

Stereoregular Polymerization of α -Olefins Catalyzed by Chiral Group 4 Benzamidinate Complexes of C_1 and C_3 Symmetry

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Abstract: The chiral lithium (–)-trimethylsilylmyrtanyl amide reacts with benzonitrile yielding the chiral benzamidinate lithium ligand ([N-trimethylsilyl][N'-myrtanyl]benzamidinate Li·TMEDA (TMEDA = tetraethylethylenediamine), [N(R*)–C–N]Li. An X-ray study shows that the ligand has a distorted tetrahedral environment in which the lithium atom is arranged symmetrically between the two benzamidinate and the two TMEDA nitrogen atoms. Equimolar addition of [N(R*)–C–N]Li to TiCl₄ in THF yields [N(R*)–C–N]-TiCl₃·THF (**1**). An X-ray study of **1** shows that it has an octahedral structure with the oxygen atom and one chlorine atom at the apical positions. [N(R*)–C–N]₃ZrCl·toluene (**2**) can be prepared in a manner related to that employed to synthesize **1**. An X-ray study of **2** shows that it has a capped octahedral geometry with the three trimethylsilyl groups in a cis position with respect to the chlorine atom and the other three myrtanyl groups arranged on the opposite side of the chlorine. Addition of MeLi·LiBr to complex **2** yields [N(R*)–C–N]₃ZrMe (**3**) which is obtained as cocrystalline with complex **2**. The X-ray structure of the cocrystalline mixture is similar to that of the chloride complex **2** exhibiting a Zr–Me distance of 2.469(10) Å. Complex **1** is an active catalyst, under pressure, for the polymerization of propylene producing elastomeric polypropylene and for the syndiotactic polymerization of styrene. Complex **2** was found to be active for the highly stereospecific polymerization of propylene.

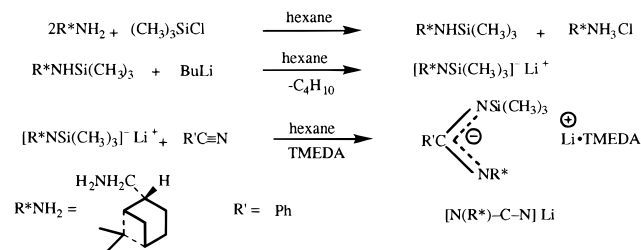
Introduction

Major advances have been achieved in the polymerization of α -olefins by “well-defined” or “single-site” catalysts.^{1,2} The majority of these catalysts belong to groups 3 and 4 of metallocene derivatives although some are known to contain one cyclopentadienyl ring and one pendant ligand.^{3–10} The tacticity of the polymers varies predictably with the structure of the metallocene catalysts. Hence, C_2 or C_1 symmetry complexes are expected to induce isotactic polyolefins, whereas C_{2v} induces atactic polymers.^{1,2,11,12} Recently, however, there has been an increased attention for other complexes containing non-Cp-spectator ligands as potential Ziegler–Natta catalysts. Chelating dialkoxo,^{13–15} chelating diamido,^{16–21} borata-

benzene,^{22,23} and benzamidinate ligands comprise some of the systems that have been recently studied.^{24–30} For group 4 benzamidinate complexes, we and others have thoroughly studied these systems as active catalysts for the polymerization of α -olefins.^{29–35} Mono(benzamidinate) group 4 complexes

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Scheme 1. Synthetic Procedure for the Synthesis of Chiral Benzamidinate Ancillary Ligands

have been found to be active catalysts for the polymerization of syndiospecific styrene and ethylene,³⁰ and the corresponding tris(benzamidinate) zirconium complexes have been found to be active catalysts able to polymerize ethylene and norbornene but unable to polymerize propylene.²⁹ We have shown that bis-(benzamidinate) group 4 halide or alkyl complexes are active precursors for the polymerization of ethylene³¹ and propylene.³⁴ Interestingly, these complexes are obtained as racemic mixtures of C_2 symmetry octahedral complexes and found to be active for the highly stereoregular polymerization of propylene under pressure.³⁶ The efficacy of complementary diastereomeric C_1 symmetry octahedral "template" ligation or the C_3 chiral ligation raises conceptual questions of applicability to asymmetric group 4 chemistry. Here we communicate the synthesis of the chiral benzamidinate lithium ligand ([*N*-trimethylsilyl][*N'*-myrtanyl]-benzamidinate) Li•TMEDA (TMEDA = tetramethylethylenediamine) [N(R*)-C-N]Li, the chiral complexes C_1 -mono([*N*-trimethylsilyl][*N'*-myrtanyl] benzamidinate)(THF)titanium trichloride (**1**), C_3 -tris([*N*-trimethylsilyl][*N'*-myrtanyl] benzamidinate)zirconium chloride (**2**), and C_3 -tris([*N*-trimethylsilyl][*N'*-myrtanyl] benzamidinate)zirconium methyl (**3**); and their reactivity as active catalytic precursors for the polymerization of α -olefins. To our knowledge, this is the first example for the synthesis and structural characterization of chiral benzamidinate ancillary ligand and complexes and their selective use, depending on the complex, as precursors for either the formation of elastomeric polypropylene or the stereoregular polymerization of propylene and styrene.

Results and Discussion

The chiral ancillary ligand, [N(R*)-C-N]Li, was prepared from the corresponding trimethylsilylmyrtanylamine after lithiation with BuLi and the concomitant reaction with benzonitrile, as described in Scheme 1. The yield of the crystalline ancillary ligand, [N(R*)-C-N]Li, is typically 40% on a scale of 10–15 g. An X-ray study of [N(R*)-C-N]Li (Figure 1, Table 1) shows that it has a distorted tetrahedral environment in which the lithium atom is arranged symmetrically between the two benzamidinate and the two TMEDA nitrogen atoms (Li–N(1) = 2.021(5) Å, Li–N(2) = 2.023(5) Å; Li–N(3) = 2.135(6) Å, Li–N(4) = 2.129(6) Å). The dissimilar electronic delocalization throughout the amidinate moiety is observed by the different C–N distances [N(1)–C(4) = 1.343(4) Å, N(2)–C(14) = 1.308(4) Å].

