon hampers a global interpretation of polymerization activities, interesting comments arise. The beneficial effect of a decreased bite angle is evidenced by the noticeable activity of the *rac*-**5** system (average activity over the first hour, $A_{1h} = 9 \times 10^4$ g of PE/(mol of Nd·h)) compared with the total inefficiency of the equivalently substituted but non-

---

(9) (a) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *B25*, 295. (b) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1970**, *B26*, 1046. (c) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(10) Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 1191.

(11) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271.

(12) All the chloroneodymocene complexes described in this paper are totally inactive toward ethylene and 1-octene at 80 °C in the absence of a dialkylmagnesium compound as a cocatalyst. *n*-BuEtMg was initially chosen as the cocatalyst because of its availability and low cost in view of potential industrial considerations.[4b] Poor results were obtained using other alkylating agents as cocatalysts in place of dialkylmagnesium compounds; of potential interest are the *rac*-**3**/*n*-BuLi (1:2) combination that gives 435 g of oligooctenes/(mol of Nd·h) with $M_n = 2500$ and $M_w/M_n = 2.87$, and the *rac*-**3**/*n*-BuLi/$AlEt_3$ (1:1:1) combination that gives 520 g of oligooctenes/(mol of Nd·h) with $M_n = 1270$ and $M_w/M_n = 2.57$.

Table 1. Crystal Data for Complexes *rac*-3, *rac*-5, and C_1-6

	rac-**3**	*rac*-**5**	C_1-**6**
formula	$C_{34}H_{62}Cl_2LiNdO_2Si_3$	$C_{32}H_{62}Cl_2LiNdO_2Si_5$	$C_{32}H_{62}Cl_2LiNdO_2Si_5$
cryst size (mm)	0.40 × 0.38 × 0.34	0.42 × 0.41 × 0.34	0.40 × 0.40 × 0.35
fw	809.19	841.35	841.35
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a, Å	13.362(19)	11.4219(12)	17.548(11)
b, Å	16.90(2)	19.2434(19)	13.481(8)
c, Å	20.24(3)	20.1127(19)	19.473(8)
α, deg	103.47(2)	90.00	90.00
β, deg	99.396(19)	90.145(4)	104.29(4)
γ, deg	101.82(2)	90.00	90.00
V, Å^3	4241(10)	4420.7(8)	4464(4)
Z	4	4	4
D_{calcd}, Mg/m^3	1.215	1.264	1.309
T, K	293(2)	100(2)	293(2)
θ range, deg	2.36−23.40	2.03−27.50	1.86−23.32
μ, mm^{-1}	1.459	1.455	1.443
no. of measd reflns	8965	36985	6381
no. of ind reflns	3969	8056	3365
goodness of fit	1.044	1.077	1.033
R (R_w) ($I > 2\sigma(I)$)	0.0816 (0.1933)	0.0363 (0.0855)	0.0800 (0.1895)

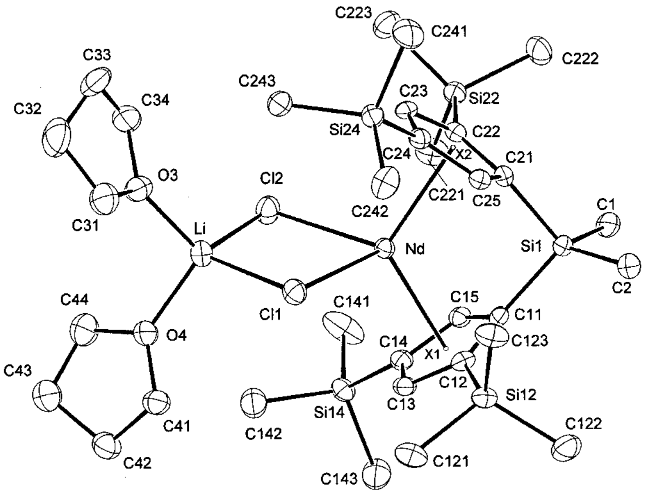


Figure 2. Molecular structure of [*rac*-{$Me_2Si(\eta^5$-2,4-$(SiMe_3)_2C_5H_2)_2$}$Nd(\mu$-$Cl)_2Li(THF)_2$] (*rac*-**5**) (hydrogen atoms omitted for clarity).

bridged system **7**. The decrease in activity going from **1** (A_{1h} = 26 × 10^4 g of PE/(mol of Nd·h)) to *rac*-**3** (A_{1h} = 7 × 10^4 g of PE/(mol of Nd·h)) shows, however, that the Cp′(centroid)−Nd−Cp′(centroid) bite angle is not the sole factor to be considered. Apparently, in this case, the presence of the bulky *t*-Bu group counterbalances unfavorably the decrease in the bite angle enforced by the $SiMe_2$ bridge.

