Heterocycle-Fused Indenyl Silyl Amido Dimethyl Titanium Complexes as Catalysts for High Molecular Weight Syndiotactic Amorphous Polypropylene

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Indenyl silyl amido titanium complexes based on indenoindoles, indenopyrrole, and 2-methylindenothiophene have been prepared and tested in propylene polymerization. The indenoindole ligand precursors were prepared in high yields by the acid-catalyzed Fischer condensation of indan-2-one and arylhydrazines. The Ti complexes dimethylsilyl(*tert*-butylamido)(*N*-methyl-2-methyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)dimethyl titanium (**1**), dimethylsilyl(*tert*-butylamido)(*N*-ethyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)dimethyl titanium (**2**), dimethylsilyl(*tert*-butylamido)(*N*-methyl-5,10*H*-indeno[1,2-*b*]indol-10-yl) dimethyl titanium (**3**), dimethylsilyl(*tert*-butylamido)(*N*-phenyl-5,10*H*-indeno[1,2-*b*]indol-10-yl)dimethyl titanium (**4**), dimethylsilyl(*tert*-butylamido)(*N*-methyl-2-methyl-1,8-dihydroindeno[2,1-*b*]pyrrol-8-yl)dimethyl titanium (**5**), and dimethylsilyl(*tert*-butylamido)(2-methyl-8*H*-indeno[2,1-*b*]thiophen-8-yl)dimethyl titanium (**6**) were prepared by reacting the ligand, a 2-fold excess of MeLi, and $TiCl_4$. The molecular structures of the amidosilylindenyl titanium complexes **2** and **6** have been determined by single-crystal X-ray diffraction analysis: the indenoindole moiety in **2** and the indenothiophene moiety in **6** are perfectly planar, implying a certain degree of delocalization of the heteroatom lone pairs into the aromatic moiety coordinated to the metal atom. Catalysts **1**, **2**, and **5** produce syndiotactic amorphous polypropylenes (*sam*-PP) of very high molecular weights, even at polymerization temperatures as high as 80 °C. Syndiotactic pentad contents range between 48 and 57% *rrrr*, and regioerrors are close to or below the detection limit of the ^{13}C NMR analysis (at 100 MHz). In toluene solution, $[Ph_3C][B(C_6F_5)_4]$ is a more efficient activator than MAO, $[HNMe_2Ph][B(C_6F_5)_4]$, or $B(C_6F_5)_3$. The catalytic activity of **5**/$[Ph_3C][B(C_6F_5)_4]$ shows an approximate first-order dependence on propylene concentration, while the tacticity and the molecular weight do not seem to change noticeably with the monomer concentration. The obtained activation energy barrier for chain release with this catalyst is $\Delta\Delta E_r^{\ddagger} = 7.7$ kcal/mol. The influence of cyclopentadienyl ligand substituents on polymerization activity has been rationalized by means of the group electronegativity of the $[Me_2Si(Cp')(t\text{-Bu-N})TiMe]$ fragment, as defined within the framework of density functional theory.

Introduction

The olefin polymerization catalysts based on cyclopentadienylsilylamido titanium complexes (the so-called "constrained geometry" catalysts, or CGC, whose prototype is $Me_2Si(Me_4C_5)(t\text{-BuN})TiCl_2$[1,2]) show some distinct advantages with respect to the metallocene-based catalysts, such as higher comonomer incorporation rates, lower chain release rates leading to higher copolymer molecular weights, and a higher thermal stability, enabling their use in high-temperature solution processes without loss of catalyst efficiency and polymer molecular weight. On the other side, they lack the stereoselecting ability easily built in the metallocene complexes by means of C_2-, C_1-, or C_s-symmetric ligand frameworks,[3] with only two relevant exceptions having

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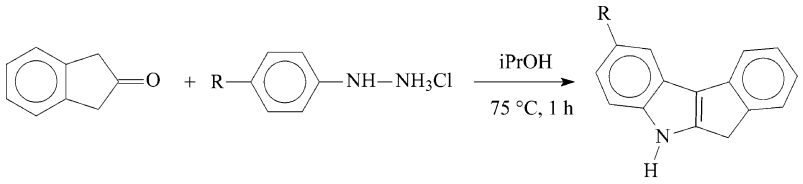
Scheme 1

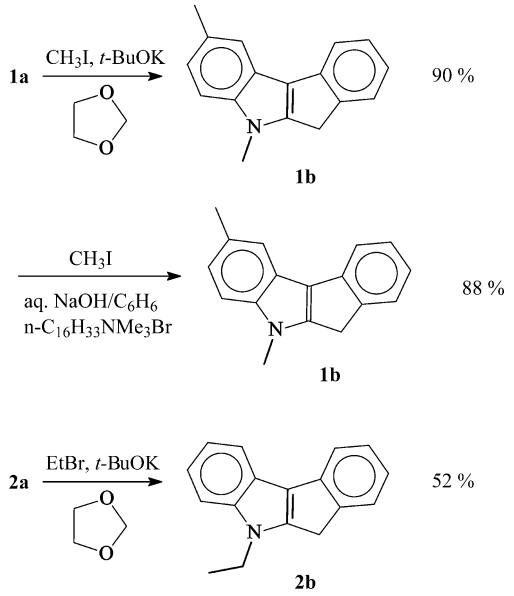


2a, R = H, 93 %
1a, R = Me, 87 %

been reported in the literature, one isospecific complex[4] and two syndiospecific fluorenyl-based complexes.[5]

Stevens has reported that the performance of "constrained geometry" catalysts improves with the electron-donating ability of either the Cp or the amido ligands, that is, increasing the electron density at the metal center.[6] In line with this insight and in order to further improve catalysts performance, electron-donating groups have been added to the cyclopentadienyl or indenyl ring: the introduction of alkoxy or amino substituents onto the indenyl ligand of $[Me_2Si(Ind)(t\text{-}BuN)]TiR_2$ (R = Cl, CH_3) has been reported to produce a dramatic increase in catalytic activity and/or molecular weight.[7,8] This observation is in striking contrast to what had been reported for bis-cyclopentadienyl complexes, for which the presence of dimethylamino- or oxygen-containing groups on Cp strongly reduces catalytic efficiency, probably due to interfering reactions of the lone pair of the heteroatom with the cationic activated metal or other components of the catalytic system.[9] To the contrary, if the heteroatom is part of an aromatic ring condensed onto the Cp ligand, such side reactions do not seem to occur while electron donation is still operating, and new complexes with different, often improved performance with respect to their all-carbon analogues have been reported.[10−12]

Scheme 2



Building on the above findings, we have prepared the first series of heterocyclic indenyl amido dimethyl titanium complexes,[13] and here we describe their synthesis and performance in propylene polymerization, both in liquid monomer and in solution at different monomer concentration and polymerization temperature.

Results and Discussion

Synthesis. As heterocycle-condensed ligands we have chosen indenoindole and indenopyrrole, whose synthesis has been developed by Nifant'ev,[11] and 2-methylindenothiophene.[13a] The indenoindole ligand precursors were prepared in high yields by the acid-catalyzed Fischer condensation of indan-2-one and arylhydrazines (Scheme 1). Both arylhydrazines and the corresponding hydrochlorides can be used in this reaction. The use of hydrochlorides is more convenient since it does not require further addition of an acid as catalyst.

Alkylation of **1a** by methyl iodide was successfully performed in an aqueous NaOH/benzene mixture in the presence of trimethylcetylammonium bromide or in 1,3-dioxolane with *t*-BuOK. Reaction of **2a** with bromoethane leads to the product in good yield (Scheme 2).

N-Methyl-2-methyldihydroindeno[2,1-*b*]pyrrole was prepared by Knorr condensation between 2-aminoin-

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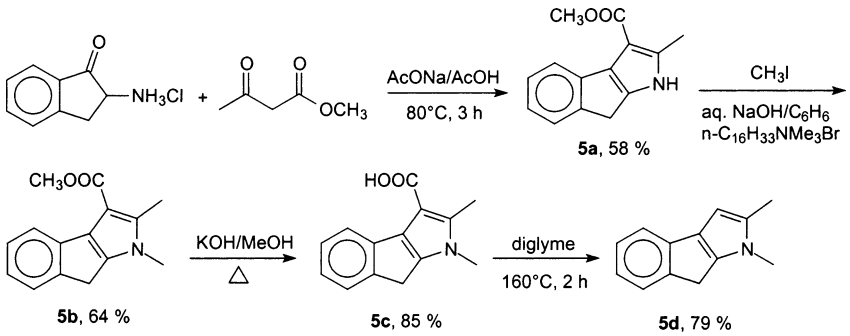
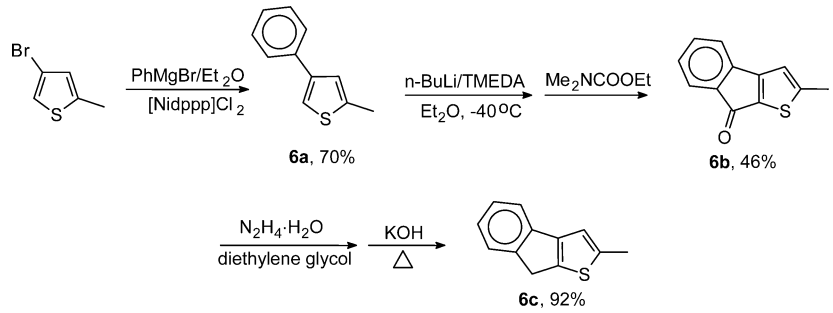
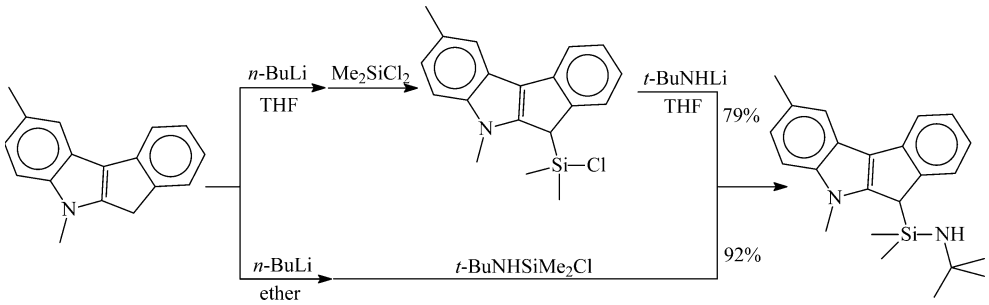
Scheme 3



Scheme 4



Scheme 5



danone hydrochloride and acetoacetic ester followed by alkylation, hydrolysis, and decarboxylation of carboxylic acid (Scheme 3).[11] It is important to note that the alternative route to *N*-methyl-2-methyldihydroindeno-[2,1-*b*]pyrrole from the carboxylic acid **5a**, e.g., hydrolysis of **5a**, then decarboxylation, and *N*-methylation, was found to be unsuitable. In that case we isolated only traces of the product **5d**.

2-Methyl-8*H*-indeno[2,1-*b*]thiophene **6c** was obtained from 2-methyl-4-phenylthiophene via dimetalation and subsequent reaction with *N*,*N*-dimethylethylcarbamate and Wolff−Kishner reduction of ketone **6b** (Scheme 4).

Preparation of the silylamine derivative of **1b** was performed in two ways (Scheme 5). Use of (*tert*-butylamino)dimethylchlorosilane seemed to be preferable, and this reagent was used for the synthesis of silylamine derivatives of other heterocyclic ligand precursors.

All the Ti complexes prepared and their isolated yields are shown in Chart 1. As a synthetic route, we used the simple and versatile protocol developed by some of us for the direct synthesis of the dimethylzirconocenes from the ligand, a 2-fold excess of MeLi, and $MtCl_4$ (Mt = Ti, Zr, Hf),[14] and successfully applied also to the silyl-bridged cyclopentadienylamido and indenylamido complexes of Ti and Zr (Scheme 6).[15,16] It is worth pointing out that in our hands the classic route to the silyl-bridged Cp-amido Ti dichloride complexes from the dilithium salt of the ligand[17] did not meet with success when applied to indenoindole-based ligands.

NMR Analysis: General Considerations. The spectra of **1**, **2**, **3**, **5**, and **6** show some common features.

The two methyls on the bridge are identified from the peak multiplicity, as they present at the base a doublet due to their coupling with ^{29}Si (I = 1/2, natural abundance = 4.7%).