Addition of equimolar amounts of [N(R*)-C-N]Li in THF at 25 °C to TiCl₄ yields the complex [N(R*)-C-N](THF)-TiCl₃ (**1**) in 89% yield. An X-ray study of complex **1** (Figure

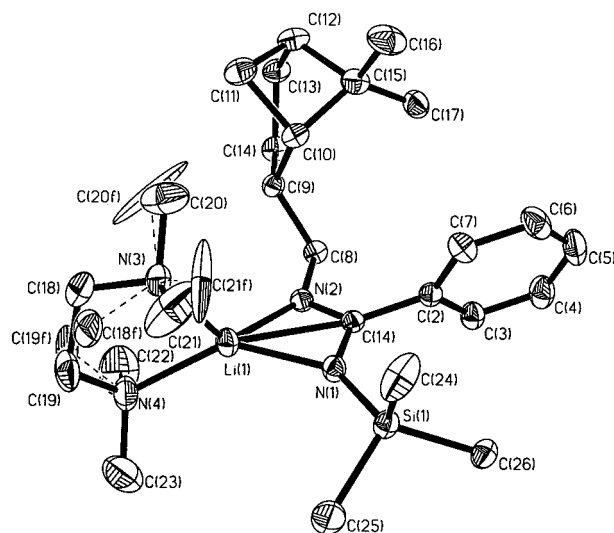


Figure 1. ORTEP diagram of the ligand [N(R*)-C-N]Li•TMEDA showing the 40% probability thermal ellipsoids for all non-hydrogen atoms.

Table 1. Selected Bond Lengths and Angles for [N(R*)-C-N]Li•TMEDA^a

bond lengths (Å)		bond angles (deg)	
Si(1)–N(1)	1.690(2)	C(14)–N(2)–Li(1)	86.4(2)
N(1)–C(14)	1.343(4)	C(14)–N(1)–Si(1)	133.7(2)
N(2)–C(14)	1.308(4)	C(14)–N(1)–Li(1)	85.7(2)
N(1)–Li(1)	2.021(5)	C(14)–N(2)–C(8)	122.4(2)
N(2)–Li(1)	2.023(5)	Si(1)–N(1)–Li(1)	140.7(2)
N(3)–Li(1)	2.135(6)	C(8)–N(2)–Li(1)	147.9(2)
N(4)–Li(1)	2.129(6)	C(14)–N(2)–Li(1)	86.4(2)
Li(1)–C(14)	2.340(5)	N(1)–Li(1)–N(2)	68.3(2)

^a Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figure 1.

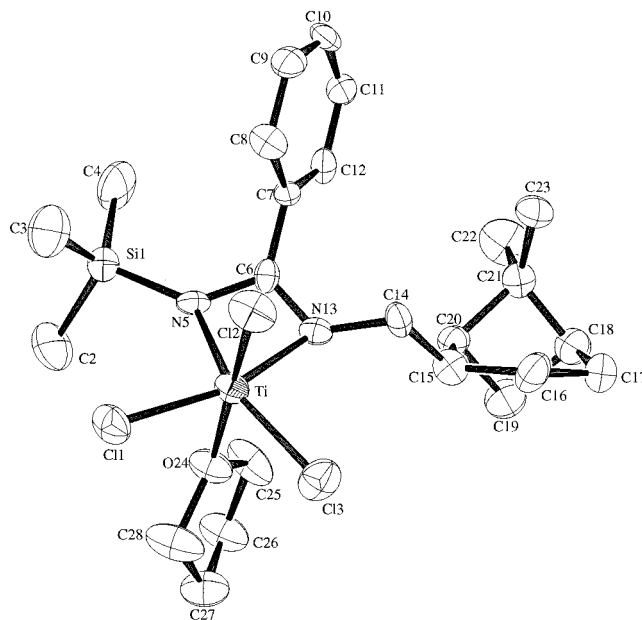


Figure 2. ORTEP drawing of complex **1** showing the 40% probability thermal ellipsoids for all non-hydrogen atoms.

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2, Table 2) shows that it has an octahedral structure with the oxygen atom and one chlorine atom at the apical positions. Interestingly, the 4-membered ring Ti–N(5)–C(6)–N(13) deviates from planarity along the Ti–C(6) vector (151.7°) more than any other benzamidinate complex (167–178°),^{34,37} in part as a

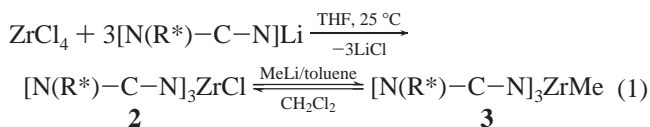
Table 2. Selected Bond Lengths and Angles for [N(R*)-C-N](THF)TiCl₃ (**1**)^a

bond lengths (Å)		bond angles (deg)	
Ti-N(5)	2.030(9)	N(5)-Ti-N(13)	64.3(4)
Ti-N(13)	2.070(9)	N(5)-Ti-O(24)	86.9(3)
Ti-O(24)	2.119(8)	N(5)-Ti-Cl(1)	95.1(3)
Ti-Cl(1)	2.280(4)	N(5)-Ti-Cl(2)	96.7(3)
Ti-Cl(2)	2.288(4)	N(5)-Ti-Cl(3)	153.9(3)
Ti-Cl(3)	2.299(4)	N(13)-Ti-Cl(3)	91.1(3)
		N(13)-Ti-Cl(1)	159.3(3)
		N(5)-C(6)-N(13)	111.0(10)

^a Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figure 2.

consequence of the different electronic effects of the different nitrogen substituents at the benzamidinate moiety.