The experimental M_n data reported in Table 3 for the final polyethylene samples recovered from systems based on **1**, *rac*-**3**, and *rac*-**5** are lower than the theoretical data ($M_{n,th}$) calculated assuming total transfer to MgR_2 (two chains per Mg) ($M_{n,th}$ = 8020, 8320, and 6580 g·mol^{-1}, respectively). This is ascribed to significant β-H elimination from monometallic [Cp'_2NdR] species after precipitation of high molecular weight Mg products,[4a,c] as revealed by the presence of vinyl terminations in the ^{1}H NMR spectra of the oligomers (ca. 10%). This phenomenon also causes a gradual deactivation and relatively large molecular weight distributions. For the C_1-**6** system, in which no precipitation was observed, the experimental data ($M_{n,exp}$ = 1690) agrees well with the theoretical data ($M_{n,th}$ = 1580) and the polydispersity is lower. Analysis of aliquot samples taken from reactions conducted with **1** and *rac*-**3** as the precursors before precipitation occurred showed similar good agreement between $M_{n,exp}$ and $M_{n,th}$ data, as well as lower molecular weight distributions (M_w/M_n = 1.2−1.4).

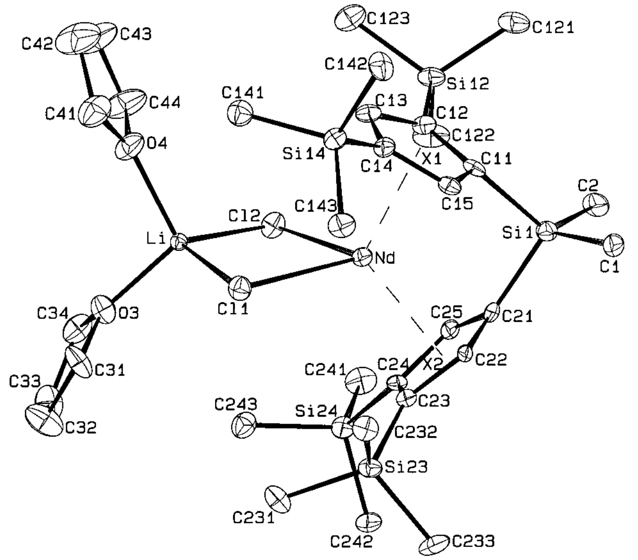


Figure 3. Molecular structure of [{$Me_2Si(\eta^5$-2,4-$(SiMe_3)_2$-$C_5H_2)(\eta^5$-3,4-$(SiMe_3)_2C_5H_2)$}$Nd(\mu$-$Cl)_2Li(THF)_2$] (C_1-**6**) (hydrogen atoms omitted for clarity).

1-Octene Oligomerization. The performances of different catalytic combinations for 1-octene oligomerization are summarized in Table 4. As initially expected, the systems based on bulky *ansa*-bis(cyclopentadienyl) ligands proved much more efficient than those derived from the simple Cp* complex **1** and the nonbridged bis(trimethylsilylcyclopentadienyl) complex **7**. The activity observed using *n*-BuEtMg as a cocatalyst decreases in the order *rac*-**3** > *rac*-**5** > C_1-**6** > **1**−**7**. Thus, the present neodymocene/dialkylmagnesium systems follow exactly the same activity order than that found for analogous divalent samarium complexes in ethylene and 1-olefin polymerization.[3c] This confirms that activity for α-olefin polymerization in this series of complexes is governed primarily by the size of the vacant space around the active metal center and suggests that coordination of

