Articles

Some Evidence of a Dual Stereodifferentiation Mechanism in the Polymerization of Propene by α-Diimine Nickel Catalysts

Daniela Pappalardo, Mina Mazzeo, Simona Antinucci, and Claudio Pellecchia*

Dipartimento di Chimica, Università di Salerno, I-84081 Baronissi (SA), Italy

Received June 5, 2000; Revised Manuscript Received October 16, 2000

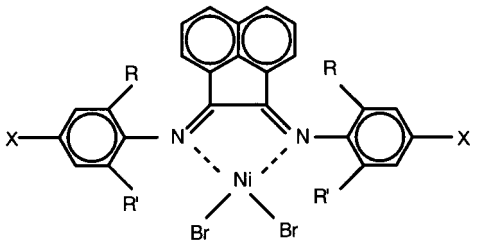
ABSTRACT: Nickel diimine compounds of general formula [{(ArN═C(X)C(X)═NAr)}$NiBr_2$] (X_2 = 1,8-naphthdiyl; Ar = 2,6-diisopropylphenyl, **1**; 2,6-dimethylphenyl, **2**; 2-isopropyl-6-methylphenyl, **3**; 2-*tert*-butyl-6-methylphenyl, **4**; 2,4-di-*tert*-butyl-6-methylphenyl, **5**) were synthesized and tested in the polymerization of propene to address the effects of the coordination environment at the nickel center on the polypropylene microstructure. Compounds **1** and **2**, having four isopropyl and four methyl ortho substituents, respectively, afford prevailingly syndiotactic polypropylenes at −45 °C (rr = 75% for **1** and rr = 61% for **2**) through a "chain-end" control mechanism. Compounds such as **3**, **4**, and **5**, having two different ortho substituents on the same aromatic ring, can exist as either *rac* or *meso* isomers. *Rac*-**3** and *rac*-**4** afford much less stereoregular polypropylenes with respect to **1** and **2** (e.g., mm = 41% and rr = 25% for *rac*-**3)**. These C_2-symmetric catalysts could provide an "enantiomorphic-site" type isotactic-specific steric control opposing the syndiospecific "chain-end" steric control. The hypothesis of a dual mechanism of steric control being operative has been supported by the synthesis of both the *rac* and the *meso* isomers of **5**, with the former still affording a polypropylene with a low stereoregularity (rr = 33% and mm = 23%) and the latter yielding a prevailingly syndiotactic polymer (rr = 66%).

Introduction

The disclosure of a novel class of catalysts based on Ni(II) or Pd(II) α-diimine compounds by Brookhart et al.[1] was a milestone in the development of homogeneous "non-Cp" and "non-group 4" olefin polymerization catalysts, stimulating considerable research efforts in this area.[2−4] In this context, we have recently reported that the homogeneous catalytic system (1,2-bis(2,6-diisopropylphenyl)ethylenediimine)nickel dibromide−methylaluminoxane (MAO) at subambient temperatures (e.g., −78 °C) affords a prevailingly syndiotactic crystalline polypropylene.[5] NMR analysis of the polymer microstructure showed the presence of isolated *m* dyads as the main stereodefects, thus suggesting that a "chain-end" mechanism of steric control is operative in this system, as found for syndiotactic-specific polymerization of propene promoted by the classical vanadium-based catalysts, first disclosed by Natta et al.[6] Although the polymerization is poorly regioselective, a largely prevailing primary monomer insertion has been assessed by NMR analysis of suitably labeled polymer end groups formed in either the initiation or the termination steps, and confirmed by the structure of low molecular weight samples.[7] A theoretical QM/MM study has provided a possible mechanism for the observed *unlike* enantioselectivity, arising mainly from an entropy-driven 2:1 preference for syndiotactic enchainments.[8]

In this contribution, we report a study concerning the effects of the coordination environment at the nickel center on the polypropylene microstructure. Thus, several nickel diimine compounds having various ortho substituents on the aromatic rings were synthesized and tested in the polymerization of propene. Comparison of the performances of C_2-symmetric precatalysts with those of C_{2v}- and C_s-symmetric ones suggests that a dual mechanism of steric control (i.e., an "enantiomorphic-site" type isospecific steric control counterbalancing the syndiospecific "chain-end" steric control) could be operative for the former.