In a similar manner, the reaction of 3 equiv of [N(R*)-C-N]Li with ZrCl₄ in THF or toluene at room temperature yields the complex [N(R*)-C-N]₃ZrCl·toluene (**2**) in 25–35% as shown in eq 1. ¹H and ¹³C NMR spectra of complex **2** suggest

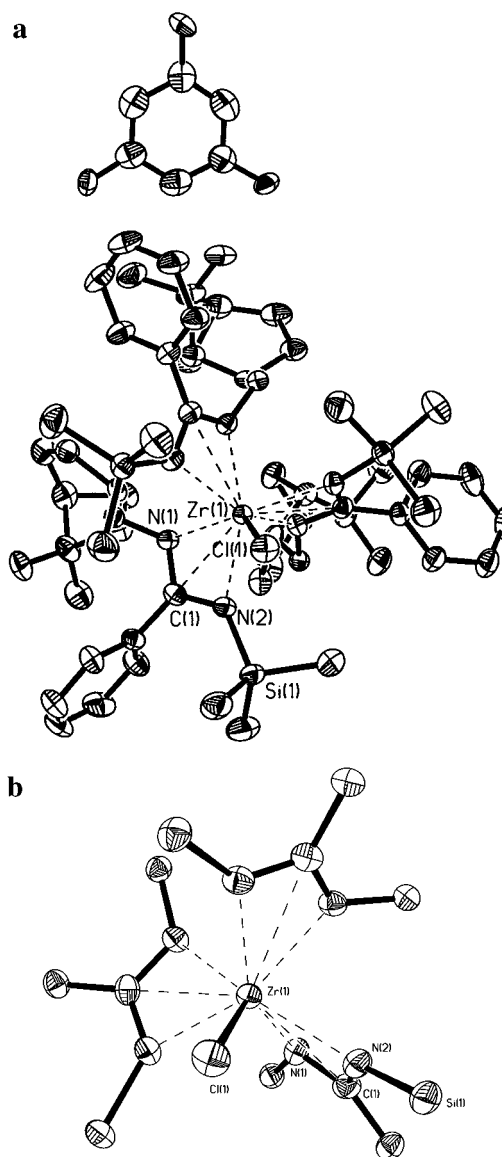


a C₃ symmetry complex. X-ray crystal structure determination of **2** revealed a “propeller”-like structure (Figure 3a and b, Table 3). The coordination geometry around the 7-coordinate zirconium atom can be described as a capped octahedral. Owing to the propeller-like structure, three trimethylsilyl groups are in a cis position with respect to the chlorine atom and the other three myrtanyl groups are arranged on the opposite side of the chlorine. The distances between the benzamidinate moiety or the chloride atom and the zirconium center are normal as compared to nonchiral group 4 and actinide benzamidinate complexes [Zr-N = 2.24–2.35 Å; Zr-Cl = 2.46–2.48 Å].^{29,37}

Alkylation of complex **2** with an excess of MeLi·LiBr in toluene, at room temperature, yields a brown solution of a mixture of complexes **2** and **3**. Crystallization of the mixture affords single cocrystals containing 70:30 of complexes **2** and **3**, respectively. The X-ray structure of the cocrystalline complex (Figure 4, Table 4) is akin to that of the chloride complex **2** with a Zr-Me distance of 2.469(10) Å.

Reaction of the cocrystalline mixture with CH₂Cl₂ yields the chloride complex **2**, which crystallizes in a different space group (P63; hexagonal crystal system) as compared to the original chloride complex, obtained from toluene, due to the presence of CH₂Cl₂ in the unit cell.

Structural comparison of complex **2** with the nonchiral tris-([bistrimethylsilyl]benzamidinate) zirconium chloride complex shows that both complexes crystallize in the hexagonal crystal system having P3 and P₃c1 space groups, respectively.²⁹ Both complexes have a capped octahedral propeller-like structure with the major difference being that in the nonchiral complex both enantiomeric propeller structures are present in the crystal structure, whereas in the chiral complex only one enantiomeric structure is observed. Structural distinctions are found in the Zr-N(1) [2.293(5) vs 2.249(4) Å], N(1)-C(1) [1.348(9) vs 1.329(5) Å], and Zr-Cl [2.475(3) vs 2.464(2) Å] bond lengths for complex **2** and the tris-([bistrimethylsilyl]benzamidinate) zirconium chloride complex, respectively (Figure 3). The major difference between the two complexes is the position of the three benzamidinate ligands as compared to that of the chloride

**Figure 3.** (a) ORTEP drawing of complex **2**. (b) View of the first coordination sphere, showing the 40% probability thermal ellipsoids for all non-hydrogen atoms.**Table 3.** Selected Bond Lengths and Angles for [N(R*)-C-N]₃ZrCl·toluene (**2**)^a

bond lengths (Å)		bond angles (deg)	
Zr-N(1)	2.293(5)	N(1)-Zr(1)-N(2)	59.3(2)
Zr-N(2)	2.249(5)	N(1)-Zr(1)-N(1')	86.8(2)
Zr-Cl(1)	2.475(3)	N(2)-Zr(1)-N(2)'	119.36(4)
Zr-C(1)	2.679(6)	N(1)-Zr(1)-N(2)'	144.4(2)
N(1)-C(1)	1.322(9)	N(2)-Zr(1)-N(1)'	81.0(2)
N(2)-C(1)	1.348(9)	N(1)-Zr-Cl(1)	127.47(13)
		N(2)-Zr-Cl(1)	85.40(14)
		N(1)-C(1)-N(1)	114.6(5)

^a Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figure 3.