Table 2. Selected Bond Lengths (Å) and Angles (deg)

	rac-**3**	*rac*-**5**	C_1-**6**
Nd−Cl(1)	2.717(8)	2.7250(8)	2.724(4)
Nd−Cl(2)	2.708(6)	2.7287(9)	2.720(4)
Nd−X1[a]	2.464(19)	2.475(3)	2.468(15)
Nd−X2[b]	2.429(29)	2.472(3)	2.470(13)
Si(1)−C(1)	1.898(24)	1.866(3)	1.900(17)
Si(1)−C(2)	1.896(28)	1.868(4)	1.907(16)
Si(12)−C(12)	1.883(27)	1.880(3)	1.858(16)
Si(22)−C(22)	1.853(27)	1.873(3)	
Si(14)−C(14)		1.871(4)	1.890(15)
Si(24)−C(24)		1.870(3)	1.870(14)
Si(23)−C(23)			1.860(15)
X1−Nd−X2[a,b]	118.9(11)	118.60(15)	116.06(64)
C(11)−Si(1)−C(21)	98.6(10)	100.33(13)	99.4(6)
C(12)−Si(12)−C(121)	116.6(11)	107.43(17)	108.3(8)
C(12)−Si(12)−C(122)	107.6(13)	109.80(17)	115.1(7)
C(12)−Si(12)−C(123)	110.0(11)	115.77(15)	105.5(8)
C(22)−Si(22)−C(221)	115.8(11)	115.59(15)	
C(22)−Si(22)−C(222)	111.9(14)	111.19(17)	
C(22)−Si(22)−C(223)	104.5(12)	106.74(16)	
C(23)−Si(23)−C(231)			115.2(7)
C(23)−Si(23)−C(232)			107.1(7)
C(23)−Si(23)−C(233)			107.8(7)

[a] X1 is the centroid for C11 to C15. [b] X2 is the centroid for C21 to C25.

Table 3. Ethylene Oligomerization by Chloroneodymocene/*n*-BuEtMg Systems[a]

entry	precursor	*t* (min)	PE (g)	M_n	M_w/M_n
1	**1**	90	31.9	4 820	1.80
2	*rac*-**3**	230	33.1	3 760	1.83
3	*rac*-**5**	230	26.1	4 520	3.12
4	C_1-**6**	90	6.15	1 690	1.44
5	**7**	60	0		

[a] Reaction conditions: $T = 80$ °C; [Nd] = 0.1 mmol; *n*-BuEtMg = 2.0 mmol; toluene = 100 mL.

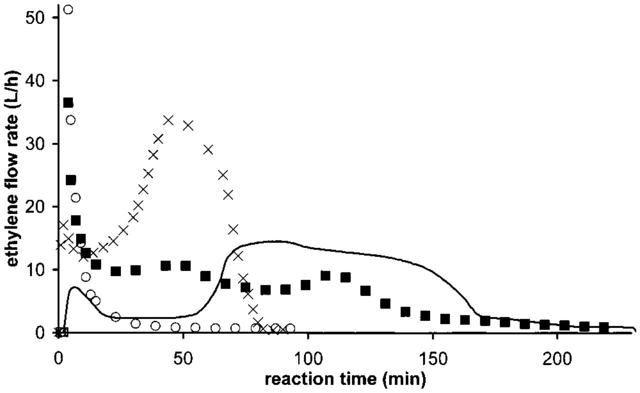


Figure 4. Ethylene flow rates for chloroneodymocene/*n*-BuEtMg systems (see Table 3 for reaction conditions): ×, **1**; –, *rac*-**3**; ■, *rac*-**5**; ○, C_1-**6**.

Table 4. 1-Octene Oligomerization by Chloroneodymocene/*n*-BuEtMg Systems: Influence of the Catalyst Precursor[a]

entry	precursor	*t* (h)	yield (%)	M_n	M_w/M_n
1	**1**	24	7	330	1.11
2	*rac*-**3**	7	20	500	1.36
3	*rac*-**3**	15	36	600	1.38
4	*rac*-**3**	24	76	950	1.31
5	*rac*-**5**	24	39	750	1.43
6	C_1-**6**	24	23	320	1.35
7	**7**	24	3	365	1.28

[a] Reaction conditions: $T = 80$ °C; [Nd] = 0.1 mmol; *n*-BuEtMg = 2.0 mmol; 1-octene = 64 mmol (neat) (7.1 g).