Scheme 1



1, R = R' = $CH(CH_3)_2$; X = H
2, R = R' = CH_3; X = H
3, R = CH_3; R' = $CH(CH_3)_2$; X = H
4, R = CH_3; R' = $C(CH_3)_3$; X = H
5, R = CH_3; R' = X = $C(CH_3)_3$

Results and Discussion

Synthesis and Characterization of the Nickel Precatalysts. The nickel diimine derivatives used in this study are displayed in Scheme 1. Compounds **1** and

* Corresponding author. E-mail: pellecchia@chem.unisa.it.

10.1021/ma000982s CCC: $19.00
Published on Web 12/26/2000

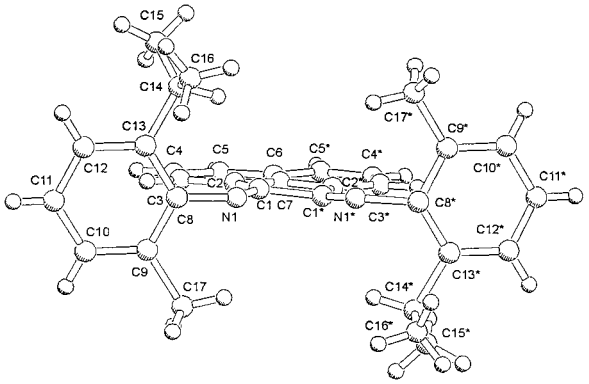


Figure 1. X-ray crystal structure of *anti*-2-isopropyl-6-methylphenylbis(imino)acenaphthene (**3′**).

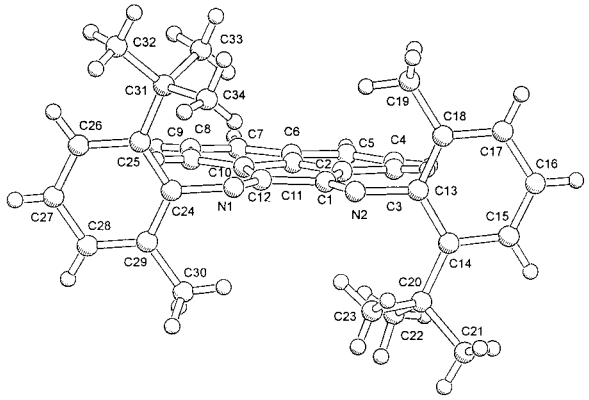


Figure 2. X-ray crystal structure of *anti*-2-*tert*-butyl-6-methylphenylbis(imino)acenaphthene (**4′**).

2, having four isopropyl and four methyl ortho substituents on the aromatic rings, respectively, have C_{2v} symmetry, while compounds **3**−**5**, having two different ortho substituents on each aromatic ring, can exist as either syn or anti isomers, having C_s or C_2 symmetry, respectively.

The corresponding diimine ligands **1′**−**5′** have been synthesized by condensation of acenaphthenequinone and 2 equiv of the proper substituted aniline, as detailed in the Experimental Section. The synthesis of **3′** from the commercially available 2-isopropyl-6-methylaniline resulted in the prevailing formation of a single product (>90%), as evidenced by NMR analysis. A single-crystal X-ray diffraction analysis indicated that it is the anti atropoisomer (see Figure 1). In the solid state, **3′** has a crystallographic C_2 symmetry and an *E,E* configuration around the imine C=N bond. The ortho-substituted phenyl rings are roughly perpendicular to the plane of the imine bond: the angle is 85.7(4)°, significantly higher than in the analogous compound *p*-tolyl-bis(imino)acenaphthene (55−60°),[9] owing to the bulkier ortho substituents. NMR monitoring of **3′** in $CDCl_3$ solution at room temperature indicated slow isomerization to the syn isomer (the anti/syn ratio shifts to 75:25 after 20 h), probably via an interconversion between (*E*,*E*) and (*E*,*Z*) forms, as previously reported for closely related compounds.[9] **4′** was obtained similarly using 2-*tert*-butyl-6-methylaniline, which was selectively synthesized adapting a literature procedure. The crude product is a mixture of the two atropoisomers, as evidenced by ^{1}H and ^{13}C NMR analysis: e.g., double signals with a ∼3:1 intensity ratio are observed for Ar−CH_3 and for the methyl and the quaternary carbons of the *tert*-butyl groups; also, two resonances with 3:1 intensity ratio are observed for the Ar−CH_3 protons. The most abundant isomer could be isolated by repeated crystallizations. An X-ray diffraction analysis showed that even in this case the anti isomer is obtained preferentially (see Figure 2). In the solid state, **4′** does not exhibit crystallographic C_2 symmetry; the latter symmetry is however roughly fulfilled at the molecular level. The bis(imino)acenaphthene skeleton is planar (rmsd 0.015 Å). The angles between each substituted phenyl ring and the acenaphthene plane are respectively 94.9° and 79.9°. **5′** was obtained from 2,4-di-*tert*-butyl-6-methylaniline (synthesized adapting a literature procedure) as a mixture of the two atropoisomers in comparable amounts. In this case, pure syn and anti isomers were isolated by chromatography on a silica gel column and identified by comparison of their NMR spectra with those of the isomers of closely related **4′**. In the case of **4′** and **5′**, NMR monitoring for 24 h showed no significant isomerization at room temperature, reasonably as a result of the increased steric bulk of the ortho substituents on the aromatic rings.