A peculiarity of the ^{1}H spectrum of these titanium complexes is the quartet structure (or in some cases an incompletely resolved quartet) of the metal-bound methyl groups.[16] The COSY experiments show a proton−proton coupling between the two methyl groups on the metal, accounting for the multiplicity of the signal. A coupling with titanium can be reasonably excluded since the observed quartet is clearly due to the coupling with a nucleus of nearly 100% abundance, while Ti has a low isotopic abundance (^{47}Ti = 7.4%, ^{49}Ti = 5.4%).

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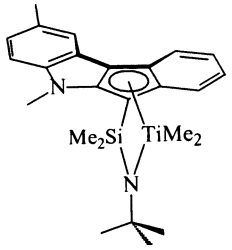
Chart 1



1

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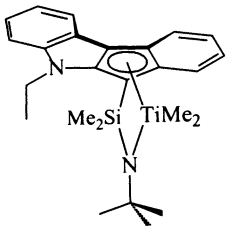

2

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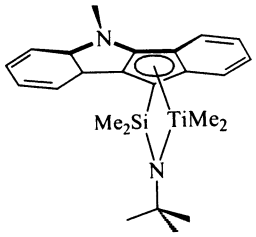

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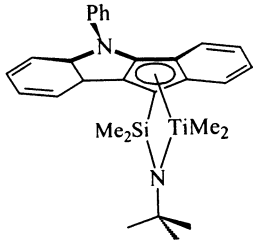

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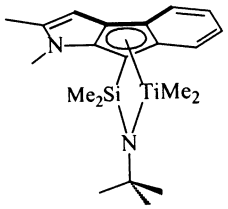

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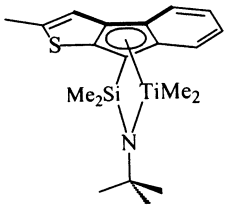
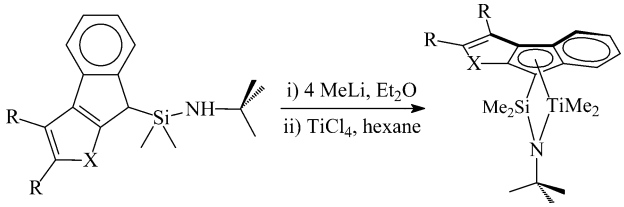


6

20%

Scheme 6[a]



[a] X = S, NMe, NEt.

A coupling between Si-methyl protons is also observed in the COSY spectra. The coupling between Si-bound methyls seems to be less strong than the titanium-bound methyls, and in fact the multiplicity of the Si-methyls is not evident in the ^{1}H NMR spectrum. The assignments of the ^{1}H NMR spectrum are based on the bidimensional COSYgs[18] and NOESY[19] spectra.

The ^{13}C NMR spectrum is assigned from DEPT-135, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC 2D experiments. Protonated carbons are assigned from their cross-peaks with directly bonded protons in the ^{1}H−^{13}C HSQC spectrum;[20,21] for quaternary carbons ^{1}H−^{13}C HMBC 2D spectra [22] are used (taking into account that in aromatic systems $J^3 \approx 7-10$ Hz and $J^2 \approx 1$ Hz). In the ^{1}H−^{13}C HMBC spectra the quaternary carbon of the *t*-Bu is identified from the cross-peaks with its methyl protons, and the cyclopentadienyl carbon bearing the $SiMe_2$ group is identified from its cross-peaks with Si-methyl protons. As an example of the procedure adopted for the assignment of the ^{1}H and ^{13}C NMR spectra of all these complexes, the case of **1** is reported. The C−H coupling constants for the metal-bound methyl groups are compared in Table 1. For more detailed NMR data on the other complexes, see the Supporting Information.

Table 1. C−H Coupling Constants for the Ti-Bound Methyl Groups

complex	$^1J_{C-H}$ (TiCH_3)	$^1J_{C-H}$ (TiCH_3) [av]
2	120.8−120.4	120.6
3	120.1−119.9	120.0
5	120.1−119.9	120.0
6	120.5−121.0	120.8
8	119.9−121.2	120.6
9	119.4−121.4	120.4

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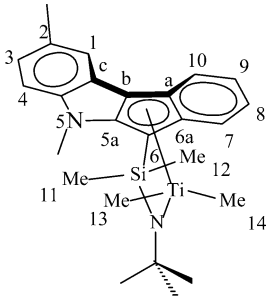
Chart 2. Atom Numbering for 1



NMR Analysis of 1. The assignments of the ^{1}H NMR spectrum, based on the numbering scheme of Chart 2, start from the NOESY spectrum. Protons H1 and H3 (a singlet and a doublet, respectively) are identified from their cross-peak with methyl protons H2, proton H4 is assigned from the cross-peak with *N*-methyl protons, proton H7 is assigned from the cross-peak with Si-methyl protons H12, and proton H10 is the remaining doublet in the aromatic region. Protons H9 and H8 are identified from their structure (being a doublet of doublets of doublets) and from cross-peaks with protons H10 and H9, respectively. Ti-methyl protons H13 and H14 are assigned from their cross-peak with protons H1 and H10, respectively. Si-methyl protons H11 are assigned to the remaining peak showing the typical doublet structure at the base. The assignments of aromatic protons are confirmed from the COSY spectrum from cross-peaks between H10−H9, H9−H8, H8−H7, and H4−H3.

Quaternary carbon C5a is assigned from a cross-peak with *N*-methyl protons, carbon C4a from cross-peaks with *N*-methyl protons, and protons H1 and H3, carbon C2 from cross-peaks with proton H4 and methyl protons H2. Owing to the low intensity of cross-peaks, only tentative assignments were obtained for C6a (from cross-peaks with protons H8 and H10), C10b (from cross-peaks with protons H1 and H10), and C10c (from cross-peak with proton H4). C10a is the remaining quaternary carbon partially overlapping with C8.

Crystal and Molecular Structure of the Titanium Complexes 2 and 6. The molecular structures of the amidosilylindenyl titanium complexes **2** and **6** have been determined by single-crystal X-ray diffraction analysis. Two ORTEP views of compounds **2** and **6** are depicted in Figures 1 and 2, respectively, along with the non-hydrogen atom labeling scheme. A list of relevant bond lengths and angles is reported in Table 2.

In both compounds the titanium atom is pseudo-tetrahedrally coordinated by the bifunctional amido-κN-silyl-η^5-indenyl ligand and the two terminal methyl groups.

The indenoindole moiety in **2** and the indenothiophene moiety in **6** are perfectly planar, the maximum deviation from the least-squares planes being 0.056(3) and 0.035(3) Å, respectively. In **2** the sum of the angles around N(5) is 360.0(2)°, consistent with an sp^2 hybridization for the nitrogen atom. The N(5)−C(5a) bond length in **2** (1.389(3) Å) and the S(1)−C(8a) bond length in **6** (1.733(3) Å) are quite short and consistent with a partial double-bond character. These evidences indicate a certain degree of delocalization of the nitrogen and sulfur lone pairs into the aromatic moiety coordinated to the metal atom.

With respect to the coordination sphere of the titanium atom, compounds **2** and **6** are remarkably similar, as shown by the values reported in Table 2. In particular, geometrical parameters usually employed in describing the metal environment in "constrained geometry" catalysts, such as the cp−Ti−N bite angle and the Ti−cp and Ti−N bond distances, are identical within the experimental error and in line with the values found for similar complexes.[6−8] Differences in catalytic activity have to be attributed to electronic effects that do not leave a clear trace in geometrical parameters.

Catalyst Evaluation in Propylene Polymerization. 1. Polymerization in Liquid Monomer. The "constrained geometry" catalysts polymerize propylene to *am*-PP with molecular weights and activities that depend on the substitution of the Cp ring. [Me_2Si-(Me_4Cp)(*t*-BuN)]$TiCl_2$ [1] and the fluorenyl-based Ti and Zr complexes [Me_2Si(Flu)(*t*-BuN)]MtX_2 (X = Cl, Me) polymerize propylene to moderately syndiotactic PP.[23] A site-controlled mechanism for such (moderately) syndiospecific polymerizations has been established.[24,25a]

Recently, [Me_2Si(2,7-*t*-Bu_2Flu)(*t*-BuN)]$TiCl_2$ and [Me_2Si(3,6-*t*-Bu_2Flu)(*t*-BuN)]$TiCl_2$ [5] were reported to give high molecular weight syndiotactic PP (*rrrr* from 56 to 81% in the T_p range 40−80 °C) with no or moderate crystallinity and also, as expected, operating by site-controlled enantioface selectivity.[25b]

The liquid propylene polymerization results obtained with MAO-activated complexes **1**−**6** are compared in Table 3, together with selected results from Dow's [$Me_2Si(Me_4Cp)$(*t*-BuN)]$TiCl_2$ (**7**), [Me_2Si(Ind)(*t*-BuN)]-$TiMe_2$ (**8**), and [Me_2Si(2-MeInd)(*t*-BuN)]$TiMe_2$ (**9**) from our previous investigation.[16]

The most relevant result is that catalysts **1**, **2**, and **5**, all having a pyrrole or indole condensed to indene with N in the back of the ligand, produce syndiotactic amorphous polypropylenes (*sam*-PP) of very high molecular weights. Syndiotactic pentad contents range between 48 and 57% *rrrr*, and regioerrors are close to or below the detection limit of the ^{13}C NMR analysis (at 100 MHz). These polypropylenes show remarkable elastic properties, which are due to a combination of their particular microstructure and the high molecular weights.[13b] The methyl region of ^{13}C NMR of a typical sample prepared with **2**/MAO is presented in Figure 3, together with that of *am*-PP prepared from **7**/MAO and of highly syndiotactic PP from Ewen's Me_2C(Cp)(Flu)-$ZrCl_2$/MAO.[24]

Syndioselectivity follows the order **1** ∼ **5** ∼ **2** > **6** > **3** ∼ **4** > **9** > **7** > **8**, while regioselectivity follows the order **1** ∼ **5** ∼ **2** ∼ **3** ∼ **4** > **6** > **9** > **7** ∼ **8**. To investigate the mechanism of stereocontrol, enantiomorphic-site or

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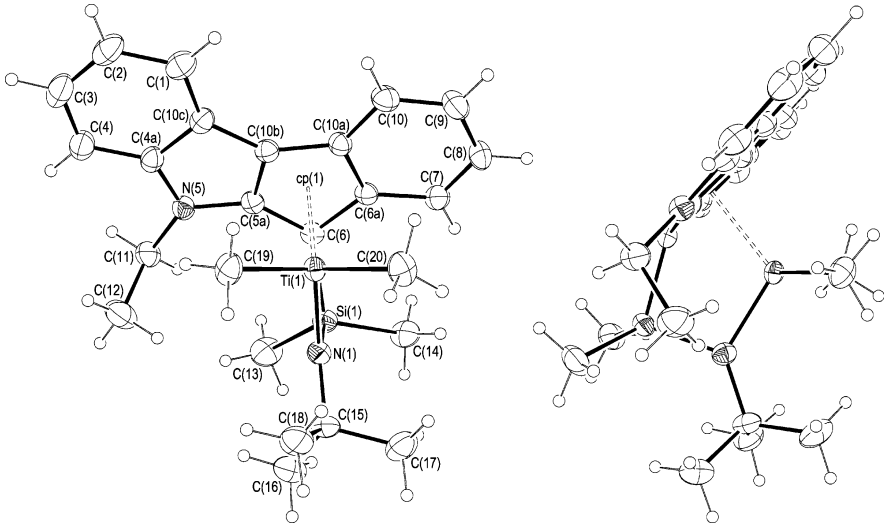

Figure 1. Frontal and lateral ORTEP views of [6-[(*tert*-butylamido-κN)dimethylsilyl]-5-ethyl-(5a,6,6a,10a,10b-η)-indeno-[2,1-*b*]indol-6-yl]dimethyltitanium, **2**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are given arbitrary radii.