Table 5. 1-Octene Oligomerization by *rac*-3/MgR$_2$ Systems[a]

entry	*T* (°C)	MgR$_2$	Mg/Nd	yield (%)	M_n	M_w/M_n
1	25	*n*-BuEtMg	20	2	330	1.14
2	60	*n*-BuEtMg	20	32	760	1.37
3	80	*n*-BuEtMg	20	76	950	1.31
4	100	*n*-BuEtMg	20	69	500	1.41
5	120	*n*-BuEtMg	20	60	400	1.32
6	80	*n*-BuEtMg	2	25	1 300	1.59
7	80	*n*-BuEtMg	5	38	1 200	1.47
8	80	*n*-BuEtMg	10	74	1 100	1.45
9	80	*n*-BuEtMg	40	54	650	1.36
10	80	(*n*,*s*-Bu)$_2$Mg	20	67	1 000	1.36
11	80	(*n*-hexyl)$_2$Mg	20	62	1 000	1.32
12	80	(Me$_3$SiCH$_2$)$_2$Mg	20	7	900	1.65

[a] Reaction conditions: $t = 24$ h; *rac*-**3** = 0.1 mmol; 1-octene = 64 mmol (neat).

the olefin monomer is the rate-determining step of the process.[1d] The activity of the *rac*-**3**/*n*-BuEtMg system over 24 h is 2250 g of oligooctene/(mol of Nd·h) at 80 °C and ca. 60 g of oligooctene/(mol of Nd·h) at 23 °C (Table 5, entry 1, vide infra). These values compare well with that reported for the equivalent Sm(II) initiator in 1-hexene polymerization, i.e., 112 g of poly(1-hexene)/(mol of Sm·h) at 23 °C.[3c] The yield in oligooctenes and the molecular weight of the latter increase regularly, but not in parallel, with time at 80 °C (Table 4, entries 2−4). The experimental M_n data of the oligooctenes obtained after hydrolysis (entry 4, $M_{n,exp} = 950$) are lower than the theoretical value calculated assuming transfer to MgR$_2$ (two chains per Mg) ($M_{n,th} = 1390$), indicating that significant β-H elimination and/or chain transfer to the monomer occurs. The ^{1}H and ^{13}C NMR spectra of these oligomers showed ca. 40−50% of unsaturated oligooctene chains, comprising more than 85% of vinylidene end groups (δ ^{1}H = 4.68, 4.73; δ ^{13}C = 108.8, 148.9; CDCl$_3$), characteristic of a 1,2-insertion mode, and less than 15% of internal insaturations (δ ^{1}H = 5.35, δ ^{13}C = 128.5, 130.2, 131.4; CDCl$_3$), characteristic of a 2,1-insertion mode.

The effect of the variation of the reaction temperature, the MgR$_2$/Nd ratio, and the nature of the dialkylmagnesium cocatalyst[12] are reported in Table 5. The oligomerization was best carried out at 80 °C with a MgR$_2$/Nd ratio in the range 10−20, as deviation from these values resulted in decreased yields and/or lower degrees of polymerization (entries 1−9). A slight decrease in activity was observed upon using higher dialkylmagnesium compounds such as *n*,*s*-Bu$_2$Mg and (*n*-hexyl)$_2$Mg, with no significant changes in the degree of polymerization and the molecular weight distribution. Thus, the higher the dialkylmagnesium reagent, the better the agreement between experimental and calculated molecular masses, e.g., entry 10: $M_{n,exp} = 1000$, $M_{n,th} = 1250$; entry 11: $M_{n,exp} = 1000$, $M_{n,th} = 1170$. These differences are presumably ascribed to the lower degree of association of higher dialkylmagnesiums in hydrocarbon solutions.[13] The variation in concentration of dissociated (monomeric) dialkylmagnesium species is expected to affect steps a and b in Scheme 1. Consistent

---

(13) (a) Weiss, E. *J. Organomet. Chem.* **1964**, *2*, 134. (b) Weiss, E. *J. Organomet. Chem.* **1965**, *4*, 101. (c) Kamiensky, C. W.; Easthmann, J. F. *J. Org. Chem.* **1969**, *34*, 1116. (d) Malpass, D. B.; Fannin, L. W. *J. Organomet. Chem.* **1975**, *93*, 1. (e) Malpass, D. B.; Fannin, L. W.; Ligi, J. J. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1981; Vol. 16, p 555. (f) Andersen, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 809.

with this hypothesis, $Mg(CH_2SiMe_3)_2$, which is known to be polymeric in hydrocarbon solutions,[13] proved inefficient (entry 12). Further investigations aimed at clarifying the influence of the dialkylmagnesium reagent and improving catalytic performances are currently under way.