ligand. Thus, in complex **2**, the blades in the propeller structure are pushed down opposite the chloride ligand as observed from the Zr-Cl vector (Figures 3 and 4) and as compared with the tris-([bistrimethylsilyl]benzamidinate) zirconium chloride complex. The angle between the propeller flap and the chloride atom in complex **2** is larger by 8° as related to the racemic complex, exhibiting a more exposed chloride ligand. This

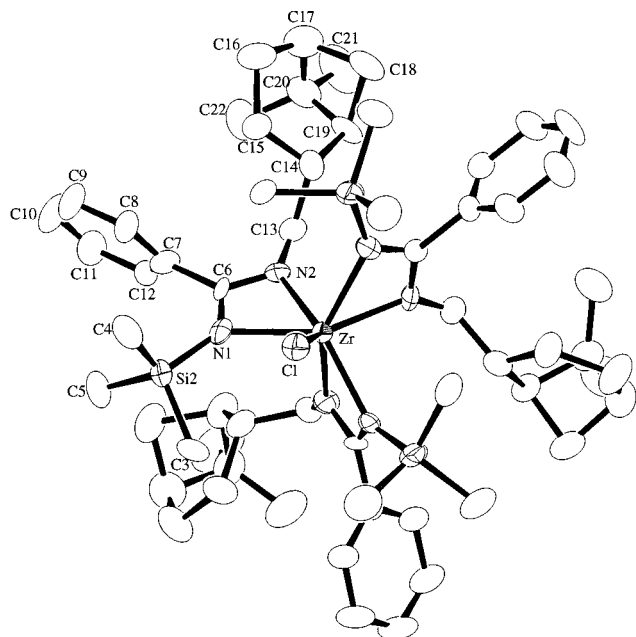


Figure 4. ORTEP drawing of complex **3** showing the 40% probability thermal ellipsoids for all non-hydrogen atoms.

Table 4. Selected Bond Lengths and Angles for $[N(R^*)-C-N]_2ZrMe$ (**3**)^a

bond lengths (Å)		bond angles (deg)	
Zr–N(1)	2.217(13)	N(1)–Zr(1)–N(2)	59.2(2)
Zr–N(2)	2.26(2)	N(2)–Zr–Cl	130.3(4)
Zr–Cl(1)	2.471(9)	N(1)–Zr–Cl	83.2(4)
Zr–C(6)	2.69(2)	N(1)–C(6)–N(2)	112.0(2)
N(1)–C(6)	1.36(3)		
N(2)–C(6)	1.31(2)		

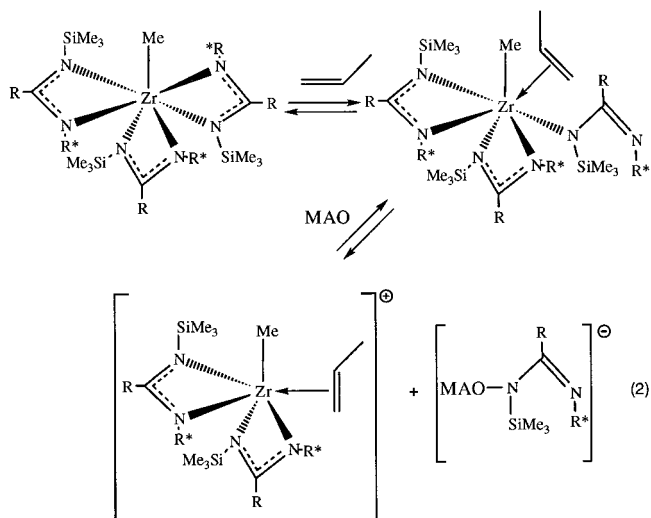
^a Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figure 4.

opened coordination is likely partially responsible for the different reactivities found between the two complexes (vide infra).

When activated with methylalumoxane (MAO), complexes **1** and **2** are active catalysts for the polymerization of propylene (Table 5). The polymerization of propylene by complex **1**, under pressure, produces a high molecular weight elastomer (*mmmm* = 35%) (at atmospheric pressure only dimer and trimers are obtained).^{38–42} Increasing the pressure/temperature or using a polar solvent (CH₂Cl₂) induces a decrease in molecular weight and activities although the polypropylene is obtained as a nonsticky elastomeric solid. In addition, complex **1** has been found to be an active catalyst for the polymerization of styrene to highly syndiotactic polystyrene (*rrrr* > 99%). It is noteworthy to point out that a nonchiral monobenzamidinate titanium complex also produces syndiotactic polystyrene with a high degree of stereoregularity.³⁰ The molecular weight of the syndiotactic polystyrene was found to exhibit a linear dependency on the used amount of MAO. It is important to point out that MAO in CH₂Cl₂, on its own, is able to induce the rapid

polymerization of styrene to a high cross-linkage polystyrene with T_g of 110 °C, whereas in toluene this reaction is not observed.

In the stereoregular polymerization of propylene, by complex **2** under pressure, isotactic polypropylenes are obtained exclusively by the site control mechanism since no *mrmm* signals were found in the ¹³C NMR analysis of the polymers (Table 5).⁴³ In contrast to group 4 metallocene complexes, larger amounts of MAO were found to decrease the activity and the molecular weight of the isotactic polypropylenes reaching a maximum activity and molecular weight at a ratio of about Zr/Al 1:600. This similar behavior has already been observed for other benzamidinate complexes.^{31,34} It is important to point out that attempts to produce polypropylene at atmospheric pressure were not successful. This result argues for a high propene concentration to allow the initiation of the polymerization. Recently, we have shown that bis(benzamidinate)zirconium dichloride complexes are able to polymerize polypropylene in an atactic fashion at atmospheric pressure and in an isospecific fashion under pressure (due to their *C*_{2v} symmetry resembling racemic mixture of *ansa*-metallocenes).³⁶ Thus, it is plausible to expect that one ancillary ligand is not acting as a spectator ligand and that MAO is able to extract one benzamidinate moiety, producing the expected chiral cationic complex.^{1,2} Taking into account that high propene concentration is required and that aluminum benzamidinate complexes are known,^{44–47} we expect that the displacement of the benzamidinate ligand should proceed most likely through a $\eta^3 \rightarrow \eta^1$ slippage mechanism (eq 2). Although two different η^1 -amido configura-



tions are possible, theoretically, the preferred configuration will be the one containing a silyl group at the β position from the metal center.^{48–51} Recently, similar isolobal (alkoxy)silylimido ligands have been found not to be inert spectator ligands and

(38) For group 4 metallocenes producing elastomers and the corresponding characterization, see refs 39–42.