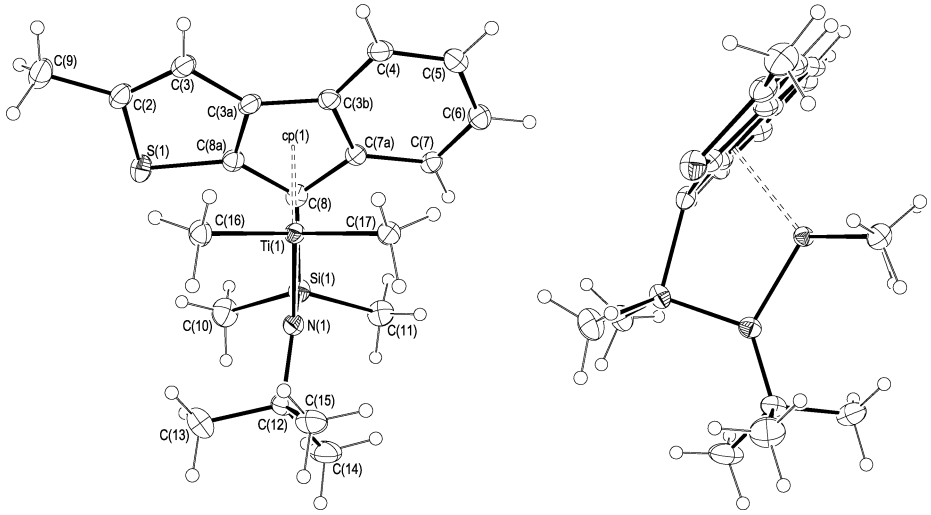

Figure 2. Frontal and lateral ORTEP views of [8-[(*tert*-butylamido-κN)dimethylsilyl]-2-methyl-(3a,3b,7a,8,8a-η)-8*H*-indeno-[2,1-*b*]thiophen-8-yl]dimethyltitanium, **6**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are given arbitrary radii.

chain-end control, we applied the statistical model for syndiospecific propagation already developed for syndiospecific polymerization by the C_s-symmetric zirconocene $Me_2C(Cp)(Flu)ZrCl_2$.[3,24,25]

Statistical modeling of pentad distributions of these *sam*-PP was satisfactorily done using a model based on enantiomorphic site control (values listed as "calc" in Table 4). The presence of isolated *m* dyads in ^{13}C NMR spectra (*rrmr* pentad), attributable to an isomerization of the site due to a "skipped" monomer insertion during chain growth, was included in the model considering the probability of site isomerization p_{bs} in the expressions for pentad distribution.[3]

For comparison, the experimental pentad distribution was also fitted with the (symmetric) Markovian model (for chain-end control) (values listed as "calc M1" in Table 4). The calculated pentads distribution for the two models are reported in Table 4 together with the values of the least-squares fitting. The least-squares of the Bernoullian fitting is always lower that the least-squares of the Markovian one, confirming that these complexes operate by enantiomorphic site-controlled syndiospecific polymerization.[3]

Activities follow the order **5** > **3** > **2** > **1** ∼ **4** > **6** ∼ **7** > **8** ∼ **9**; in addition **6**/MAO shows a very fast decay. Molecular weights are remarkably high, with **5**, **2**, and **6** producing molecular weights around 10^6 at the high (for propylene) polymerization temperatures of 70−80 °C. The order of molecular weights is approximately **5** > **2** ∼ **6** > **1** ∼ **3** ∼ **4** ∼ **7** ∼ **9** ≫ **8**. Given the outstanding performance of **5**, this catalyst was further investigated by low-pressure polymerization in toluene solution.

2. Polymerization in Solution. Propylene polymerizations in solution were carried out in toluene in a 250 mL pressure glass reactor. The results are reported in Table 5. Both **5** and **2** were tested in combination with $[Ph_3C][B(C_6F_5)_4]$ as cocatalyst, and they show very similar activity values (compare entries 17 and 22 in Table 5). **2** was also used in the presence of MAO and $[PhNHMe_2][B(C_6F_5)_4]$: the catalytic activity is the same with both the cocatalysts, but much lower than with $[Ph_3C][B(C_6F_5)_4]$. Note that MAO produces the highest

Table 2. Selected Bond Lengths [Å] and Angles [deg] for the Titanium Complexes 2 and 6[a]

2		6	
Ti(1)−cp(1)	2.1040(16)	Ti(1)−cp(1)	2.1063(15)
Ti(1)−N(1)	1.936(2)	Ti(1)−N(1)	1.929(3)
Ti(1)−C(19)	2.094(3)	Ti(1)−C(16)	2.109(3)
Ti(1)−C(20)	2.116(3)	Ti(1)−C(17)	2.107(3)
Ti(1)−C(6)	2.271(3)	Ti(1)−C(8)	2.270(3)
Ti(1)−C(6a)	2.370(3)	Ti(1)−C(8a)	2.388(3)
Ti(1)−C(5a)	2.418(3)	Ti(1)−C(7a)	2.398(3)
Ti(1)−C(10a)	2.541(3)	Ti(1)−C(3a)	2.548(3)
Ti(1)−C(10b)	2.557(3)	Ti(1)−C(3b)	2.556(3)
cp(1)−Ti(1)−N(1)	110.54(7)	cp(1)−Ti(1)−N(1)	110.73(9)
cp(1)−Ti(1)−C(19)	110.48(9)	cp(1)−Ti(1)−C(16)	113.09(10)
cp(1)−Ti(1)−C(20)	116.48(10)	cp(1)−Ti(1)−C(17)	114.48(10)
N(1)−Ti(1)−C(19)	111.92(11)	N(1)−Ti(1)−C(16)	108.62(13)
N(1)−Ti(1)−C(20)	107.59(12)	N(1)−Ti(1)−C(17)	109.72(12)
C(19)−Ti(1)−C(20)	99.38(13)	C(16)−Ti(1)−C(17)	99.60(14)
Ti(1)−N(1)−Si(1)	101.98(10)	Ti(1)−N(1)−Si(1)	101.54(13)
Ti(1)−N(1)−C(15)	130.51(18)	Ti(1)−N(1)−C(12)	131.9(2)
Si(1)−N(1)−C(15)	126.99(18)	Si(1)−N(1)−C(12)	126.3(2)

[a] cp refers to the centroid of the five-membered rings of the organic ligand coordinated to the metal.

syndioselectivity among the three activators. It can be seen that in the presence of $[PhNHMe_2][B(C_6F_5)_4]$ the catalytic activity threshold is quite high. The same behavior toward the cocatalysts is also shown by **9** and other indenyl amido titanium dimethyl complexes, as already reported in our previous investigation.[16]

High molecular weight *sam*-PP was produced in all cases, and 2,1-propylene insertions are practically absent. Selected samples were analyzed by GPC and showed the narrow molecular weight distributions expected for single-center catalysts ($M_w/M_n = 2-2.5$).

The catalyst **5**/$[Ph_3C][B(C_6F_5)_4]$ was also tested in the range 0.9−3.7 mol/L as propylene concentration in liquid phase. As already revealed for **9**,[16] the catalytic activity increases (in an approximately linear manner) with the propylene concentration in liquid phase, while syndiotacticity and molecular weight do not seem to change noticeably with the monomer concentration.

As the molecular weight of a polyolefin prepared with a single-center catalyst is given by the ratio between the overall rate of propagation and the sum of all rates of chain release reactions,[3,26,27] and assuming a first-order reaction rate with respect to monomer concentration for the overall rate of propagation,[28] the observed independence of molecular weight from monomer concentration indicates that the rate of chain release is first-order in monomer. End-group analysis is obviously impossible for such high molecular weights, but ^{1}H NMR analysis of the 4−6 ppm region on a low molecular weight sample obtained at high temperature and low [propylene] shows the presence of only vinylidene end groups. Whether this chain release is due to direct β-H transfer to the coordinated monomer or to associative displacement following a unimolecular β-H transfer[27] cannot be established at this time.

For **5**/$[Ph_3C][B(C_6F_5)_4]$ the effect of the polymerization temperature was also determined, by performing polymerization tests in the range 20−80 °C under identical monomer concentration (1.85 mol/L). The stereoregularity markedly decreases as the polymerization temperature increases, while 2,1 insertions were again not observed. The catalyst activity and PP molecular weights also strongly decrease with temperatures. The Arrhenius plot of $\ln(\bar{P}_n)$ versus $1/T$ for **5** is compared in Figure 4 to those from **8** and **9**.[16]

$\bar{P}_n$ values for *sam*-PP from **5** are higher than for **8** and **9**, and the temperature effect is more marked. The obtained activation energy barriers for chain release with the three catalysts are $\Delta\Delta E_r^{\ddagger}$(**8**) = 3.4 kcal/mol, $\Delta\Delta E_r^{\ddagger}$(**9**) = 6.3 kcal/mol, and $\Delta\Delta E_r^{\ddagger}$(**5**) = 7.7 kcal/mol. We attribute the observed increase in $\Delta\Delta E_r^{\ddagger}$ on going from **8** to **9** to **5** to the increase of electron-donating ability of the substituents on the Cp ring, which reduces proton affinity of the metal center.

Influence of Cyclopentadienyl Ligand Substituents on Polymerization Activity. The catalytic performance of formally 14-electron complexes of type $Me_2Si(Cp')(t\text{-BuN})TiMe_2$, where Cp′ is a generically substituted cyclopentadienyl ligand, is strictly related to the extent of cation−anion interactions in the activated species, assumed to be the 12-electron cation $[Me_2Si(Cp')(t\text{-BuN})TiMe]^+$, generated from the precatalyst by σ-ligand abstraction. Intuitively, if the Cp′ ligand is a good electron donor, it will stabilize the cation and reduce cation−anion electrostatic interactions by reducing the positive charge on the metal. Various physical and chemical quantities have been proposed as a measure of the electron donor capability of the Cp′ ligand in attempts to quantify the substituent electronic effect on the metal center.[29] Here we propose as a direct *computational* measure of this effect the group electronegativity of the $[Me_2Si(Cp')(t\text{-BuN})TiMe]$ fragment (for computational details see below). Group electronegativity[30] can be defined, within the framework of density functional theory, as a tendency of a group of atoms to attract electrons to itself from another group of atoms. An electron-donating Cp′ ligand, increasing the electron density at the metal center, should decrease the electronegativity of the $[Me_2Si(Cp')(t\text{-BuN})TiMe]$ fragment, while an electron-withdrawing ligand should increase it.

A set of 10 molecules has been considered: three complexes in which Cp′ is tetramethylcyclopentadienyl (**7**), indenyl (**8**), and 2-methylindenyl (**9**), respectively, taken as reference species; two complexes containing the indenopyrrolyl moiety both [2,1-*b*] (**5**) and [1,2-*b*] (**10**) fused; two complexes containing the indenoindolyl moiety both [2,1-*b*] (**1**) and [1,2-*b*] (**3**) fused; a complex containing the indeno[2,1-*b*]thiophenyl moiety (**6**); and two complexes related to those prepared by Klosin, namely, 2-(dimethylamino)cyclopentadienyl (**11**) and 3-(dimethylamino)cyclopentadienyl (**12**).[31]

The geometry of the 10 $Me_2Si(Cp')(t\text{-BuN})TiMe_2$ complexes **1**, **3**, and **5**−**12** have been fully optimized at the

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(27) Liu, Z.; Somsook, E.; White, C. B.; Rosaaen, K. A.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 11193.

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(29) (a) Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406. (b) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525. Dealing with dimethyltitanium species, a proposed measure of the electron-richness of the titanium center is the C−H coupling constant of the Ti-CH_3 group. However, for complexes **1**−**9** a clear relation does not seem to exist between the measured $^1J_{CH}$ and either the polymerization activity or the polymer molecular weight.