Nickel derivatives were synthesized from (DME)$NiBr_2$ by ligand exchange with the mentioned diimines under mild conditions. Thus, we assume that the original geometry of the diimine is substantially maintained in the nickel compounds, although crystal structures of the latter have not been obtained, and a detailed NMR analysis was precluded by the paramagnetism of these compounds.[1,3c] The structures and symmetries of the nickel complexes are summarized in Figure 3.

Polymerizations. Polymerizations of propene were carried out with the nickel precatalysts activated by methylaluminoxane in toluene at −45 °C. The main polymerization data are summarized in Table 1. Under these conditions, precatalyst **1** affords a prevailingly syndiotactic polymer with a rr triad content = 75%, in agreement with previous results.[5,7] Precatalyst **2** also affords a prevailingly syndiotactic polymer, although with a reduced stereoselectivity (rr = 61%). In both cases, the polymers are poorly regioregular.[10] As discussed in previous papers,[5,7,8] the stereospecific polymerization is attributable to 1,3-*unlike* asymmetric induction from the last monomer unit of the primary growing chain to the incoming monomer. In a theoretical QM/MM study,[8] three nearly isoenergetic transition states have been located for propene insertion into a growing chain of a given chirality, two corresponding to an *unlike* (syndiotactic) enchainment and only one corresponding to a *like* (isotactic) enchainment. Calculations have also shown that this mainly entropy-driven preference for syndiospecific propagation is only marginally affected by the size of the ortho substituents on the aromatic rings of the ligand. The lower enantioselectivity of **2** with respect to **1** would be attributable to slightly lower energy differences between the mentioned transition states corresponding to *unlike* and *like* propagations, owing to a less crowded coordination sphere in **2**.

In apparent contrast with the above discussion, catalyst **3** affords a much less stereoregular polymer, having a higher content of mm rather than rr triads (41 vs 25%).[10] The ^{13}C NMR spectra of polypropylene samples produced by catalysts **1**−**3** are compared in Figure 4. A possible explanation of the peculiar behavior of **3** results from acknowledgment of its C_2 symmetry, which is compatible with an isotactic enantioselectivity through an enantiomorphic site control mechanism

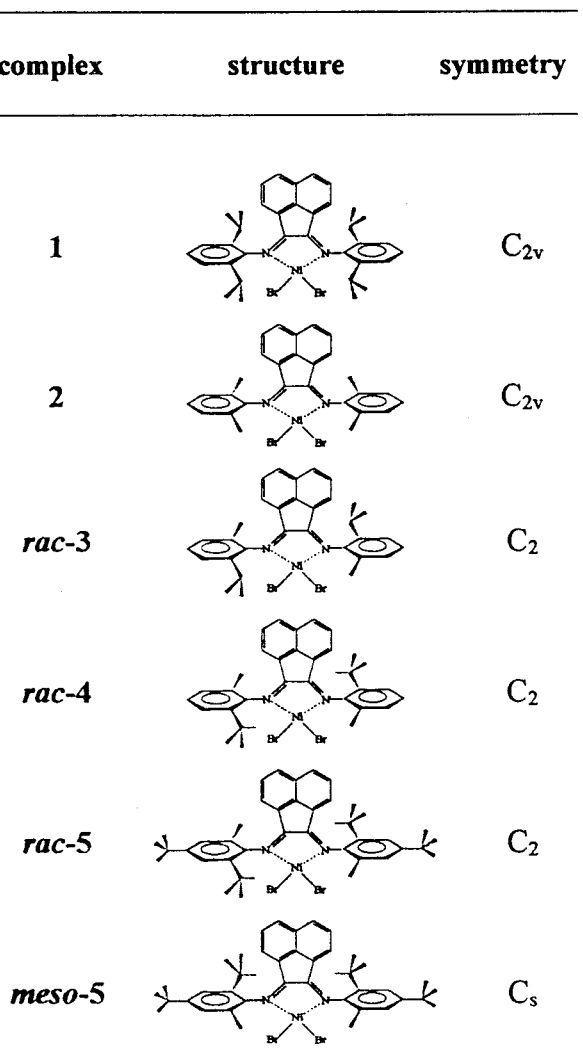


Figure 3. Structures and symmetries of nickel complexes.