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Table 5. Activity, Molecular Weight, and Melting Point Data for the Polymerization of Propylene and Styrene by Complexes **1** and **2**

entry	cat.	olefin	solvent	[MAO]/[cat.] ^a	pressure (atm)	temp (K)	<i>M_v</i> ^c	activity ^b	<i>mmmm</i> (%)	mp ^d (°C)
1	1	propylene	toluene	200	5.0	293	100 145	85 000	35	— ^e
2	1	propylene	toluene	200	7.2	333	27 650	4 910	23	— ^e
3	1	propylene	CH ₂ Cl ₂	200	5.0	293	31 379	1 382	27	— ^e
4	2	propylene	toluene	280	12.0	353	7 750	9 230	79.5 ^f	128.5
5	2	propylene	toluene	280	8.6	323	10 250	716	92.8 ^g	135.0
6	2	propylene	toluene	280	5.1	273	31 800	200	98.9 ^h	145.0
7	2	propylene	toluene	560	8.6	323	33 650	1 060	95.0 ⁱ	140.0
8	2	propylene	toluene	830	8.6	323	7 250	105	93.8 ^j	139.4
9	2	propylene	CH ₂ Cl ₂	280	8.6	323	930 ^k	5 290	—	— ^l
10	1	styrene	toluene	200	1.0	293	15 200 ^e	470 000	(>99) ^m	264; 270
11	1	styrene	toluene	1000	1.0	293	67 400 ^e	320 000	(>99) ^m	263.4

^a Methylaluminoxane, solvent removed from a 20% solution in toluene (Schering) at 25 °C/10⁻⁶ torr. ^b Grams total polymer/mole catalyst·hour. ^c By viscosimeter technique in 1,2,4-trichlorobenzene at 130 °C ($K = 1.37 \times 10^{-2}$; $\alpha = 0.7$). ^d Measured by DSC of the second thermogram. ^e The polypropylene is obtained as a noncrystalline elastomer. ^f *mmmm* = 8.9%, *mmrr* = 8.9%, *mrrm* = 2.7%. ^g *mmmm* = 3.3%, *mmrr* = 3.3%, *mrrm* = 0.6%. ^h *mmmm* = 0.6%, *mmrr* = 0.5%. ⁱ *mmmm* = 2.3%; *mmrr* = 2.3%, *mrrm* = 0.4%. ^j *mmmm* = 3.1%; *mmrr* = 3.1%. ^k *M_n*. ^l Atactic polypropylene. ^m Syndiotactic polystyrene (*rrrr*, %).

to be quite reactive.^{52,53} In addition, we have recently shown that metallocene complexes with amido, phosphido, and arsenido ligands bearing a silyl group at the β -position, are easily cleaved with MAO, allowing the formation of the active cationic metallocenes for the polymerization of propylene.^{18,54}

Interestingly, in the polymerization of propylene by either complex **1** or **2**, the only chain termination mechanism operative in these systems appears to be the chain transfer to aluminum since we have been unable to observe any olefinic resonances in the proton or carbon NMR spectra of the polymeric or oligomers prepared with these catalytic systems. Thus, it seems that if the aluminum cocatalyst is replaced by a perfluorophenylborate anion or other strong Lewis acid cocatalyst able to remove one of the benzamidinate moieties, a living system could be achieved.²⁰

Conclusions

In summary, new catalytic chiral systems for the polymerization of α -olefins has been introduced. C₃ symmetry chiral complexes allow the highly stereoregular polymerization of propylene, whereas the monosubstituted group 4 complex is able to polymerize either styrene or propylene toward highly syndiotactic or elastomeric polypropylenes, respectively. The use of perfluoroborane cocatalysts and the copolymerization of styrene and propylene are presently under investigation.

Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line or interfaced to a high vacuum (10⁻⁵ Torr) line or in a nitrogen filled Vacuum/Atmospheres glovebox with a medium capacity recirculator (1–2 ppm O₂). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents were distilled under argon from sodium benzophenone ketyl. Hydrocarbon solvents (THF-*d*₈, toluene-*d*₈, benzene-*d*₆, C₆D₁₂) were distilled under nitrogen from an Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over an Na/K alloy in resealable bulbs. Benzonitrile, TMSCl, BuLi, and myrtanylamine (Aldrich) were used without further purification. CH₂-Cl₂ was freshly distilled over P₂O₅. Propylene was purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular-sieve column. TMEDA was dried and distilled over Na/K. Styrene

was dried and freshly distilled over CaH₂ and stored for a maximum of 24 h at –25 °C under Ar, in darkness, until utilization. NMR spectra were recorded on Bruker AM 200 and Bruker AM 400 spectrometers. Chemical shifts for ¹H NMR and ¹³C NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. The polypropylene NMR experiments were conducted in 1,2,4-trichlorobenzene at 130 °C with 20% DMSO-*d*₆. Pentad analysis was evaluated as described in the literature.⁴³ For elastomeric polypropylenes, C₆H₁₂ at reflux temperatures was used as the solvent. Syndiotactic polystyrene NMR experiments were conducted in 1,2,4-trichlorobenzene at 120 °C with 10% of 1,1,2,2-tetrachloro-1,2-dideuterioethane. Melting points of the polymers were measured by DSC (Polymer Laboratories). The second heating thermogram was used to correct the melting points of the polymers (5 deg/min). Elemental analysis was performed by the microanalytical laboratory at the Hebrew University of Jerusalem. Optical rotations were measured using Digital Polarimeter Jasco-DIP 370.