(30) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

Table 3. Liquid Propylene Polymerization Results[a]

run	catalyst	μmol Ti	MAO/Ti molar	T_p °C	time min	$kg_{PP}/(mmol_{Ti} \times h)$	$\bar{M}_w$ [b]	rr	rrrr	2,1
1	**1**	2.3	500	50	60	18.2	1 311 500	73.3	57.5	<0.3
2	**1**	2.3	1000	60	30	43.3	548 500	72.1	52.9	<0.3
3	**1**	1.6	1000	70	60	26.9	529 600	69.2	48.4	<0.3
4	**2**[c]	0.7	1000	60	60	49.7	1 915 000	73.5	57.5	≈0.3
5	**2**[c]	1.1	1000	70	60	46.5	1 309 000	72.8	54.1	<0.3
6	**3**	2.3	500	70	60	61.6	515 600	54.5	28.3	<0.3
7	**4**	2.1	500	70	60	29.2	567 500	54.3	29.0	<0.3
8	**5**	1.3	500	70	60	41.2	1 900 000			
9	**5**	1.3	500	80	60	124.3	1 034 000	71.2	52.0	<0.3
10	**6**	1.3	500	60	60	10.2	2 822 000			
11	**6**	5.1	500	80	60	17.6	981 000	61.4	39.0	0.5
12	**7**	2.7	3000	50	60	12.9	1 191 000	52.3	26.8	1.3
13	**7**	5.4	1000	60	60	10.9	650 300	50.0	25.3	1.3
14	**7**	5.4	1000	70	60	11.6	420 100	48.0	22.7	1.6
15	**8**	6.2	1000	60	60	4.0	135 400	36.3	12.5	1.5
16	**9**	3.0	1000	60	60	6.2	550 800	51.3	28.3	0.6

[a] Polymerization conditions: 2 L reactor, 600 g of propylene, 2 mmol of Al(*i*-Bu)$_3$. [b] From intrinsic viscosity. [c] Catalyst injection at 30 °C, polymerization temperature reached in 5−7 min.

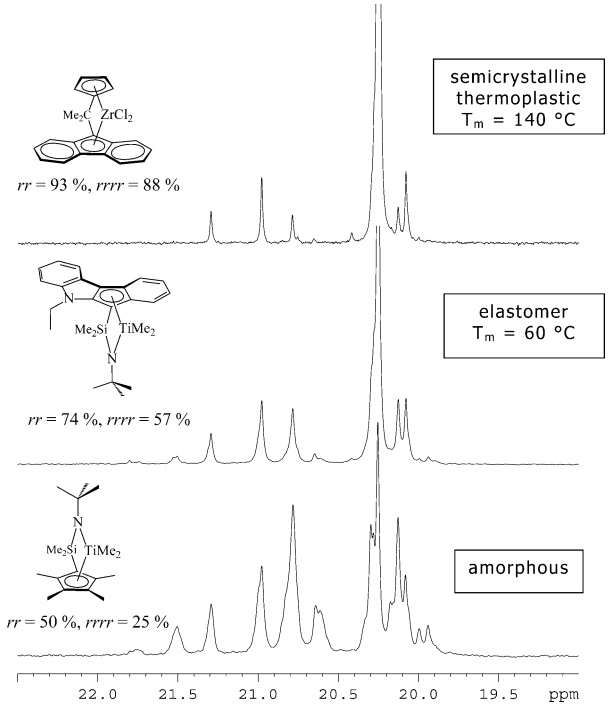

Figure 3. Methyl pentad region of ^{13}C NMR spectra ($C_2D_2Cl_4$, 120 °C) of *s*-PP from $Me_2C(Cp)(Flu)ZrCl_2$/MAO (top, sample polymerized at 0 °C), of *sam*-PP obtained from **2**/MAO (middle, sample 4), and of *am*-PP obtained from **7**/MAO (bottom, sample 13).

HF/3-21G(*) level. This level of theory has been recently demonstrated to give an adequate description of the geometry of group 4 metallocene polymerization catalysts.[32] Geometries have been optimized in redundant internal coordinates,[33] employing the GDIIS algorithm,[34] until the maximum (root-mean-square) force was less than 0.00045 (0.00030) au. Calculations have been done without the imposition of any symmetry constraints; however **7** resulted to possess C_s symmetry (as the related dichloro derivative [$SiMe_2(C_5Me_4)$(*t*-BuN)$TiCl_2$] in the solid state[35]). Group electronegativity has been computed as minus the energy of the semioccupied molecular orbital (SOMO) of the open-shell species [$SiMe_2$(Cp′)(*t*-BuN)TiMe].[36] This single-point computation has been done at the spin-unrestricted B3LYP/3-21G(*) level of theory.[37] The geometry of this fragment has been obtained from that of the corresponding dimethyl complex by eliminating one of the two methyl group. Since the two methyl groups are, in general, not equivalent, electronegativity has been computed for the two possible fragments and the two values have been averaged. All the computations have been performed with Gaussian 98.[38]

Table 7 collects the computed group electronegativity values for the 10 [Me_2Si(Cp′)(*t*-BuN)TiMe] fragments, together with some computed geometric parameters for the Me_2Si(Cp′)(*t*-BuN)$TiMe_2$ precatalysts.

Assuming that the lower the group electronegativity, the higher the predicted activity, we foresee the following order of activity: **10** > **5** > **3** > **1** ≫ **6** ≫ **8** ≈ **9**, which is in good accordance with the experimental results.

The fusion of the indenyl moiety with a nitrogen-containing heterocycle determines a significant lowering of the group electronegativity: the effect is greater for pyrrole than for indole. This observation can be explained considering that the nitrogen p-electrons are more delocalized in indole (in which aromaticity involves also a benzo fused ring) than in pyrrole.

Values reported in Table 7 show also that the [1,2-*b*] fusion of the rings (which results in a 3-N substitution of the indenyl ring) is only slightly more effective than the [2,1-*b*] one (which results in a 2-N substitution). This is in accordance with our experimental findings but seems to contrast with the observation of Klosin that the 3-amino-substituted indenyl complexes are much more active than the 2-amino-substituted ones.[7,8] However, in all four compounds **5**, **10**, **1**, and **3** the nitrogen

(31) Klosin actually compared 2-(dimethylamino)indenyl and 3-pyrrolidinoindenyl.[7−9] To avoid the problem of the conformation of the five-membered ring, we model the pyrrolidino substituent with a dimethylamino one.

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(38) *Gaussian 98*, revision A.11.3; Gaussian, Inc.: Pittsburgh, PA, 2002.

Table 4. Pentad Distributions

	sample	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*mmrm* + *rmrr*	*rmrm*	*rrrr*	*rrrm*	*mrrm*	*a*	P_{bs}	ls
expt	2	0.55	1.72	4.67	8.70	9.53	2.72	52.86	15.43	3.82			
calc		0.54	2.06	4.67	9.82	10.34	2.02	53.21	16.09	1.24	0.9241	0.06	9.72×10^{-4}
calc M1		0.04	0.47	1.44	2.88	18.24	2.88	54.83	17.78	1.44			1.37×10^{-2}
expt	4	0.83	1.58	3.96	9.02	8.90	2.40	57.48	14.10	1.71			
calc		0.43	1.66	4.41	9.21	9.02	1.60	57.69	14.98	0.99	0.9323	0.05	2.39×10^{-4}
calc M1		0.02	0.31	1.14	2.27	16.77	2.27	59.63	16.45	1.14			1.28×10^{-2}
expt	6	1.08	3.59	3.85	8.72	20.93	7.33	28.27	20.33	5.90			
calc		0.92	3.96	4.37	9.29	22.05	6.88	28.32	20.50	3.71	0.9460	0.23	7.04×10^{-4}
calc M1		0.54	2.92	3.92	7.83	23.91	7.83	28.13	20.99	3.92			4.58×10^{-2}
expt	7	0.96	3.27	4.13	8.92	21.30	7.12	28.98	20.41	4.90			
calc		0.86	3.80	4.29	9.11	21.99	6.75	29.01	20.55	3.64	0.9488	0.23	2.57×10^{-4}
calc M1		0.51	2.80	3.83	7.67	23.82	7.67	28.84	21.03	3.83			1.03×10^{-3}
expt	9	0.48	1.69	2.95	6.73	13.82	3.09	52.03	16.22	2.97			
calc		0.31	1.69	3.34	7.16	14.17	2.38	52.26	17.25	1.43	0.9524	0.10	4.49×10^{-4}
calc M1		0.05	0.53	1.56	3.12	18.73	3.12	53.15	18.20	1.56			4.78×10^{-3}
expt	11	0.65	2.63	3.46	8.02	18.21	5.65	39.01	17.44	4.94			
calc		0.58	2.83	3.90	8.44	18.55	4.39	39.02	19.77	2.51	0.9424	0.16	1.34×10^{-3}
calc M1		0.19	1.44	2.73	5.46	22.12	5.46	39.18	20.68	2.73			3.95×10^{-3}
expt	13	1.40	4.20	5.81	10.27	20.01	8.27	25.29	19.09	5.65			
calc		1.49	5.28	5.07	10.95	21.19	7.01	25.26	19.44	3.92	0.89915	0.21	8.74×10^{-4}
calc M1		0.76	3.62	4.33	8.65	24.29	8.65	24.69	20.67	4.33			2.87×10^{-3}

Table 5. Propylene Polymerization in Solution with 5[a]

run	catalyst	μmol	cocatalyst	*P*, bar-g	T_p, °C	[propylene], mol/L	time, min	yield, g	kg_{PP}/($mmol_{Ti} \times h$)	% triads mm	mr	rr	% 2,1	$\bar{M}_w$ [b]
17	**2**	1.0	$[Ph_3C][B(C_6F_5)_4]$	3	50	2.26	10	1.5	9.3	11.8	39.6	48.6	0.0	665 200
18	**2**	1.0	MAO	3	50	2.26	15	0.6	2.4	8.8	31.3	59.8	0.0	450 000
19	**2**	4.5	$[PhNHMe_2][B(C_6F_5)_4]$	3	50	2.26	10	1.8	2.4	12.1	37.8	50.1	0.0	682 800
20	**5**	2.0	$[Ph_3C][B(C_6F_5)_4]$	1	50	0.87	15	1.5	2.9	7.7	38.1	54.2	0.0	613 400
21	**5**	2.0	$[Ph_3C][B(C_6F_5)_4]$	2	50	1.57	10	1.5	4.5					647 800
22	**5**	2.0	$[Ph_3C][B(C_6F_5)_4]$	3	50	2.26	10	3.1	9.2	7.7	38.5	53.8	0.0	572 300
23	**5**	1.5	$[Ph_3C][B(C_6F_5)_4]$	4	50	2.95	10	2.4	9.6					891 000
24	**5**	1.5	$[Ph_3C][B(C_6F_5)_4]$	5	50	3.65	10	3.9	15.4	7.4	36.1	56.6	0.0	748 800
25	**5**	1.0	$[Ph_3C][B(C_6F_5)_4]$	0.85	20.5	1.85	15	1.6	6.3	5.7	23.8	70.5	0.0	2 594 400
26	**5**	1.0	$[Ph_3C][B(C_6F_5)_4]$	1.9	41.5	1.85	10	1.6	9.4					1 252 300
27	**5**	1.0	$[Ph_3C][B(C_6F_5)_4]$	3.3	60.0	1.85	10	0.9	5.3					577 100
28	**5**	1.0	$[Ph_3C][B(C_6F_5)_4]$	5.0	77.5	1.85	10	0.1	0.7	9.4	42.5	48.2	0.0	303 500

[a] Polymerization conditions: 260 mL Büchi glass autoclave, 100 mL of toluene, 0.5 mmol of Al(*i*-Bu)$_3$ as scavenger in toluene, B/Ti = 1 (mol/mol), Al/Ti = 1000 (mol/mol), precontact in toluene (5 mL); 30 s (time necessary to transfer the catalytic solution into the reactor). [b] From intrinsic viscosity.

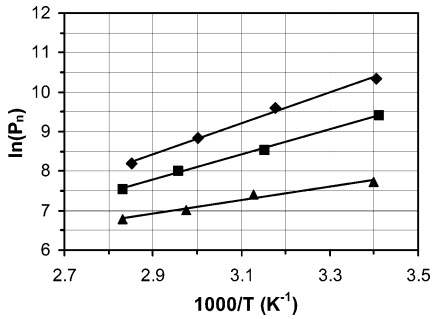


Figure 4. Arrhenius plots of $\ln(\bar{P}_n)$ versus 1000/*T*. (◆) **5** ($\Delta\Delta E_r^{\ddagger} = 7.7 \pm 0.4$ kcal/mol, $R = 0.997$); (■) Me_2Si(2-MeInd)(*t*-BuN)$TiMe_2$ ($\Delta\Delta E_r^{\ddagger} = 6.3 \pm 0.2$ kcal/mol, $R = 0.999$); (▲) Me_2Si(Ind)(*t*-BuN)$TiMe_2$ ($\Delta\Delta E_r^{\ddagger} = 3.4 \pm 0.4$ kcal/mol, $R = 0.987$). Cocatalyst $Ph_3CB(C_6F_5)_4$, [propylene] = 1.85 mol/L.

atom of the heterocycle effectively delocalizes its p-electrons into the indenyl moiety. This is confirmed by the value of the computed N−C bond lengths (from 1.372 to 1.376 Å, see Supporting Information), which are consistent with a partial double-bond character and are similar to those computed for the 3-dimethylamino-substituted complex **12** (1.366 Å). The same consideration can be done analyzing the pyramidalization of the nitrogen atom, measured by the sum of the angles around it: the values computed for **5**, **10**, **1**, and **3** (from 359.28° to 360.00°) and for **12** (359.34°) are consistent with a sp^2 hybridization. For the 2-dimethylamino-substituted complex **11** we compute a substantially higher value of the group electronegativity: indeed, in this complex the nitrogen atom is sp^3 hybridized and cannot delocalize its p-electrons into the indenyl moiety (computed N−C bond lengths: 1.407 Å; sum of the angles around N: 343.06°). It can be concluded that in complex **11** steric interactions between the dimethylamino group in position 2 and the $SiMe_2$ bridge preclude a planar configuration of the nitrogen atom, while in **5** and **1** the planarity is granted by the aromaticity of the heterocycle.