analogous to that commonly involved in C_2-symmetric *ansa*-metallocene catalysts.[11] Of course, in the present case the extent of the enantiomorphic site control would be limited, and the polymer microstructure would result from overlap of a weak *isospecific* site control and a weak *syndiospecific* chain-end control. A double stereodifferentiating mechanism, partly site control and partly chain-end control, both isospecific, has been previously involved in the polymerization of propene with an unbridged metallocene catalyst by Erker and co-workers.[12] These authors analyzed the polypropylene microstructure applying the usual statistical treatment, obtaining the relative contributions and the probability parameters for the two mechanisms. In our case, a similar treatment was precluded by the concurrent presence of a high content of regioirregularly arranged monomer units.[10]

Catalyst **4** was synthesized to investigate the possible effects of the increase of steric bulk difference in the two halves of the coordination sphere of Ni. However, the microstructure of the obtained polypropylene does not show any increase of the isotactic triad content with respect to the polymer produced by **3**, although syndiotacticity is still significantly reduced with respect to **1** and **2**. Moreover, the polymer contains a high fraction of 1,3 inserted monomer units, apparently owing to an increased rate of "chain-running" vs the rate of monomer insertion, the latter being slowed by the bulky *tert*-butyl substituents.

Support to the hypothesis of a double stereodifferentiating mechanism comes from comparison of the performances of *rac*-**5** (C_2-symmetric) and *meso*-**5** (C_s-symmetric). In fact, while the former produces a polypropylene similar to that produced by **4** (rr = 33%; mm = 23%), the latter yields a largely prevailingly syndiotactic polymer (rr = 66%; mm = 6%), in agreement with the absence of any possible *isospecific* site control. In both cases, the polymers contain a high fraction of 1,3 inserted monomer units, as observed for **4**. It is also worth mentioning that the polypropylene samples produced by all the tested catalysts have unimodal and narrow molecular weight distributions (see Table 1), confirming the "single-site" nature of these catalytic systems.

In conclusion, variation of the coordination environment at the metal center in nickel diimine catalysts has been shown to significantly affect the microstructure of the resulting polypropylenes. In particular, comparison of the performances of C_2- and C_s-symmetric Ni precatalysts, the former affording polypropylenes having a significantly higher mm triad content with respect to the latter, suggests the hypothesis that a dual mechanism of steric control (partly site control, partly chain-end control) is operative for the former catalysts. These results encourage the search for novel stereospecific "non-metallocene" catalysts.

Experimental Section

General. Manipulations of sensitive materials were carried out under a dry nitrogen atmosphere using Schlenk or glovebox techniques. Polymerization grade propylene was used after distillation over triisobutylaluminum. Toluene was refluxed over metallic sodium and distilled under a nitrogen atmosphere. Methylaluminoxane (Aldrich) was purchased as a 10 wt % solution in toluene and stored as a solid in a glovebox after the solvent was removed under reduced pressure. NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer. Molecular weights were measured vs atactic polystyrene standards by GPC in 1,2,4-trichlorobenzene at 50 °C using a Waters 150-C instrument. EI MS were obtained on a Finnigan Thermoquest GCQ Plus 2000 spectrometer, using a direct exposure probe.

Synthesis of the Diimine Ligands. The diimine ligands were synthesized adapting literature procedures.[1a,9]