Experimental Section

General Considerations. All operations were performed under dry argon by using standard Schlenk techniques and a glovebox. Solvents were distilled from sodium benzophenone ketyl (toluene, THF) or Na/K alloy (pentane, hexane) under nitrogen and thoroughly degassed prior to use. Ethylene (Air Liquide) was prepurified by passage through a moisture filter (Chrompack, no. 7971). 1-Octene (Aldrich) was distilled over Na and degassed prior to use. *n*-Butylethylmagnesium, di(*n*-hexyl)magnesium (both 20 wt % solution in heptane from Texas alkyl), and *n*,*s*-dibutylmagnesium (1.0 m solution in heptane from Aldrich) were used as received. $NdCl_3$ (Strem) was used as received. Lanthanidocenes $[(\eta^5\text{-}C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(Et_2O)_2]$ (**1**)[14] and $[(\eta^5\text{-}1,3\text{-}(SiMe_3)_2C_5H_3)_2Nd(\mu\text{-}Cl)_2Li(THF)_2]$ (**7**)[10] were prepared according to the literature procedures. Bulky ligands $Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}t\text{-}Bu\text{-}C_5H_3)_2$ (**2**)[6a] and $Me_2Si((SiMe_3)_2C_5H_3)_2$ (**4**)[3c] were prepared according to published methods. ^1H and ^{13}C NMR spectra were recorded on a AC 300 Bruker or a AM 400 Bruker spectrometer at 23 °C, unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported vs $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent peaks. The average molecular masses and polydispersity of polyethylene and oligo(1-octene) samples were measured by size exclusion chromatography (SEC). Measurements for polyethylene samples were performed in 1,3,5-trichlorobenzene at 135 °C using a Waters 150C Plus chromatograph equipped with a refractometer, a Waters 150R Plus Retrofit viscometer, and Waters styragel columns (HT3-HT6). Measurements for oligo(1-octene) samples were performed in THF at 20 °C using a Waters SIS HPLC-pump, a Waters 410 refractometer, and Waters styragel columns (HR2, HR3, HR4, HR5E). In both cases, M_n and M_w/M_n values were calibrated from polystyrene standards. The M_n values of oligo(1-octene) samples were determined in a parallel manner by vapor pressure osmometry (VPO) using toluene as solvent at 60 °C with a Osmomat 070 (Gonotec) apparatus. SEC and VPO techniques gave consistent results within 10% error.