The thiophene derivative **6** shows an activity intermediate between that of the nitrogen-substituted and that of the unsubstituted indenyls. This can be explained considering that the p-electrons of sulfur are too diffuse and high in energy to be as effective as those of nitrogen to donate to the indenyl moiety.

The prototype complex **7** seems to deviate from the correlation between group electronegativity and activity: indeed, its computed electronegativity is similar to that of the nitrogen-substituted complexes, but experimentally it shows an activity similar to **6**. However, from a steric point of view, **7** is quite different from the other complexes of Table 7 because all the cyclopentadienyl atoms bear a sp^3 substituent. This leaves a clear trace in the computed geometric parameters, in particular in the Ti−Me bond lengths that are quite elongated in this complex. Hence, the behavior of this

Table 6. Summary of Crystal Data, Data Collection, and Structure Refinement Parameters for 2 and 6

	2	**6**
formula	$C_{25}H_{34}N_2SiTi$	$C_{20}H_{29}NSSiTi$
fw	438.53	391.49
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	*Pbcn* (No. 60)
a (Å)	10.742(6)	23.208(5)
b (Å)	10.964(6)	12.423(3)
c (Å)	11.486(6)	14.280(3)
α (deg)	79.00(1)	
β (deg)	69.61(1)	
γ (deg)	72.21(1)	
V (Å^3)	1202.0(11)	4117.1(16)
Z	2	8
F(000)	468	1664
density (g cm^{-3})	1.212	1.263
abs coeff (mm^{-1})	0.419	0.577
cryst color	orange	red
cryst size (mm)	0.26 × 0.23 × 0.20	0.35 × 0.28 × 0.20
θ range (deg)	$1.9 \le \theta \le 23.3$	$2.3 \le \theta \le 23.3$
index ranges	$-11 \le h \le 11$	$-25 \le h \le 10$
	$-12 \le k \le 12$	$-13 \le k \le 12$
	$-12 \le l \le 12$	$-14 \le l \le 15$
intensity decay (%)	none	none
transmn factors (min, max)	0.886, 0.921	0.818, 0.893
no. of measd reflns	8902	15681
no. of ind reflns	3475	2930
R_{int}, R_σ[α]	0.0720, 0.0716	0.0438, 0.0322
no. of reflns with $I > 2\sigma(I)$	2930	2394
no. of data/parameters	2930/271	2394/225
weights (*a*, *b*)[b]	0.05, 0.65	0.03, 5.00
goodness-of-fit $S(F^2)$[c]	1.049	1.154
$R(F)$[d]	0.0372	0.0430
$wR(F^2)$[e]	0.0913	0.0866
largest diff peak, hole (e Å^{-3})	0.262, −0.292	0.272, −0.227

[a] $R_{int} = \sum|F_o^2 - F_{mean}^2|/\sum|F_o^2|$; $R_\sigma = \sum|\sigma(F_o^2)|/\sum|F_o^2|$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [c] $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters. [d] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

species can be explained taking into account its steric properties besides its electronic effect, as measured by group electronegativity.

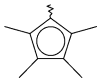
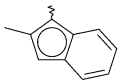
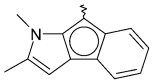
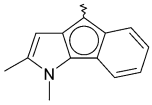
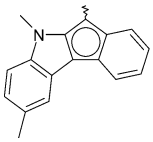
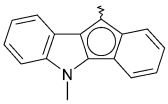
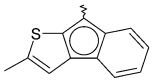
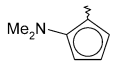
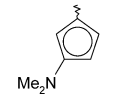
These results allow us to conclude that the group electronegativity of the [$SiMe_2$(Cp′)(*t*-BuN)TiMe] fragment is a suitable, and easy to compute, measure of the substituent electronic effects for this class of catalysts.

Conclusions

We have described a new family of indenyl silyl amido titanium complexes based on indenoindoles, indenopyrrole, and 2-methylindenothiophene. The indenoindole ligand precursors are especially simple to prepare in high yields by the acid-catalyzed Fischer condensation of indan-2-one and the hydrochlorides of arylhydrazines. All the Ti complexes were prepared as their dimethyl derivatives by reacting the ligand, a 2-fold excess of MeLi, and $TiCl_4$. The molecular structures of the amidosilylindenyl titanium complexes **2** and **6** have been determined by single-crystal X-ray diffraction analysis: the indenoindole moiety in **2** and the indenothiophene moiety in **6** are perfectly planar.

Catalysts **1**, **2**, and **5**, all having a pyrrole or indole condensed to indene with N in the back of the ligand, produce syndiotactic amorphous polypropylenes (*sam*-

Table 7. Computed Group Electronegativities (χ) for the [Me_2Si(Cp′)(*t*-BuN)TiMe] Fragments and Computed Geometric Parameters for the $SiMe_2$(Cp′)(*t*-BuN)$TiMe_2$ Molecules

	Cp′	χ[a] eV	cp–Ti–N[b] °	Ti–cp[b] Å	Ti–N Å	Ti–Me Å
7		4.126	107.55	2.088	1.944	2.112 2.112
8		4.428	107.66	2.135	1.923	2.095 2.102
9		4.433	107.87	2.127	1.928	2.095 2.105
5		4.107	110.58	2.159	1.916	2.095 2.104
10		4.050	110.95	2.175	1.910	2.100 2.109
1		4.189	109.49	2.151	4.917	2.090 2.101
3		4.140	110.69	2.182	1.907	2.099 2.101
6		4.310	109.76	2.181	1.909	2.095 2.097
11		4.221	107.28	2.113	1.920	2.108 2.114
12		3.986	107.86	2.115	1.928	2.112 2.114

[a] Mean value (see text). [b] cp refers to the centroid of the five-membered ring coordinated to the metal.

PP) of very high molecular weights, even at polymerization temperatures as high as 80 °C. Syndiotactic pentad contents range between 48 and 57% *rrrr*, and regioerrors are close to or below the detection limit of the ^{13}C NMR analysis (at 100 MHz). In toluene solution, $[Ph_3C][B(C_6F_5)_4]$ is by far a better activator than MAO, $[HNMe_2Ph][B(C_6F_5)_4]$, or $B(C_6F_5)_3$.

For **5**/$[Ph_3C][B(C_6F_5)_4]$ the catalytic activity shows an approximate first-order dependence on propylene concentration, while the tacticity and the molecular weight do not seem to change noticeably with the monomer concentration. On the other side, stereoregularity, catalyst activity, and PP molecular weights decrease as the polymerization temperature increases. The obtained activation energy barrier for chain release with this catalyst is $\Delta\Delta E_r^{\ddagger} = 7.7$ kcal/mol.

Experimental Section

General Procedures. If not otherwise indicated, all operations were performed under nitrogen by using conventional Schlenk-line techniques. Solvents were purified by degassing

with N_2 and passing over activated (8 h, N_2 purge, 300 °C) Al_2O_3, and stored under nitrogen. MeLi, *n*-BuLi, $TiCl_4$, Me_2SiCl_2, *t*-$BuNH_2$, 1-indanone, *p*-tolyl-hydrazine hydrochloride, phenyl-hydrazine hydrochloride, 1,1-diphenylhydrazine hydrochloride, 1,3-dioxolane (all from Aldrich), 2-indanone (Chemische Fabrik Berg, 98%), *t*-BuOK (Fluka), MeI (Acros), NH_4Cl (Carlo Erba RPE, 99.5%), EtBr (Fluka, 99%), $B(C_6F_5)_3$ (Boulder Scientific), $[Ph_3C][B(C_6F_5)_4]$, and $[PhNHMe_2][B(C_6F_5)_4]$ (Austin) were used as received. Al(*i*-Bu)$_3$ (Witco) was used as 1 M in hexane (liquid propylene tests) or in toluene, and MAO (methylalumoxane, 10 wt % solution in toluene, Witco) was used as received (liquid propylene tests) or dried under vacuum to remove most of the free trimethylaluminum and then redissolved in toluene as a 1 M solution. Polymerization grade propylene was obtained from the Basell Ferrara plant.

^{1}H and ^{13}C NMR Analysis. The proton and carbon spectra of ligands and metallocenes were obtained using a Bruker DPX 200 spectrometer operating in the Fourier transform mode at room temperature at 200.13 and 50.323 MHz, respectively. The samples were dissolved in $CDCl_3$, CD_2Cl_2, C_6D_6, or $C_6D_5CD_3$. The residual peak of $CHCl_3$, $CHDCl_2$, C_6D_5H, or $C_6D_5CH_3$ in the ^{1}H spectra (7.25, 5.35, 7.15, and 2.10 ppm, respectively) and the central peak of the solvent in the ^{13}C spectra (77.00 ppm for $CDCl_3$ and 128.00 ppm for C_6D_6) were used as references. Proton spectra were acquired with a 15° pulse and 2 s of delay between pulses; 16 or 32 transients were stored for each spectrum. The carbon spectra were acquired with a 45° pulse and 6 s of delay between pulses; about 512 transients were stored for each spectrum. C_6D_6 (Aldrich, 99.6 atom % D), CD_2Cl_2 (Aldrich, 99.8 atom % D), and $CDCl_3$ (Aldrich, 99.8 atom % D) were dried and stored over activated molecular sieves (4−5 Å).

GC−MS. GC−MS analyses were carried out on a HP 5890-series 2 gas chromatograph and a HP 5989B quadrupole mass spectrometer.

Dimethylsilyl(*tert*-butylamido)(*N*-methyl-2-methyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)dimethyl Titanium (1). First Synthetic Route. 2-Methyl-5,6-dihydroindeno[2,1-*b*]indole (1a). All operations were carried out in air, with out-of-the bottle solvents and reagents: 2-propanol, RPE Carlo Erba (99%); 2-indanone, Chemische Fabrik Berg (98%); *p*-tolyl-hydrazine hydrochloride, Aldrich (98%). In a 1 L jacketed glass reactor (Büchi) with a magnetically driven, three-blade stirrer, connected to a thermostat for temperature control, were charged 85.0 g of 2-indanone (0.63 mol), 102.0 g of *p*-$MeC_6H_4NHNH_2$·HCl (0.63 mol), and 0.5 L of *i*-PrOH. The thick suspension was warmed to 80 °C in about 30 min, and the slurry darkened to dark brown under stirring. The mixture was stirred at 80 °C for 1 h and then was cooled to room temperature in about 30 min. The slurry was siphoned into 1.2 L of water containing 1.5 equiv of $NaHCO_3$, thus obtaining a fine dispersion of a dark green product (no heat evolution was observed). The slurry was then filtered on a G3 frit, washed with water, and dried in air under moderate vacuum, then in the rotating evaporator at 80 °C, and finally under high vacuum (mechanical pump). A total of 121.2 g of the target product was obtained with a yield of 87.3% (purity of 99.6% by GC). ^{1}H NMR ($CDCl_3$, δ, ppm): 2.52 (s, 3H, CH_3); 3.70 (s, 2H, CH_2); 7.01−7.66 (m, 7H, Ar); 8.13 (bs, 1H, *N*-H). ^{13}C NMR (CD_2Cl_2, δ, ppm): 21.62 (*C*H_3); 31.48 (*C*H_2); 111.81; 118.49; 119.26; 121.58; 122.72 (2*C*); 123.22; 125.05; 127.26; 129.99; 139.31; 140.41; 143.09; 146.98. Mp: 191.8−195.1 °C. *m*/*z* (%): 219 (100) [M^+]; 204 (86); 189 (14); 108 (25). Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.62; H, 5.94; N, 6.44.