Synthesis of (CH₃)₃SiH(N-myrtanyl). A flame-dried 1-L Schlenk flask containing 300 mL of dried hexane was charged under argon with 10 g (65.2 mmol) of (–)-*cis*-myrtanylamine. Over a period of 1.5 h at room temperature, 7.82 g (72 mmol) of (CH₃)₃SiCl was slowly added using a dropping funnel. A precipitate was immediately formed, and the reaction was warmed to reflux for 17 h. The solid myrtanylammmonium chloride salt was filtered and washed with hexane, dried under vacuum, and recycled. The washing hexane solutions were combined, and the chiral (CH₃)₃SiHNH(myrtanyl) was distilled at 83 °C at 0.05 mbar as a transparent oil to obtain 6.1 g (82%). ¹H NMR (CDCl₃, 200 MHz) δ 2.63 (dd, ²*J* = 6.0 Hz, 2H, CH₂N); 2.25 (m, 1H, NCH₂CH); 1.80–2.06 (m, 8H); 1.40 (m, 1H, NH); 1.14 (s, 3H, CH₃); 0.090 (s, 3H, CH₃); 0.08 (s, 9H, SiMe₃).

Synthesis of [C₆H₅C(N-TMS)(N-myrtanyl)]Li·TMEDA. To a solution of 100 mL of hexane containing 6 g (26.8 mmol) of freshly distilled (CH₃)₃Si(H)N-myrtanyl was slowly added dropwise under argon, during 1 h, at room temperature, 16.75 mL (26.8 mmol) of a solution of 1.6 M BuLi in hexane. The reaction was stirred for an additional hour, and 2.76 g (26.8 mmol) of freshly distilled benzonitrile was added at –10 °C. The mixture was allowed to warm to room temperature and stirred for an additional 17 h. To the reaction mixture was carefully added 5.3 mL (35 mmol) of TMEDA (tetramethylethylenediamine), and the mixture was cooled to 0 °C to obtain 11.7 g (40%) of large, yellowish crystals of the ligand. $[\alpha]_D^{20} = -66^\circ$ ($c = 2.44 \times 10^{-2}$; hexane). Found: C 69.08, H 10.55, N 12.19; calcd for C₂₆H₄₇LiN₄Si (450.70): C 69.29, H 10.51, N 12.43. ¹H NMR (C₆D₆, 200.13 MHz): δ 7.30 (m, 5H, *ph*), 3.10 (m, 2H, N–CH₂CH), 2.31 (m, 1H, NCH₂CH), 2.29 (m, 2H CH₂(CH)₂), 2.11 (s, 12H, NCH₃), 1.95 (m, 6H, CHCH₂CH₂ + CH₂(CH)₂), 1.85 (s, 4H, CH₂CH₂N), 1.25 (s, 3H, CH₃), 0.85 (s, 3H, CH₃), 0.15 (s, 9H, Si(CH₃)₃). ¹³C NMR (C₆D₆): δ 144.1 (N=C), 129.5 (arom CH), 128.4 (arom CH), 127.5 (arom CH), 126.0 (arom C), 57.2 (CH₂NCH₃), 56.8 (CHCH₂N), 46.5 (CHCH₂N), 45.5 (CH₂NCH₃), 44.5 (CH₃), 42.5 (CH₃), 39.0 (C(CH₃)₂), 35.1 (CH₂CH₂CH), 28.5 (CH₂CH₂CH), 27.5 (CH₂CH₂CH), 23.5 (CH(CH₂)₂), 21.5 (CH₂(CH)₂), 4.6 (Si(CH₃)₃).

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Table 6. Crystal Data and Structure Refinement for the Ligand [NR*—C—N]Li·TMEDA and the Complexes **1**, **2**, and **3**