Preparation of [*rac*-{$Me_2Si(\eta^5\text{-}2\text{-}SiMe_3\text{-}4\text{-}t\text{-}BuC_5H_2)_2$}$Nd(\mu\text{-}Cl)_2Li(THF)_2$] (*rac*-3). To a stirred solution of bis[2-(trimethylsilyl)-4-tertbutylcyclopentadiene]dimethylsilane[6a] (7.7 g, 17.3 mmol) in THF (50 mL) was added *n*-BuLi (22.7 mL of a 1.6 M solution in hexane, 36.3 mmol) dropwise at 0 °C. The reaction mixture was stirred for 5 h at 23 °C, and the solution was evaporated to dryness. The product was washed with hexane, affording the dilithium salt **2** in 95% yield as a pale brown powder. ^1H NMR (300 MHz, $C_6D_6 + d_8$-THF): δ 6.71 (s, 2H, Cp H), 6.60 (s, 2H, Cp H), 1.49 (s, 18H, *t*-Bu), 0.87 (s, 6H, $SiMe_2$), 0.49 (s, 18H, $SiMe_3$). ^{13}C NMR ($C_6D_6 + d_8$-THF): δ 137.5, 120.8, 115.7, 34.5, 32.8, 6.0, 3.7. A THF solution (25 mL) of the dilithium salt **2** (2.28 g, 5.0 mmol) was added to a THF suspension (25 mL) of $NdCl_3$ (1.5 g, 6.0 mmol). After the resulting reaction mixture was refluxed for 24 h, the solution was evaporated. Hexane (90 mL) was then added to the residue, and the mixture was stirred for 24 h at 23 °C. Insoluble material was removed by decantation, and the solution was concentrated in vacuo to ca. 30 mL. Recrystallization of the clear solution at −17 °C afforded *rac*-**3** as blue crystals in 50% yield. ^1H NMR (400 MHz, C_6D_6): δ 35.43 (s, 2H, Cp H), 6.32 (s, 8H, THF-α), 3.07 (s, 8H, THF-β), 2.17 (s, 6H, $SiMe_2$), 1.66 (s, 18H, CMe_3), −7.70 (s, 18H, $SiMe_3$), −24.13 (s, 2H, Cp H). ^{13}C NMR (99 MHz, C_6D_6): δ 288.5, 259.1, 252.5, 205.2, 191.0 (all Cp C), 71.6 (THF-α), 48.2 (C*Me*$_3$), 27.5 (THF-β), 23.6 (*C*Me$_3$), −4.8, −11.8 ($SiMe_2$, $SiMe_3$). Anal. Calcd for $C_{34}H_{62}Cl_2LiNdO_2Si_3$: C, 50.46; H, 7.72. Found: C, 51.0; H, 7.54.

Preparation of [*rac*-{$Me_2Si(\eta^5\text{-}2,4\text{-}(SiMe_3)_2\text{-}C_5H_2)_2$}Nd-$(\mu\text{-}Cl)_2Li(THF)_2$] (*rac*-5) and [{$Me_2Si(\eta^5\text{-}2,4\text{-}(SiMe_3)_2\text{-}C_5H_2)$-$(\eta^5\text{-}3,4\text{-}(SiMe_3)_2\text{-}C_5H_2)$}$Nd(\mu\text{-}Cl)_2Li(THF)_2$] ($C_1$-6). To a stirred solution of bis[bis(trimethylsilyl)cyclopentadiene]dimethylsilane[3c] (mixture of isomers, 6.3 g, 13.2 mmol) in THF (50 mL) was added *n*-BuLi (17.3 mL of a 1.6 M solution in hexane, 27.7 mmol) dropwise at 0 °C. The reaction mixture was stirred for 5 h at 23 °C, and the solution was evaporated to dryness. The product was washed with hexane, affording the dilithium salt **4** as a pale brown powder (6.1 g, 95% yield). ^1H NMR (300 MHz, $C_6D_6 + d_8$-THF): δ 6.78 (s, 2H, Cp H), 6.67 (s, 2H, Cp H), 0.31 (s, 36H, $SiMe_3$), 0.23 (s, 6H, $SiMe_2$). A THF solution (25 mL) of the dilithium salt **4** (2.44 g, 5.0 mmol) was added to a THF suspension (25 mL) of $NdCl_3$ (1.5 g, 6.0 mmol). After the resulting reaction mixture was refluxed for 24 h, the solution was evaporated. Hexane (90 mL) was then added to the residue, and the mixture was stirred with a magnetic bar for 24 h at 23 °C. Insoluble material (mostly C_1-**6**) was removed by decantation, and the solution was concentrated in vacuo to ca. 30 mL. Recrystallization of the clear solution at −17 °C afforded a first crop of blue crystals of C_1-**6** (0.85 g, 20% yield). ^1H NMR (400 MHz, C_6D_6): δ 37.74 (s, 1H, Cp H), 7.21 (s, 8H, THF-α), 4.51 (s, 3H, $SiMe_2$), 3.87 (s, 9H, $SiMe_3$), 3.57 (s, 8H, THF-β), −0.77 (s, 6H, $SiMe_2$), −2.20 (s, 9H, $SiMe_3$), −2.46 (s, 9H, $SiMe_3$), −9.96 (s, 9H, $SiMe_3$), −10.36 (s, 1H, Cp H), −15.71 (s, 1H, Cp H), −20.42 (s, 1H, Cp H). ^{13}C NMR (99 MHz, C_6D_6): δ 277.1, 276.0, 257.3, 253.1, 241.3, 228.7, 227.5, 215.6, 193.3, 178.0 (all Cp C), 72.6 (THF-α), 27.9 (THF-β), 10.6, 5.2, 4.0, −9.0, −10.1, −10.7 (all SiMe). Further crystallization at −17 °C of the previous solution afforded blue crystals of *rac*-**5** (1.04 g, 25% yield). ^1H NMR (400 MHz, C_6D_6): δ 34.64 (s, 2H, Cp H), 5.95 (s, 8H, THF-α), 2.85 (s, 8H, THF-β), 2.04 (s, 6H, $SiMe_2$), 1.03 (s, 18H, $SiMe_3$), −8.61 (s, 18H, $SiMe_3$), −21.38 (s, 2H, Cp H). Anal. Calcd for $C_{32}H_{62}Cl_2LiNdO_2Si_5$: C, 45.68; H, 7.43. Found: C, 46.0; H, 7.65.