*Synthesis of 2-Isopropyl-6-methylphenyl-bis(imino)acenaphthene (**3′**).* Acenaphthenequinone (6.3 g, 34.6 mmol) and 2-isopropyl-6-methylaniline (11 mL, 69.2 mmol) were stirred 18 h at room temperature in 200 mL of methanol containing 3 mL of formic acid. The precipitated orange solid was collected by filtration and dried (10.5 g). A second fraction (1.9 g) is obtained by cooling the mother solution at −20 °C. Yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, 2H), 7.38 (t, 2H), 7.27 (dd, 2H), 7.16 (2d, 4H), 6.68 (d, 2H), 3.07 (heptet, 2H, C*H*$(CH_3)_2$, 2.12 (s, 6H, ArC*H*$_3$), 1.26, 0.97 (2d, 12 H, CH(C*H*$_3)_2$). ^{13}C NMR ($CDCl_3$, selected resonances): δ 161.2 (*C*=N), 148.5 (ipso-*C*(Ar)), 136.2 (*C*(Ar)−CH$(CH_3)_2$), 124.7 (*C*(Ar)−CH_3), 28.8 (*C*H$(CH_3)_2$), 24.0, 23.0 (CH(*C*H$_3)_2$), 18.2 (Ar*C*H$_3$). A second isomer (<10%) is detected: ^{13}C NMR ($CDCl_3$, selected resonances): δ 29.1 (*C*H$(CH_3)_2$), 23.6, 22.8 (CH(*C*H$_3)_2$). NMR monitoring at room temperature shows slow isomerization, leading to a ca. 3:1 ratio between the isomers after 12 h.

*Synthesis of 2-tert-Butyl-6-methylphenyl-bis(imino)acenaphthene (**4′**).* 2-*tert*-Butyl-6-methylaniline was synthesized by selective ortho methylation of 2-*tert*-butylaniline adapting a literature procedure.[13] Then, acenaphthenequinone (1.56 g, 8.5 mmol) and 2-*tert*-butyl-6-methylaniline (3.2 g, 20 mmol) were allowed to react 24 h in 10 mL of boiling acetic acid.[9] After cooling at room temperature, the precipitated orange solid was

Table 1. Polymerization Conditions and Results[a]

run	catalyst	yield, g	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	% triad composition[b]			% regioinverted monomer units[c]	% 1,3 inserted monomer units[d]
					mm	mr	rr		
1	**1**	1.5	150	1.7	1	24	75	7	<1
2	**2**	0.2	130	2.3	8	31	61	23	<1
3	*rac*-**3**	0.4	69	2.5	41	34	25	24	3
4	*rac*-**4**	0.2	32	1.8	24	42	34	11	19
5	*rac*-**5**	1.6[e]	111	1.8	23	44	33	8	14
6	*meso*-**5**	0.3[e]	75	2.2	6	28	66	10	20

[a] Polymerization conditions: toluene = 35 mL, Ni 30 μmol, MAO = 6 mmol, T = −45 °C, liquid propene = 10 mL, time = 5 h. [b] Estimated by ^{13}C NMR, neglecting the effects due to regioinversions and 1,3 insertions. [c] Evaluated by ^{13}C NMR. [d] Evaluated by ^{1}H NMR. [e] Polymerization time = 24 h.

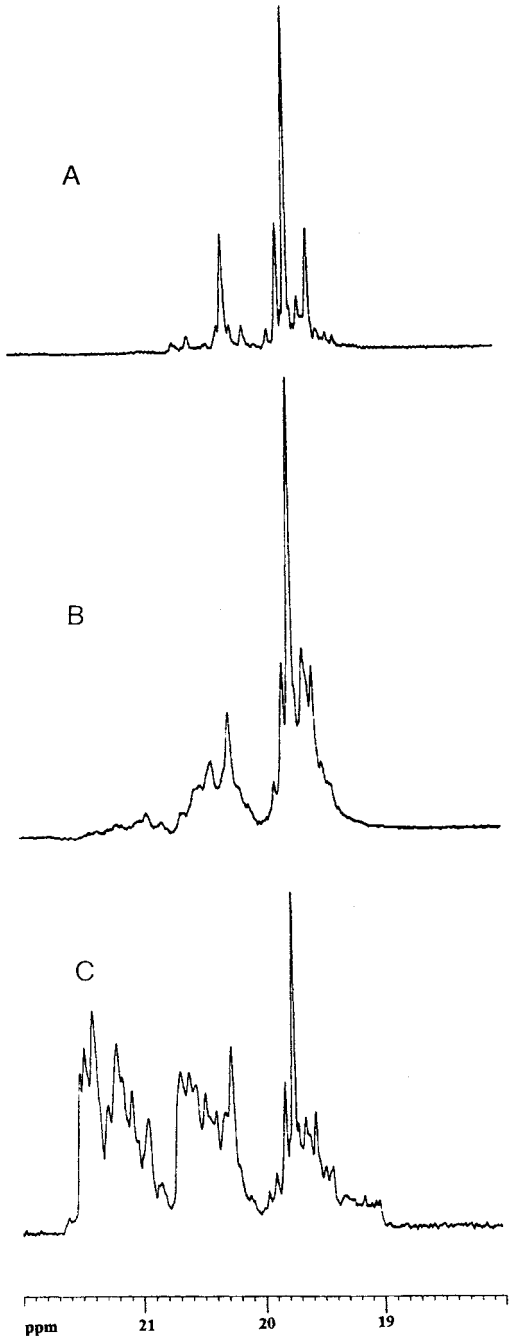


Figure 4. Methyl region of the ^{13}C NMR spectra of polypropylene samples produced by catalyst **1** (A), **2** (B), and **3** (C).