compd	[NR*—C—N]Li·TMEDA	1	2	3
empirical formula	C ₂₆ H ₄₃ LiN ₄ Si	C ₂₄ H ₃₉ Cl ₃ N ₂ SiTi	C ₆₀ H ₉₃ ClN ₆ Si ₃ Zr	C ₆₀ H ₉₃ N ₆ Si ₃ ZrCl _{0.7} Me _{0.3}
formula weight	446.67	553.91	1109.36	1103.23
temperature	210.0(1) K	200.0(1) K	210.0(1) K	200.0(2) K
wavelength	0.710 73 Å	0.710 73 Å	0.710 73 Å	0.710 73 Å
crystal system	monoclinic	monoclinic	hexagonalic	hexagonalic
space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁	<i>P</i> 3	<i>P</i> 6 ₃
unit cell dimensions	<i>a</i> = 9.7279(8) Å α = 90° <i>b</i> = 15.9000(13) Å β = 112.71 (1)° <i>c</i> = 10.0932(8) Å γ = 90°	<i>a</i> = 10.658 (5) Å α = 90° <i>b</i> = 18.883 (9) Å β = 103.14 (5)° <i>c</i> = 7.312 (3) Å γ = 90°	<i>a</i> = 13.3493 (8) Å α = 90° <i>b</i> = 13.3493 (8) Å β = 90° <i>c</i> = 12.1353 (11) Å γ = 120°	<i>a</i> = 14.634 (7) Å α = 90° <i>b</i> = 14.634 (7) Å β = 90° <i>c</i> = 18.318 (9) Å γ = 120°
volume	1440.0 (2) Å ³	1433.0 (11) Å ³	1872.8 (2) Å ³	3397.3 (3) Å ³
Z	2	2	2	6
density (calcd)	1.030 mg/m ³	1.284 mg/m ³	1.273 mg/m ³	1.204 mg/m ³
absorption coefficient	0.100 mm ⁻¹	0.639 mm ⁻¹	0.498 mm ⁻¹	0.355 mm ⁻¹
<i>F</i> (000)	488	584	1520	1308
crystal size	0.4 × 0.4 × 0.3 mm	0.58 × 0.34 × 0.17 mm	0.42 × 0.41 × 0.36 mm	0.26 × 0.32 × 0.41 mm
θ -range for data collection	2.19 to 25.96°	2.16 to 25.02°	1.68 to 25.88°	2.22 to 25.05°
index ranges	-10 ≤ <i>h</i> ≤ 11; -10 ≤ <i>k</i> ≤ 19; -12 ≤ <i>l</i> ≤ 12	-12 ≤ <i>h</i> ≤ 12; 0 ≤ <i>k</i> ≤ 22; 0 ≤ <i>l</i> ≤ 8	-12 ≤ <i>h</i> ≤ 16; -14 ≤ <i>k</i> ≤ 15; -14 ≤ <i>l</i> ≤ 16	-17 ≤ <i>h</i> ≤ 15; 0 ≤ <i>k</i> ≤ 17; 0 ≤ <i>l</i> ≤ 21
reflections collected	6813	2825	6317	6339
independent reflections	3894 (<i>R</i> _{int} = 0.0330)	2619 (<i>R</i> _{int} = 0.0786)	3482 (<i>R</i> _{int} = 0.0397)	2046 (<i>R</i> _{int} = 0.0612)
refinement method	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²
data/restraints/parameters	3894/1/451	2618/1/313	3480/1/272	2046/1/250
goodness of fit on <i>F</i> ²	1.072	1.130	1.081	1.113
final <i>R</i> indices <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0407, w <i>R</i> 2 = 0.1090	<i>R</i> 1 = 0.0742, w <i>R</i> 2 = 0.1601	<i>R</i> 1 = 0.0571, w <i>R</i> 2 = 0.1401	<i>R</i> 1 = 0.1089, w <i>R</i> 2 = 0.2622
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0514, w <i>R</i> 2 = 0.1253	<i>R</i> 1 = 0.1275, w <i>R</i> 2 = 0.1891	<i>R</i> 1 = 0.0755, w <i>R</i> 2 = 0.1791	<i>R</i> 1 = 0.1272, w <i>R</i> 2 = 0.2782
absolute structure parameter	-0.1(2)	0.01(11)	0.03(8)	-0.3(3)
largest diff. peak and hole	0.158 and -0.222 e Å ⁻³	0.450 and -0.628 e Å ⁻³	0.875 and -0.410 e Å ⁻³	1.673 and -1.723 e Å ⁻³

Synthesis of [C₆H₅C(N-TMS)(N-myrtanyl)]₃TiCl. To a stirred solution of 0.692 g (3.7 mmol) of TiCl₄ in 20 mL of tetrahydrofuran was added dropwise at room temperature, a solution of 1.7 g (3.7 mmol) of C₆H₅C(NTMS)(N-myrtanyl)Li·TMEDA in 10 mL of tetrahydrofuran. The reaction mixture was stirred overnight, the solvent was removed by vacuum, and the residue was extracted four times with 80 mL of toluene. LiCl was removed by filtration through a thin layer of dried Celite filter-aid. The clear filtrate was evaporated to dryness, washed with 30 mL of hexane, and dried under vacuum to obtain 1.83 g (89.2%) of red microcrystalline complex. Single crystals for X-ray diffraction were obtained by recrystallizing from toluene or hexane and cooling at -5 °C. [α]_D²⁰ = -13.4° (*c* = 1.28 × 10⁻²; toluene). Found: C 51.47, H 7.03, N 4.74. Calcd for C₂₄H₃₉N₂SiTiCl₃O (553.93): C 52.04, H 7.09, N 5.06. ¹H NMR (C₇D₈, 200.13 MHz): δ 7.25 (m, 5H, *ph*), 3.81 (m, 4H, OCH₂), 2.35 (m, 2H NCH₂), 1.6–1.8 (m, 6H, CH₂CHCH₂CH), 1.68 (m, 4H, OCH₂CH₂), 1.37 (s, 3H, CH₃), 1.25–1.36 (m 3H, CHCH₂), 1.26 (s, 3H, CH₃), 0.35 (s, 9H, Si(CH₃)₃). ¹³C NMR (C₇D₈): δ 177.5 (C=N), 133.4 (arom CH), 129.6 (arom C), 128.4 (arom CH), 126.2 (arom CH), 69.5 (OCH₂), 50.0 (CHCH₂N), 44.4 (CH₃), 42.5 (CH₃), 41.0 (CHCH₂N), 33.8 (C(CH₃)₂), 33.5 (CH₂CH₂CH), 26.1 (CH₂CH₂CH), 25.7 (CH₂CH₂CH), 23.4 (OCH₂CH₂), 20.9 (CH(CH₂)₂), 20.0 (CH₂(CH₂)₂), 2.9 (SiCH₃).