Structure Solution and Refinement for Complexes *rac*-3, *rac*-5, and C_1-6. All the diffraction measurements were performed on a Bruker-AXS SMART-CCD area detector diffractometer with graphite-monochromatized Mo Kα radiation. Selected crystals were mounted on glass fiber using perfluoropolyether to protect them from air and humidity. Diffraction data were collected at 293(2) K for *rac*-**3** and C_1-**6** using a quick procedure (240 frames of 1.5° width, 20 s exposure time) and at 100(2) K for *rac*-**5** using a nitrogen gas stream cooling device. Diffraction data were collected using a standardized procedure which returns redundant data from a hemisphere of reciprocal space. The crystal structures were determined using direct methods as implemented in SHELXS-97. Full-matrix least-squares refinement as implemented in SHELXL-97 was used to refine all non-hydrogen atoms including anisotropic displacement parameters. For *rac*-**5**, hydrogen atom positions were calculated using idealized geometry parameters and forced to ride on the corresponding carbon atom allowing for an isotropic displacement of 1.2 times the equivalent displacement parameter of the attached carbon atom for nonterminal carbons and 1.5 times for methyl groups, respectively. Crystal data and details of data collection and structure refinements are given in Table 1. Selected bond distances and angles are listed in Table 2. Further details are included in the Supporting Information.

Typical Procedure for Ethylene Oligomerization. Toluene (95 mL) was introduced in a 250 mL Schlenk tube equipped with a mechanic stirrer rotating at speeds up to 1500 rpm. The reaction vessel was heated to 80 °C, and toluene was saturated with ethylene (1.1 atm, kept constant via a back-

---

[14] Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267.

pressure regulator). In a parallel manner, a mixture of chloroneodymocene (0.1 mmol) and *n*-butylethylmagnesium (2.0 mmol) in toluene (5 mL) was stirred for 1 h at 23 °C. The resulting clear blue solution was then transferred via syringe into the reactor under stirring. The ethylene flow rate was monitored using a mass flowmeter (Aalborg, GFM17) connected to a totalizing controller (KEP) which acts as a flow rate integrator. The reaction was quenched by the addition of 1 L of a 5% HCl methanol solution to the mixture. The resulting precipitate was filtered, washed with methanol, and dried under vacuum.

Typical Procedure for 1-Octene Oligomerization. A mixture of chloroneodymocene (0.1 mmol) and dialkylmagnesium (20 wt % solution in heptane, 2.0 mmol) was stirred for 1 h at 23 °C. To the resulting clear blue solution was added freshly distilled 1-octene (10.0 mL, 64 mmol) via syringe, and the reaction mixture was stirred at 80 °C. After 24 h, the reaction was stopped by addition of 50 mL of a 5% HCl methanol solution. Volatiles were removed with a rotavapor, and the residue was extracted with hexane (3 × 50 mL). After drying over Na_2SO_4, hexane was removed under vacuum to yield an oily residue.

Acknowledgment. This work was supported by the Ministère de l'Enseignement Supérieur et de la Recherche (Ph.D. grant to S.B.) and the CNRS.

Supporting Information Available: Crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters for complexes *rac*-**3**, *rac*-**5**, and C_1-**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0006357