collected by filtration and dried. Yield 2.1 g, 52%. Two isomers were identified by NMR analysis in a ca. 3:1 ratio. Repeated crystallizations from toluene afforded the pure major isomer (identified as the anti isomer by X-ray analysis): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, 2H), 7.41 (d, 2H), 7.37 (t, 2H), 7.16 (d, 2H), 7.10 (d, 2H), 6.64 (d, 2H), 2.04 (s, 6H, ArCH_3), 1.33 (s, 18 H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, selected resonances): δ 160.8 (*C*═N), 149.7 (ipso-*C*(Ar)), 35.4 (*C*(CH$_3$)$_3$, 30.15 (C(*C*H$_3$)$_3$), 18.3$_2$ (Ar*C*H$_3$). Syn isomer: ^{1}H NMR (400 MHz, $CDCl_3$ selected resonances): δ 2.09 (s, 6H, ArCH_3), 1.36 (s, 18H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, selected resonances): δ 35.5 (*C*(CH$_3$)$_3$, 30.0 (C(*C*H$_3$)$_3$), 18.2$_8$ (Ar*C*H$_3$).

Synthesis of 2,4-Di-tert-butyl-6-methylphenylbis(imino)-acenaphthene (**5′**). 2,4-Di-*tert*-butyl-6-methylaniline was synthesized adapting a literature procedure,[14] by nitration of 3,5-di-*tert*-butyltoluene, affording selectively 2-nitro-3,5-di-*tert*-butyltoluene, and its subsequent reduction. Then, acenaphthenequinone (0.82 g, 4.5 mmol) and 2,4-di-*tert*-butyl-6-methylaniline (2.2 g, 10 mmol) were allowed to react 24 h in 15 mL of boiling acetic acid.[9] After cooling at room temperature, the precipitated orange solid was collected by filtration and dried. Yield 1.5 g, 58%. Two isomers were identified by NMR analysis in ca. 1:1 ratio. Separation was achieved via column chromatography (20 g silica gel, petroleum ether/toluene 1:2). The first eluted isomer was identified as the anti isomer (in agreement with a lower polarity resulting in a higher R_f) by comparison with the NMR spectrum of **4′**. Anti isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, 2H), 7.40 (d, 2H), 7.36 (t, 2H), 7.14 (d, 2H), 6.66 (d, 2H), 2.01 (s, 6H, ArCH_3), 1.40 (s, 18 H, p−C(CH_3)$_3$), 1.33 (s, 18 H, o−C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, selected resonances): δ 161.5 (*C*═N), 146.3 (ipso-*C*(Ar)), 36.0 (p-*C*(CH$_3$)$_3$), 34.7 (o-*C*(CH$_3$)$_3$), 31.9 (p-C(*C*H$_3$)$_3$), 30.5 (o-C(*C*H$_3$)$_3$), 18.9 (Ar*C*H$_3$). Syn isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, 2H), 7.40 (d, 2H), 7.36 (t, 2H), 7.14 (d, 2H), 6.57 (d, 2H), 2.07 (s, 6H, ArCH_3), 1.41 (s, 18 H, p-C(CH_3)$_3$), 1.35 (s, 18 H, o-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, selected resonances): δ 161.5 (*C*═N), 146.3 (ipso-*C*(Ar)), 36.9 (p-*C*(CH$_3$)$_3$), 34.7 (o-*C*(CH$_3$)$_3$), 31.9 (p-C(*C*H$_3$)$_3$), 30.3 (o-C(*C*H$_3$)$_3$), 18.9 (Ar*C*H$_3$).