***N*-Methyl-2-methyl-5,6-dihydroindeno[2,1-*b*]indole (1b).** A 22.37 g sample of 2-methyl-5,6-dihydroindeno[2,1-*b*]indole (99.6% by GC, 101.6 mmol) was dissolved in 220 mL of 1,3-dioxolane (Aldrich) at room temperature, and to this was added 11.46 g of *t*-BuOK (Aldrich, 101.6 mmol). The solution changed color from green to dark brown and was stirred at room temperature for 10 min; then 6.33 mL of MeI (Acros, d = 2.280, 101.6 mmol) was added. After 15 min stirring, a solid started forming. Stirring was continued for 1 h, then the reaction mixture was poured into water containing 8 g of NH_4Cl (Carlo Erba RPE, purity 99.5%). After 2 h stirring, the formed solid was isolated by filtration and dried in vacuo to give 23.2 g of a brown powder, which was analyzed by NMR spectroscopy and GC−MS. The GC−MS analysis showed a purity in the desired product of 91.5% (yield = 89.5%). 2-Methyl-5,6-dihydroindeno[2,1-*b*]indole and *N*-methyl-2,6-methyl-5,6-hydroindeno[2,1-*b*] indole were also present, in percentages of 2.6% and 3.7%, respectively. An aliquot of the product (9.98 g) was suspended in 150 mL of MeOH. After 30 min stirring at room temperature, a dark brown microcrystalline powder was isolated by filtration (9.18 g). The GC−MS analysis shows a higher purity (99.0%) in the desired product. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.53 (s, 3H, CH_3); 3.65 (s, 2H, CH_2); 3.76 (s, 3H, *N*-CH_3); 7.00−7.60 (m, 7H, Ar). ^{13}C NMR ($CDCl_3$, δ, ppm): 21.52 (*C*H_3); 29.98 (*C*H_2); 31.08 (*N*-*C*H_3); 109.38; 118.11; 119.13; 121.83; 122.14; 122.26; 124.62; 126.95; 129.11 (2C); 139.59; 140.50; 142.14; 148.87. Mp: 192.6−195.9 °C. *m*/*z* (%): 233 (100) [M^+]; 218 (35). Anal. Calcd for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.45; H, 6.44; N, 6.11.

Chlorodimethyl(*N*-methyl-2-methyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)silane. A 9.5 mL sample of a 2.5 M solution of *n*-BuLi in hexane (23.75 mmol) was added dropwise to a solution of 5.1 g of *N*-methyl-2-methyl-5,6-dihydroindeno-[2,1-*b*]indole, obtained as reported above (purity 98.2%, 21.46 mmol; indenoindole/*n*-BuLi, 1:1.1), in 70 mL of THF, previously cooled to −78 °C. At the end of the addition, the brown solution was allowed to warm to room temperature and stirred for 6 h. Then it was cooled again to −78 °C and added dropwise to a solution of dichlorodimethylsilane (d = 1.064, 2.6 mL, 21.43 mmol; indenoindole/Me_2SiCl_2, 1:1) in 20 mL of THF, previously cooled to −78 °C. At the end of the addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. The solvents were evaporated under reduced pressure to give a brown sticky solid, which with ^{1}H NMR analysis resulted to be the target product, with few byproducts. The product was used in the subsequent step without further purification. ^{1}H NMR ($CDCl_3$, δ, ppm): −0.13 (s, 3H, Si-CH_3); 0.48 (s, 3H, Si-CH_3); 2.53 (s, 3H, CH_3); 3.44 (s, 1H, CH); 3.88 (s, 3H, *N*-CH_3); 6.90−7.71 (m, 7H, Ar).

6-[Dimethylsilyl(*tert*-butylamino)]*N*-methyl-2-methyl-5,6-dihydroindeno[2,1-*b*]indole. A 3.96 g sample of chlorodimethyl(*N*-methyl-2-methyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)silane (12.15 mmol), obtained as described above, was dissolved in 50 mL of toluene and added at −78 °C to a solution of *t*-$BuNH_2$ (3.0 mL, d = 0.696, 28.55 mmol) in 20 mL of toluene. At the end of the addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 days to give a black suspension, which was filtered to remove the ammonium salt formed. The filtrate was concentrated under vacuum, obtaining 3.49 g of the target product, as a black sticky solid (crude yield = 79.2%). ^{1}H NMR ($CDCl_3$, δ, ppm): −0.15 (s, 3H, Si-CH_3); −0.04 (s, 3H, Si-CH_3); 1.23 (s, 9H, *t*-Bu); 2.52 (s, 3H, CH_3); 3.44 (s, 1H, CH); 3.86 (s, 3H, *N*-CH_3); 6.90−7.71 (m, 7H, Ar). Anal. Calcd for$C_{23}H_{30}N_2Si$: C, 76.19; H, 8.34; N, 7.73.Found: C, 76.05; H, 8.40; N, 7.71.

Dimethylsilyl(*tert*-butylamido)(*N*-methyl-2-methyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)dimethyl Titanium. A 25.3 mL portion of a 1.6 M solution of MeLi in diethyl ether (40.48 mmol) was added dropwise at room temperature to a solution of 3.49 g of 6-[dimethylsilyl(*tert*-butylamino)]*N*-methyl-2-methyl-5,6-dihydroindeno[2,1-*b*]indole (9.62 mmol), obtained as reported above, in 45 mL of Et_2O. The reaction mixture was stirred overnight: an increasing turbidity developed with final formation of a black suspension. Then 1.05 mL of $TiCl_4$ (d = 1.730, 9.62 mmol) in 40 mL of pentane was slowly added at room temperature, and the resulting mixture was stirred overnight. The solvents were removed under reduced pressure

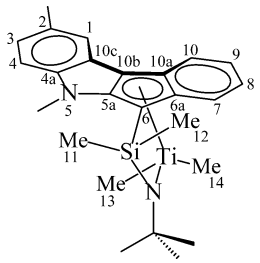
to give a black sticky solid, which was extracted with 50 mL of toluene. The extract was then concentrated, yielding 3.02 g of the desired compound as a dark powder (crude yield 71.6%). ^{1}H NMR (C_6D_6, δ, ppm): −0.02 (s, 3H, Ti-CH_3); 0.07 (s, 3H, Ti-CH_3); 0.56 (s, 3H, Si-CH_3); 0.74 (s, 3H, Si-CH_3); 1.41 (s, 9H, *t*-Bu); 2.45 (s, 3H, CH_3); 3.12 (s, 3H, *N*-CH_3); 6.90−7.94 (m, 7H, Ar).

This product was further purified by extraction with hexane (3 × 70 mL). The hexane solution was concentrated to a final volume of 50 mL, toluene (30 mL) was added, and the mixture was kept at room temperature for 10 h. The dark red crystalline product was separated from the mother solution, washed twice with cold pentane, and finally dried. Yield: 2.86 g.

Second Synthetic Route. (*tert*-Butylamino)dimethylchlorosilane. A 15.7 mL portion of Me_2SiCl_2 (d = 1.07, 130.21 mmol) in 20 mL of Et_2O was added dropwise at 0 °C to a solution of 20.0 g of *t*-$BuNH_2$ (d = 0.696, 273.44 mmol, *t*-$BuNH_2$/Me_2SiCl_2, 2.1:1) in 40 mL of Et_2O. The resulting solution was allowed to warm to room temperature and stirred for 1.5 h. A color change from yellow to light yellow with final formation of a white milky suspension was observed. The suspension was filtered and the filtrate concentrated in vacuo to give 18.93 g of a light yellow oil, which was shown by ^{1}H NMR analysis to be mainly the target product, together with di(*tert*-butylamino)dimethylsilane byproduct. The product was used in the subsequent step without further purification. Yield: 65.8% (purity by ^{1}H NMR = 75.0% mol). ^{1}H NMR (CD_2Cl_2, δ, ppm): 0.48 (s, 6H, Si-CH_3); 1.26 (s, 9H, *t*-Bu); 1.42 (bs, 1H, NH).

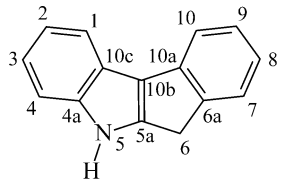
6-[Dimethylsilyl(*tert*-butylamino)]-*N*-methyl-2-methyl-5,6-dihydroindeno[2,1-*b*]indole. A 6.66 mL sample of *n*-BuLi 2.5 M in hexane (16.65 mmol) was added dropwise at 0 °C to a solution of 3.53 g of *N*-methyl-2-methyl-5,6-dihydroindeno[2,1-*b*]indole (purity 99.0%, 15.13 mmol) in Et_2O. At the end of the addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 h. (*tert*-Butylamino)dimethylchlorosilane (3.34 g, purity 75.0% mol, d = 0.887, 20.17 mmol) was added to the Li salt suspension at 0 °C, and the mixture was allowed to warm to room temperature. After 3 h stirring, the solvents were evaporated under reduced pressure and the residue was dissolved in 50 mL of toluene, obtaining a dark brown suspension, which was filtered. The filtrate was evaporated to dryness under reduced pressure, obtaining 5.86 g of a dark brown oil, which resulted to be 90.7 wt % pure (calculated by ^{1}H NMR). Yield = 96.9%. ^{1}H NMR (C_6D_6, δ, ppm): −0.14 (s, 3H, Si-CH_3); −0.13 (s, 3H, Si-CH_3); 0.99 (s, 9H, *t*-Bu); 2.54 (s, 3H, CH_3); 3.27 (s, 3H, *N*-CH_3); 3.40 (s, 1H, CH); 7.10−7.90 (m, 7H, Ar). *m*/*z* (%): 362 (39) [M^+]; 232 (16); 130 (100); 74 (18).

Dimethylsilyl(*tert*-butylamido)(*N*-methyl-2-methyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)dimethyl Titanium. A 19.14



mL (30.63 mmol) portion of MeLi 1.6 M in diethyl ether was added dropwise at 0 °C to a solution of 2.76 g of 6-[dimethylsilyl(*tert*-butylamino)]*N*-methyl-2-methyl-5,6-dihydroindeno-[2,1-*b*]indole (7.62 mmol) in Et_2O; the dark brown suspension obtained was stirred for 1.5 h at room temperature. Then 0.84 mL (7.63 mmol) of $TiCl_4$ in 4 mL of pentane was slowly added at room temperature to the lithium salt, and the resulting black mixture was stirred for 1.5 h (light exothermic reaction with gas evolution). The solvents were removed under reduced pressure to give a black sticky solid, which was extracted with 50 mL of toluene. The extract (3.07 g) was washed with 70 mL of pentane, obtaining 2.22 g of a light brown powder, wich resulted to be 97.0 wt % pure desired product by ^{1}H NMR analysis. Traces of starting ligand (3.0 wt %) were also present. Yield: 64.4%. ^{1}H NMR (C_6D_6, δ, ppm): −0.03 (q, 3H, Ti-CH_3-(13), J = 0.36 Hz); 0.07 (q, 3H, Ti-CH_3(14), J = 0.36 Hz); 0.55 (s, 3H, Si-CH_3(11)); 0.74 (s, 3H, Si-CH_3(12)); 1.40 (s, 9H, *t*-Bu); 2.45 (s, 3H, 2-CH_3); 3.11 (s, 3H, *N*-CH_3); 6.91 (d, 1H, H4, J = 8.31 Hz); 7.02 (ddd, 1H, H8, J = 8.61, 6.87, 1.17 Hz); 7.13 (ddq, 1H, H3, J = 8.31, 1.57, 0.59 Hz); 7.31 (ddd, 1H, H9, J = 8.61, 6.87, 0.96 Hz); 7.80 (dt, 1H, H7, J = 8.61, 0.96 Hz); 7.77−7.79 (m, 1H, H1); 7.92 (dt, 1H, H10, J = 8.61, 1.17 Hz). ^{13}C NMR (C_6D_6, δ, ppm): 6.82 (*C*-Si(12)); 7.27 (*C*-Si(11)); 21.56 (2-*C*H_3); 32.92 (*N*-*C*H_3); 34.53 (*t*-Bu); 55.47 (*C*-Ti(13)); 57.15 (*C*-Ti(14)); 57.93 (*C*-*t*-Bu); 68.65 (*C*6); 109.34 (*C*-H4); 114.36 (*C*-10b); 120.67 (*C*-H1); 123.66 (*C*-10c); 124.08 (*C*-H8); 124.18 (*C*-H10); 124.20 (*C*-10a); 125.13 (*C*-H9); 125.67 (*C*-H3); 128.44 (*C*-H7); 129.63 (*C*-2); 134.93 (*C*-6a); 145.31 (*C*-4a); 148.05 (*C*-5a). Anal. Calcd for $C_{25}H_{34}N_2SiTi$: C, 68.47; H, 7.81. Found: C, 67.3; H, 7.5. *m*/*z* (%) by "direct insertion probe" technique: 439 (32) [M^+ +1]; 424 (37); 423 (100); 407 (26), 391 (21). A powdery sample of **1** proved stable under nitrogen atmosphere by gradual increase of the temperature from 25 °C to 80 °C. ^{1}H NMR analyses in C_6D_6 have been done at 25, 40, 50, 60, 70, and 80 °C. Similarly, a sample of **1** dissolved in C_6D_6 was slowly heated in a water bath from 25 °C to 60 °C. The solution was kept at this temperature for 3 h. ^{1}H NMR analyses showed that the complex is stable after prolonged heating at 60 °C under nitrogen atmosphere.