Synthesis of [C₆H₅C(N-TMS)(N-myrtanyl)]₃ZrCl. To a stirred solution of 5.2 g (22.2 mmol) of ZrCl₄ in 130 mL of tetrahydrofuran was added dropwise at room temperature, a solution of 30 g (66.6 mmol) of C₆H₅C(NTMS)(N-myrtanyl)Li·TMEDA in 100 mL of tetrahydrofuran. The reaction mixture was stirred overnight, the solvent was removed by vacuum, and the residue was extracted with 80 mL of toluene. LiCl was removed by filtration through a thin layer of dried Celite filter-aid. The clear filtrate was evaporated to dryness, washed with 30 mL of hexane, and dried under vacuum to obtain 20.3 g (23%) of yellow microcrystalline complex. Single crystals for X-ray diffraction were obtained by recrystallization from toluene–hexane at -10 °C. [α]_D²⁰ = 3.9° (*c* = 1.28 × 10⁻²; toluene). Found: C 65.73, H 8.61, N 7.57, Cl 3.00. Calcd for C₆₀H₉₃N₆Si₃ZrCl (1109.36): C 65.03, H 8.45, N 6.67, Cl 3.20. ¹H NMR (CDCl₃, 200.13 MHz): δ 7.25 (m, 5H, *ph*), 3.18 (m, 2H, N-CH₂CH), 2.35 (m, 2H CH₂CHCH), 2.11 (m, 1H, CH₂CHCH₂), 1.80 (m, 4H, CHCH₂CH₂), 1.25 (m, 1H, CHCH₂CH), 1.15 (s, 3H, CH₃), 0.95 (m, 1H, CHCH₂CH), 0.35 (s, 3H, CH₃), 0.05 (s, 9H, Si(CH₃)₃). ¹³C NMR (C₆D₆): δ 177.1 (N=C), 136.4 (arom

CH), 128.6 (arom C), 128.4 (arom CH), 128.2 (arom CH), 128.0 (arom CH), 127.4 (arom CH), 55.4 (CHCH₂N), 43.4 (CH₃), 42.8 (CH₃), 41.5 (CHCH₂N), 38.4 (C(CH₃)₂), 34.1 (CH₂CH₂CH), 27.6 (CH₂CH₂CH), 26.6 (CH₂CH₂CH), 22.1 (CH(CH₂)₂), 21.4 (CH₂(CH₂)₂), 2.55 (SiCH₃).

Synthesis of 0.3[C₆H₅C(N-TMS)(N-myrtanyl)]₃ZrMe·0.7[C₆H₅C(N-TMS)(N-myrtanyl)]₃ZrCl. To a stirred solution of 1.08 g (1.32 mmol) of C₆H₅C(N-TMS)(N-myrtanyl)]₃ZrCl in 50 mL of toluene was added dropwise at room temperature, a solution of 1.76 mL (2.64 mmol) of 1.5 M of MeLi in diethyl ether. The reaction mixture was stirred for 24 h, and the solvent was removed by vacuum. Hexane was vacuum-transferred to the mixture, and LiCl was removed by filtration through a thin layer of dried Celite filter-aid. The clear filtrate was evaporated to dryness to obtain 0.4 g (85%) of colorless microcrystalline complex. Crystals for X-ray diffraction were obtained by recrystallization of the complex from toluene–hexane at -25 °C. [α]_D²⁰ = 2.2° (*c* = 0.76 × 10⁻²; toluene). Found: C 65.82, H 8.54, N 7.04, Cl 2.24. Calcd for C₆₀H₉₃N₆Si₃Zr(0.7Cl + 0.3CH₃) (1103.23): C 65.66, H 8.57, N 7.67, Cl 2.25. ¹H and ¹³C NMR (C₆D₆, 200.13 MHz): The same spectra are obtained as for the chloride complex with the additional signals of the Zr-CH₃ at 1.05 and 14.3 ppm for the ¹H and ¹³C NMR, respectively.

Propylene Polymerizations. The general procedure is as follows: A 100-mL heavy-wall glass reactor with a strong magnetic stirrer and flame-dried under vacuum for a few hours, was charged with 5 mg of the catalyst and a specific amount of MAO into the glovebox. The reactor was connected to a high-vacuum line, and 20 mL of CH₂Cl₂ (dried over P₂O₅) or toluene (dried over Na/K) were condensed by vacuum transfer. After equilibration of the temperature, the reactor was cooled to -150 °C, and an excess of propylene (purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column) was introduced into the reactor. The temperature was raised and equilibrated through a thermostated bath, and the pressure was measured by means of a manometer. The reaction was stirred strongly for a period of few hours. The polymerization was quenched by exhausting the excess propylene into a well-ventilated hood, followed by the fast introduction of 30 mL of methanol/HCl. The isotactic polypropylene was filtered, washed several times with hexane and acetone, and dried under vacuum at 0.001 mmHg at 60 °C for few hours. The filtrate solutions containing any atactic or low molecular

weight polymers were combined and dried under vacuum at 0.001 mmHg at 60 °C for few hours.

Styrene Polymerizations. Polymerizations were carried out in 100-mL glass reactors (fully covered against light) equipped with magnetic stirring bars and thermostated to the desired temperature. The reactor was charged with 5 mg of the catalyst and a specific amount of MAO into the glovebox. The reactor was connected to a high vacuum line, and 20 mL of toluene (dried over Na/K) were condensed by vacuum transfer. After equilibration of the temperature, a measured amount of freshly distilled styrene (kept at -20 °C and covered against light) was introduced into the reactor by mean of a gastight syringe. The temperature was raised and equilibrated through a thermostated bath. The reaction was stirred strongly for a period of few hours. The polymerization was quenched by the fast introduction of 30 mL of methanol/HCl. The polymer was filtered, washed several times with hexane and acetone, and dried under vacuum at 0.001 mmHg at 60 °C for few hours.

X-ray Crystallography. General Procedure. X-ray crystallographic studies were carried out on a Siemens CCD diffractometer with graphite-monochromized Mo K α ($\lambda = 0.71073 \text{ \AA}$) controlled by a pentium-based PC running the SMART software package.⁵⁵ Single crystals were mounted at room temperature on the ends of quartz fibers in Parathone N oil, and the data were collected at the corresponding temperature in a stream of cold N₂.

(55) SMART Version 4.0; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

Data collection and reduction protocols are described in detail elsewhere.⁵⁶ The structures were solved by direct methods and refined on F^2 by using SHELXTL software package.⁵⁷ Relevant crystallographic information is summarized in Table 6.

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Supporting Information Available: Full crystallographic tables for the ligand and complexes **1**, **2**, and **3** (31 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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