X-ray Structural Analysis. Orange prismatic crystals of $C_{32}H_{32}N_2$ (compound **3′**) and $C_{34}H_{36}N_2$ (compound **4′**) having approximately dimensions of 0.2 × 0.3 × 0.5 mm and 0.2 × 0.3 × 0.4 mm, respectively, were studied using a Rigaku AFC7S single-crystal diffractometer with a graphite monochromated Mo Kα radiation at a temperature of 25 °C. Data for **3′** are as follows: space group *Pnn2*; lattice constants a = 12.330(5) Å, b = 12.637 (5) Å, c = 8.749 (5) Å; V = 1363 (9) Å^3; Z = 2; D_x = 1.083 g/cm^3. A total of 1559 unique reflections were collected ($\omega/2\theta$ scan, 2θ < 60.0°, scan width 1.21 + 0.35 tan θ, scan speed 16.0°/min). The structure was solved by means of SIR92[15] and refined using SHELXL93[16] package, performing rigid-body refinement both for the acenaphthene skeleton and the phenyl rings. The R disagreement index (reflections with F_{obs} < 4σ(F_{obs})) lowers only to 0.25 using isotropic thermal parameters and to 0.14 using anisotropic displacement parameters for non-H atoms. This poor result could be due either to the presence of disorder in the crystalline phase or to a small distortion from the exact C_2 molecular symmetry. Improvement of the structural model is in progress. Data for **4′** are as follows: space group $P2_1$; lattice constants a = 9.201(7) Å, b = 12.449 (7) Å, c = 12.51 (1) Å, β = 101.15 (6)°; V = 1405 (1) Å^3; Z = 2; D_x = 1.12 g/cm^3. A total of 1393 unique reflections were collected ($\omega/2\theta$ scan, 2θ < 40.0°, scan width 1.84 + 0.35 tan θ, scan speed 16.0°/min). The structure was solved by SIR92[15] and refined using the TEXSAN package. The non-H atoms were refined isotropically; the H atoms were

included in idealized positions and not refined. The final disagreement R index based on reflections with $I > 3\sigma(I)$ was 0.11.

Synthesis of the Nickel Complexes. Nickel compounds **1** and **2** were prepared as described in the literature.[17] The remaining nickel complexes were synthesized according to the same literature procedure,[1a,17] as detailed below.

Synthesis of ***3***. 1.1 g of **3′** (2.5 mmol) and 0.70 g of (DME)$NiBr_2$ (2.25 mmol) were dissolved in 40 mL of anhydrous CH_2Cl_2 and allowed to react at room temperature over 24 h. The resulting precipitate was collected by filtration, washed several times with anhydrous petroleum ether, and dried in vacuo, affording 1.3 g of **3** as an orange-brown solid (yield 87%). EI MS (35 eV); *m*/*z*: 660, 662, 663 [M^+]; 581, 583, 584, 585 [$M^+ - Br$]; 502 [$M^+ - 2\,Br$].

Synthesis of ***4***. The synthesis was carried out as for **3**, using 0.60 g of **4′** (1.27 mmol) and 0.35 g of (DME)$NiBr_2$ (1.14 mmol). Yield 0.62 g (82%) of an orange-red solid. EI MS (35 eV); *m*/*z*: 690, [M^+]; 609, 611 [$M^+ - Br$]; 530 [$M^+ - 2\,Br$].

*Synthesis of rac-****5***. The synthesis was carried out as for **3**, using 0.30 g of anti-**5′** (0.51 mmol) and 0.15 g of (DME)$NiBr_2$ (0.49 mmol). Yield 0.31 g (79%) of an orange-red solid. EI MS (35 eV); *m*/*z*: 802, [M^+]; 721, 723 [$M^+ - Br$]; 642 [$M^+ - 2\,Br$].

*Synthesis of meso-****5***. The synthesis was carried out as for **3**, using 0.40 g of syn-**5′** (0.68 mmol) and 0.20 g of (DME)$NiBr_2$ (0.65 mmol). Yield 0.42 g (80%) of an orange-red solid. EI MS (35 eV); *m*/*z*: 802, [M^+]; 721, 723 [$M^+ - Br$]; 642 [$M^+ - 2\,Br$].

Polymerizations. The polymerization runs were carried out in 100 mL, magnetically stirred glass flasks, which were thermostated at −45 °C and charged under nitrogen sequentially with toluene, the nickel precatalyst, propene, and MAO, as detailed in Table 1. The runs were stopped by pouring the reaction mixtures into a large excess of acidified ethanol, and the precipitated polymers were recovered by filtration, washed with fresh ethanol, and dried in vacuo. The main polymerization data are summarized in Table 1. Several other polymerization runs under similar conditions were carried out to check reproducibility of the results. The polypropylene samples were analyzed by ^1H and ^{13}C NMR in $CDCl_3$ at 25 °C; the spectra were referenced vs TMS using the solvent residual resonances as chemical shift reference.