Dimethylsilyl(*tert*-butylamido)(*N*-ethyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)dimethyl Titanium (2). 5,6-Dihydroindeno[2,1-*b*]indole (2a). All operations were carried out



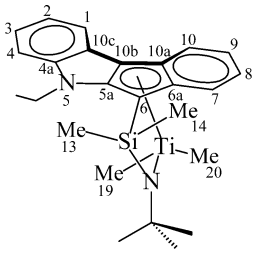
in air, with out-of-the-bottle solvents and reagents. In a 1 L glass reactor with magnetically driven stirrer, connected to a thermostat for temperature control, were charged 36.55 g of 2-indanone (Aldrich, 276.6 mmol) and 40.00 g of hydrazine hydrochloride $C_6H_4NHNH_2$·HCl (Aldrich, 99%, 276.6 mmol) in 300 mL of *i*-PrOH Carlo Erba RPE. The suspension was warmed to 80 °C in about 30 min, and the slurry changed color from yellow to dark under stirring. The reaction mixture was stirred at 80 °C for 1.5 h and then was cooled to room temperature in about 30 min. The slurry was siphoned into an aqueous solution containing 34.85 g of $NaHCO_3$ (414.9 mmol), thus obtaining a green suspension. The slurry was then filtered on a G4 frit, and the residue was washed abundantly with water and dried in air under moderate vacuum for 24 h, thus obtaining 52.81 g of the target product with a yield of 92.84% (purity of 99.8% by GC). ^{1}H NMR ($CDCl_3$, δ, ppm): 3.72 (s, 2H, CH_2); 7.12 (td, 1H, H8, J = 7.48, 1.17 Hz); 7.16−7.29 (m, 2H, H2, H3); 7.31−7.39 (m, 2H, H1, H9); 7.42 (dt, 1H, H7, J = 7.48, 1.17 Hz); 7.66 (dt, 1H, H10, J = 7.48, 1.17 Hz); 7.85−7.89 (m, 1H, H4); 8.26 (bs, 1H, *N*-H). ^{13}C NMR ($CDCl_3$, δ, ppm): 31.51 (*C*H_2); 112.18 (*C*-H1); 118.77 (*C*-H10); 119.56 (*C*-H4); 120.73, 121.84 (*C*-H2, *C*-H3); 122.47 (*C*10c); 122.91 (*C*-H8); 125.05 (*C*-H7); 127.38 (*C*-H9); 140.32 (*C*10b); 140.93 (*C*4a); 142.88 (*C*6a, *C*10a); 146.44 (*C*5a). Mp: 205.0 °C. *m*/*z* (%): 206 (14) [M^+ + 1]; 205 (100) [M^+]; 204 (72); 203 (13); 176 (16); 103 (13); 102 (15).

***N*-Ethyl-5,6-dihydroindeno[2,1-*b*]indole (2b).** In a 500 mL glass reactor with magnetically driven stirrer were charged

15.00 g of 5,6-dihydrondeno[2,1-*b*]indole (99.8% by GC, 73.1 mmol) in 200 mL of 1,3-dioxolane and 8.28 g of *t*-BuOK (Fluka, 99.0%, 73.1 mmol), obtaining a brown solution. After 30 min stirring at room temperature, 5.51 mL (8.04 g) of EtBr (Fluka, 99.0%, d = 1.46, 73.1 mmol) was added dropwise in the solution, obtaining a brown suspension. It was stirred for 2 h, then the reaction mixture was poured into water containing 8 g of NH_4Cl (Carlo Erba RPE, purity 99.5%), and the stirring was continued for 2 h. The formed solid was isolated by filtration, on a G4 frit, and dried in vacuo to give 8.98 g of a green powder, which shows a purity of 98.9% by ^{1}H NMR. Yield: 52.1%. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.48 (t, 3H, CH_3, J = 7.26 Hz); 3.73 (s, 2H, CH_2); 4.24 (q, 2H, CH_2, J = 7.26 Hz); 7.04−7.90 (m, 8H, Ar).

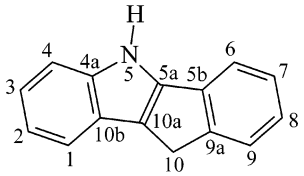
6-[Dimethylsilyl(*tert*-butylamino)]*N*-ethyl-5,6-dihydroindeno[2,1-*b*]indole. A 8.02 mL portion of a 2.5 M *n*-BuLi solution in hexane (20.04 mmol) was added dropwise at 0 °C in a solution of 4.30 g of *N*-ethyl-5,6-dihydrondeno[2,1-*b*]indole (98.9%, 18.22 mmol) in Et_2O, obtaining a dark brown solution. After 2 h stirring at room temperature, the lithium salt was siphoned at 0 °C into a solution of 4.87 mL (4.32 g) of (*tert*-butylamino)dimethylchlorosilane (83.7 wt %, d = 0.887, 21.86 mmol) in Et_2O. After 3 h stirring at room temperature, the solvent was dried in vacuo and the crude residue (8.73 g) was extracted with 50 mL of toluene, obtaining 7.48 g of a sticky brown solid, which was washed with pentane, obtaining 4.32 g of a light brown powder. The ^{1}H NMR spectrum shows a purity in the target product of 96.6 wt % and 3.4 wt % of starting *N*-ethyl-5,6-dihydroindeno[2,1-*b*]indole. Yield: 63.2%. ^{1}H NMR (C_6D_6, δ, ppm): −0.23 (s, 3H, Si-CH_3); −0.01 (s, 3H, Si-CH_3); 0.41 (bs, 1H, *N*-H); 0.99 (s + t, 12H, *t*-Bu + CH_3); 3.56 (s, 1H, C-H); 4.07 (m, 2H, CH_2); 7.15−8.07 (m, 8H, Ar). ^{1}H NMR ($CDCl_3$, δ, ppm): −0.13 (s, 3H, Si-CH_3); 0.03 (s, 3H, Si-CH_3); 0.75 (bs, 1H, *N*-H); 1.26 (s, 9H, *t*-Bu); 1.37 (t, 3H, CH_3, J = 7.14 Hz); 3.84 (s, 1H, C-H); 4.50 (m, 2H, CH_2); 6.90−8.00 (m, 8H, Ar). *m*/*z* (%): 363 (12) [M^+ + 1]; 362 (31) [M^+]; 232 (12); 131 (13); 130 (100).

Dimethylsilyl(*tert*-butylamido)(*N*-ethyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)dimethyl Titanium. A 16.13 mL portion of MeLi 1.6 M (25.80 mmol) in diethyl ether was added dropwise at 0 °C to a solution of 2.30 g of 6-[dimethylsilyl-(*tert*-butylamino)]*N*-ethyl-5,6-dihydroindeno[2,1-*b*]indole (6.34 mmol) in 40 mL of Et_2O, obtaining a dark brown suspension. After 3 h stirring at room temperature 0.7 mL (1.21 g) of $TiCl_4$ (6.34 mmol) in 40 mL of pentane was slowly added to the lithium salt. The dark brown suspension was stirred for 1 h at room temperature, then the solvents were removed under reduced pressure to obtain a crude residue of 4.63 g, which was extracted with 50 mL of toluene. The extract (2.27 g of a sticky dark brown powder containing the desired complex) was further washed with pentane and the residue dried, giving a brown powder as product (1.70 g). Purity by ^{1}H NMR analysis resulted to be 97.6 wt %. Starting ligand (2.4 wt %) was also present. Yield: 79.7%. ^{1}H NMR (C_6D_6, δ, ppm): −0.002 (q, 3H, Ti-CH_3(19), J = 0.41 Hz); 0.09 (q, 3H, Ti-CH_3(20), J = 0.41 Hz); 0.61 (s, 3H, Si-CH_3(13)); 0.73 (s, 3H, Si-CH_3(14)); 1.05 (t, 3H, CH_3, J = 7.26 Hz); 1.41 (s, 9H, *t*-Bu); 3.78 (q, 2H, CH_2, J = 7.26 Hz); 6.98−7.06 (m, 2H, H4, H8); 7.24−7.33 (m, 3H, H2, H3, and H9); 7.80 (dt, 1H, J = 8.67, 1.04 Hz, H7); 7.88−7.93 (m, 2H, H1, H10). ^{13}C NMR (C_6D_6, δ, ppm): 6.62 (Si-CH_3(13)); 7.63 (Si-CH_3(14)); 14.48 (CH_3); 34.51 (*t*-Bu); 40.00 (CH_2); 56.90 (Ti-CH_3(19)); 57.01 (Ti-CH_3(20)); 57.81 (*C*-*t*-Bu); 67.98 (*C*6); 109.81 (*C*-H4); 114.56 (*C*-10b); 120.48 (*C*-H1); 120.59 (*C*-H2); 123.67 (*C*-10c); 124.08 (*C*-H10); 124.30 (*C*-10a); 124.32 (*C*-H8); 124.49 (*C*-H3); 125.27 (*C*-H9); 128.62 (*C*-H7); 134.89 (*C*6a); 145.50 (*C*4a); 147.34 (*C*5a). $^1J_{CH}$ (TiCH_3, Hz) [av]: 120.6. Orange crystals were grown from concentrated toluene solutions cooled at −20 °C. Anal. Calcd for $C_{25}SiN_2TiH_{34}$: C, 68.47; H, 7.81. Found: C, 67.25; H, 7.35. This synthesis was repeated starting with a larger amount of reagents, using 6.84 g (18.86 mmol) of ligand, 47.75 mL (76.40 mmol) of MeLi 1.6 M in Et_2O, and 2.07 mL (18.86 mmol) of $TiCl_4$. A total of 6.80 g of the target product was obtained as a brown powder. Purity by ^{1}H NMR was 92.7 wt %. Yield: 76.2%. A sample of **2** dissolved in C_6D_6 was slowly heated in a water bath from 25 °C to 60 °C. The solution was kept at this temperature for 3 h. ^{1}H NMR analyses showed that the complex is stable after prolonged heating at 60 °C under nitrogen atmosphere.



Dimethylsilyl(*tert*-butylamido)(*N*-methyl-5,10*H*-indeno[1,2-*b*]indol-10-yl) dimethyl titanium (3). 2,3-Dihydro-1*H*-inden-1-one Phenylhydrazone. A mixture of phenylhydrazine (3.76 mL, 0.038 mol), 1-indanone (5.0 g, 0.038 mol), 2-propanol (50 mL), and *p*-toluenesulfonic acid (0.3 g) was refluxed for 40 min and then was cooled to 0 °C. The precipitate was filtered and washed with cold 2-propanol. Thus 7.38 g of the product was obtained as colorless crystals (88%). ^{1}H NMR (C_6D_6, 20 °C, δ, ppm): 7.99 (d, 1H); 7.15 (m, 8H, Ar); 6.55 (s, 1H, *N*-H); 2.52 (s, 2H, CH_2); 1.79 (s, 2H, CH_2).