Acknowledgment. This work was supported by the Italian Ministry of University and Research (MURST, PRIN 98). We also thank Dr. Gianpiero Nicoli and Dr. Giuseppe Leo for some synthetic work, Professor Attilio Immirzi and Dr. Consiglia Tedesco for discussions of the X-ray results, Mr. Ennio Comunale for the GPC analyses, and Mr. Raffaele Miranda for the MS measurements.

Supporting Information Available: Tables of crystallographic data, atomic coordinates, bond lengths, bond angles, torsion angles for **3′** and **4′**, and ^{13}C NMR spectra of the polypropylene samples. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

(2) (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (b) Johnson, L. K.; Killian, C. M.; Arthur, S. D.; Feldman, J.; McCord, E. F.; McLain, S. J.; Kreutzer, K. A.; Bennett, A. M. A.; Coughlin, E. B.; Ittel, S. D.; Parathasarathy, A.; Tempel, D. J.; Brookhart, M. S. PCT Int. Appl. WO9623010, 1996 (to DuPont); *Chem. Abstr.* **1996**, *125*, 222773. (c) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (d) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320.

(3) (a) de Souza, R. F.; Mauler, R. S.; Simon, L. C.; Nunes, F. F.; Vescia, D. V. S.; Cavagnolli, A. *Macromol. Rapid Commun.* **1997**, *18*, 795. (b) McLain, S. J.; McCord, E. F.; Johnson, L. K.; Ittel, S. D.; Nelson, L. T. J.; Arthur, S. D.; Halfhill, M. J.; Teasley, M. F. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1997**, *38*, 772. (c) Schleis, T.; Spaniol, T. P.; Okuda, J.; Heinemann, J.; Mülhaupt, R. *J. Organomet. Chem.* **1998**, *569*, 159. (d) Held, A.; Bauers, F. M.; Mecking, S. *Chem. Commun.* **2000**, 301. (e) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.

(4) (a) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849. (b) For a review on "non-metallocene" catalysts, see: Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428.

(5) Pellecchia, C.; Zambelli, A. *Macromol. Rapid Commun.* **1996**, *17*, 333.

(6) (a) Natta, G.; Pasquon, I.; Zambelli, A. *J. Am. Chem. Soc.* **1962**, *84*, 1488. (b) Zambelli, A.; Allegra, G. *Macromolecules* **1980**, *13*, 42.

(7) (a) Pellecchia, C.; Zambelli, A.; Oliva, L.; Pappalardo, D. *Macromolecules* **1996**, *29*, 6990. (b) Pellecchia, C.; Zambelli, A.; Mazzeo, M.; Pappalardo, D. *J. Mol. Catal. A: Chem.* **1998**, *128*, 229.

(8) Milano, G.; Guerra, G.; Pellecchia, C.; Cavallo, L. *Organometallics* **2000**, *19*, 1343.

(9) Van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Pays-Bas* **1994**, *113*, 88.

(10) The rr triad contents of all polypropylene samples were evaluated by neglecting the regioinversions. As discussed in a previous paper,[7b] the resonances of the $P_{\beta\gamma}$ carbons overlap with some resonances of the $P_{\beta\beta}$ carbons used for the measurement of the triads. A more precise microstructural analysis, taking into account also the tacticity of the regioirregular sequences, is precluded by the poor resolution of the spectra, due to the high content of regioerrors. However, while this approximation can lead to overestimate the rr triads, it certainly does not invalidate the main result of this study, i.e., the unexpected high content of mm triads of polymers produced by some of the nickel catalysts.

(11) See, e.g.: Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

(12) Erker, G.; Nolte, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 628.

(13) Gassman, P. G.; Gruetzmacher, G. *J. Am. Chem. Soc.* **1973**, *95*, 586.

(14) Yang, K.; Lachicotte, R. J.; Eisenberg, R. *Organometallics* **1997**, *16*, 5234.

(15) Altomare, A.; Burla M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *2*, 435.

(16) Sheldrick, G. M. *SHELX93. Program for the Refinement of Crystal Structure*; University of Göttingen, Germany, 1993.

(17) tom Dieck, H.; Svoboda, M.; Greiser, T. *Z. Naturforsch., B: Chem. Sci.* **1981**, *36*, 823.

(18) Ward, L. G. L. *Inorg. Synth.* **1972**, *12*, 154.

MA000982S