5,10-Dihydroindeno[1,2-*b*]indole. A mixture of 2,3-dihydro-1*H*-inden-1-one phenylidrazone (8.40 g, 0.038 mol), 2-propanol (60 mL), and sulfuric acid (4 mL) was refluxed for 10 h, cooled, and poured into 200 mL of a 2% KOH water solution. The precipitate was filtered and recrystallized from benzene to give 5.20 g of the product as colorless crystals (67%). ^{1}H NMR ($CDCl_3$, 20 °C, δ, ppm): 8.28 (s, 1H, *N*-H); 7.67−7.12 (m, 8H, Ar); 3.72 (s, 2H, CH_2).

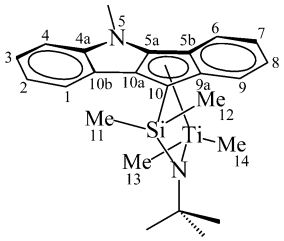


5-Methyl-5,10-dihydroindeno[1,2-*b*]indole. A mixture of 21.9 g (107 mmol) of 5,10-dihydroindeno[1,2-*b*]indole, prepared as reported above, and 9.4 mL (150 mmol) of methyl iodide was added to a well-stirred mixture of 150 mL of water, 150 mL of benzene, 150 g of NaOH, and l.0 g of *n*-$C_{16}H_{33}NMe_3Br$ (2.7 mmol). The resulting mixture was stirred at 40 °C for 2 h, under vigorous stirring. Then the reaction mixture was cooled to room temperature, the organic phase was separated and washed with water, and the solvent was evaporated. The residue was recrystallized from hexane, thus obtaining 17.3 g of the product as colorless crystals (yield = 74%). ^{1}H NMR ($CDCl_3$, 20 °C, δ, ppm): 7.62 (t, 2H, Ar); 7.52 (d, 1H, Ar); 7.34 (m, 2H, Ar); 7.17 (m, 3H, Ar); 4.01 (s, 3H, *N*-CH_3); 3.68 (s, 2H, CH_2).

10-[Dimethylsilyl(*tert*-butylamino)]*N*-methyl-5,10-dihydroindeno[1,2-*b*]indole. A 9.38 mL sample of a 1.6 M *n*-BuLi solution in hexane (0.015 mol) was added dropwise at −20 °C under stirring to a suspension of 2.19 g of 5-methyl-5,10-dihydroindeno[1,2-*b*]indole (0.010 mol) in 45 mL of Et_2O. At the end of the addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 h. Then it was quickly treated at −70 °C with 2.40 mL of Me_2SiCl_2 (0.020 mol) in 10 mL of Et_2O. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then 40 mL of Et_2O was added, the precipitate of LiCl was filtered, and the solvent was removed under vacuum. The red oil obtained was redissolved in 50 mL of Et_2O and treated at −70 °C with

9 mL (0.085 mol) of *tert*-butylamine in 10 mL of Et_2O. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The solution was separated from the *tert*-butylamine hydrochloride and evaporated. A dark red oil was obtained as product (3.19 g, 91% yield based on 5-methyl-5,10-dihydroindeno[1,2-*b*]indole). ^{1}H NMR (C_6D_6, δ, ppm): 0.06 (s, 3H, Si-CH_3); 0.24 (s, 3H, Si-CH_3); 1.18 (s, 9H, *t*-Bu); 3.42 (s, 3H, *N*-CH_3); 3.80 (s, 1H, CH); 7.20−7.40 (m, 5H, Ar); 7.59 (d, 1H, Ar); 7.81 (d, 1H, Ar); 8.02 (m, 1H, Ar). Anal. Calcd for $C_{22}H_{28}N_2Si$: C, 75.81; H, 8.10; N, 8.04. Found: C, 75.75; H, 8.10; N, 8.01.

Dimethylsilyl(*tert*-butylamido)(*N*-methyl-5,10*H*-indeno-[1,2-*b*]indol-10-yl)dimethyl Titanium (3). A solution of



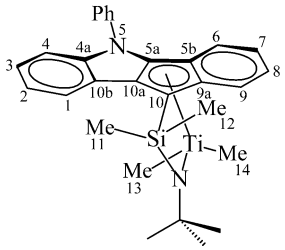
MeLi 1.34 M in ether (34.3 mL, 46.0 mmol) was added at −40 °C under stirring to a solution of 3.19 g (9.2 mmol) of 10-[dimethylsilyl(*tert*-butylamino)]*N*-methyl-5,10-dihydroindeno-[1,2-*b*]indole in 42 mL of ether. The reaction mixture was allowed to warm to room temperature and stirred for 1.5 h and then under reflux for 4 h. Then it was cooled to −60 °C, and a solution of 1.00 mL (9.2 mmol) of $TiCl_4$ in 42 mL of hexane was added. At the end of the addition the reaction mixture was allowed to warm to room temperature and stirred overnight. Then the solvents were evaporated, and the residue was extracted with hexane (3 × 50 mL). The hexane solution was concentrated to a final volume of 10 mL and kept within 10 h at room temperature. The crystalline product was separated from the mother solution, washed twice with cold pentane, and dried. Yield: 1.01 g (26%) of dark red crystals. ^{1}H NMR (CD_2Cl_2, δ, ppm): −0.62 (bq, 3H, Ti-CH_3(13)); −0.42 (bq, 3H, Ti-CH_3(14)); 0.87 (bs, 3H, Si-CH_3(12)); 0.93 (bs, 3H, Si-CH_3(11)); 1.43 (s, 9H, *t*-Bu); 4.16 (s, 3H, *N*-CH_3); 7.12−7.22 (m, 2H, H2 and H8); 7.36−7.49 (m, 3H, H3, H4, and H7); 7.73 (dt, 1H, J = 8.61, 0.98 Hz, H9); 7.90 (dt, 1H, J = 7.83, 0.78 Hz, H1); 8.05 (dt, 1H, J = 8.61, 0.98 Hz, H6). ^{1}H NMR (C_7D_8, δ, ppm): −0.31 (s, 3H); −0.07 (s, 3H); 0.74 (s, 3H); 0.85 (s, 3H); 1.38 (s, 9H); 3.36 (s, 3H); 6.93−7.01 (m, 2H); 7.07−7.16 (m, 2H); 7.23 (t, 1H); 7.59 (dt, 1H); 7.71 (dt, 1H); 7.98 (d, 1H). ^{13}C NMR (CD_2Cl_2, δ, ppm): 6.22 (Si-*C*H_3(12)); 6.49 (Si-*C*H_3(11)); 34.45 (*t*-Bu); 52.64 (Ti-*C*H_3(13)); 54.25 (Ti-*C*H_3(14)); 54.88 (*C*-*t*-Bu); 58.31 (*C*10); 109.77 (*C*-H4); 118.36 (*C*-5b); 119.53 (*C*-H2); 122.13 (*C*-H6); 122.67 (*C*-10a and *C*-H1); 124.46 (*C*-H7); 125.00 (*C*-10b); 125.16 and 125.20 (*C*-H3 and *C*-H8); 129.02 (*C*-H9); 136.71 (*C*-9a); 138.89 (*C*-5a); 147.25 (*C*-4a). $^1J_{CH}$ (Ti*CH*$_3$, Hz) [av]: 120.0. Anal. Calcd for $C_{24}H_{32}N_2SiTi$: C, 67.91; H, 7.60; N, 6.60. Found: C, 67.75; H, 7.81; N, 6.51.

Dimethylsilyl(*tert*-butylamido)(*N*-phenyl-5,10*H*-indeno-[1,2-*b*]indol-10-yl)dimethyl Titanium (4). 2,3-Dihydro-1*H*-inden-1-one Diphenylhydrazone. A mixture of 1,1-diphenylhydrazine (9.2 g, 0.05 mol), 1-indanone (6.6 g, 0.05 mol), 2-propanol (50 mL), and *p*-toluenesulfonic acid (0.1 g) was refluxed for 1 h and then was cooled to 0 °C. The precipitate was filtered and washed with cold 2-propanol. Thus 10.8 g of the product was obtained as yellow crystals (73%). ^{1}H NMR ($CDCl_3$, 20 °C, δ, ppm): 8.00 (d, 1H); 7.25 (m, 13H, Ar); 2.95 (t, 2H, α-CH_2); 2.36 (s, 2H, β-CH_2).

5-Phenyl-5,10-dihydroindeno[1,2-*b*]indole. A mixture of 10.8 g (0.036 mol) of 2,3-dihydro-1*H*-inden-1-one diphenylhydrazone, prepared as reported above, 40 mL of 2-propanol, and 2 mL of sulfuric acid was refluxed for 1 h, under vigorous stirring. Then the reaction mixture was cooled to room temperature, poured into 100 mL of water, and extracted with $CHCl_3$ (3 × 30 mL). The resulting organic phase was washed with water, dried over Na_2SO_4, and then dried. The residue was recrystallized from ethanol, thus obtaining 6.7 g of the product as colorless crystals (yield = 66%). ^{1}H NMR ($CDCl_3$, 20 °C, δ, ppm): 3.87 (s, 2H, CH_2); 7.14−7.76 (13H, Ar). Anal. Calcd for $C_{21}H_{15}N$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.55; H, 5.42; N, 5.03.

10-[Dimethylsilyl(*tert*-butylamino)]-*N*-phenyl-5,10-dihydroindeno[1,2-*b*]indole. A 4.00 mL portion of a 1.6 M *n*-BuLi solution in hexane (6.4 mmol) was added dropwise at −25 °C under stirring to a solution of 1.69 g of 5-phenyl-5,10-dihydroindeno[1,2-*b*]indole (6.0 mmol) in 40 mL of Et_2O. At the end of the addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 h. Then it was quickly treated at −70 °C with 0.78 mL of Me_2SiCl_2 (6.5 mmol) in 5 mL of Et_2O. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then 2.7 mL (25.7 mmol) of *tert*-butylamine in 7 mL of Et_2O was added at −70 °C under stirring. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The solution was separated from the *tert*-butylamine hydrochloride and evaporated. The residue was treated with 60 mL of hexane, and the solution was isolated and dried to give a dark red oil as crude product (2.27 g, 92% yield based on 5-phenyl-5,10-dihydroindeno[1,2-*b*]indole). ^{1}H NMR (C_6D_6, δ, ppm): 0.01 (s, 3H, Si-CH_3); 0.29 (s, 3H, Si-CH_3); 1.18 (s, 9H, *t*-Bu); 3.92 (s, 1H, CH); 7.15−7.52 (m, 11H, Ar); 7.80 (d, 1H, Ar); 8.07 (d, 1H, Ar). Anal. Calcd for $C_{27}H_{30}N_2Si$: C, 78.97; H, 7.36; N, 6.82. Found: C, 78.79; H, 7.29; N, 6.81.

Dimethylsilyl(*tert*-butylamido)(*N*-phenyl-5,10*H*-indeno-[1,2-*b*]indol-10-yl)dimethyl Titanium (4). A solution of



MeLi 1.34 M in ether (20.0 mL, 26.8 mmol) was added at −40 °C under stirring to a solution of 2.27 g (5.5 mmol) of 10-[dimethylsilyl(*tert*-butylamino)]*N*-phenyl-5,10-dihydroindeno-[1,2-*b*]indole in 25 mL of ether. The reaction mixture was allowed to warm to room temperature and stirred for 1.5 h and then under reflux for 4 h. Then it was cooled to −60 °C, and a solution of 0.60 mL (5.5 mmol) of $TiCl_4$ in 25 mL of hexane was added. At the end of the addition the reaction mixture was allowed to warm to room temperature and stirred overnight. Then the solvents were evaporated, and the residue was extracted with hexane (3 × 50 mL). The hexane solution was concentrated to a final volume of 7 mL and kept within 10 h at room temperature. The crystalline product was separated from the mother solution, washed twice with cold pentane, and dried. Yield: 0.83 g (31%) of dark yellow crystals. The complex is not stable at room temperature under nitrogen atmosphere in CD_2Cl_2 solution. ^{1}H NMR (C_7D_8, δ, ppm): 0.02 (s, 3H); 0.03 (s, 3H); 0.78 (s, 3H); 0.89 (s, 3H); 1.42 (s, 9H); 6.89 (m, 1H); 6.98 (m, 1H); 7.04−7.19 (m, 6H); 7.30 (m, 1H); 7.44 (m, 2H); 7.74 (dt, 1H); 8.06 (m, 1H). ^{1}H NMR (CD_2Cl_2, δ, ppm): −0.41 (bq, 3H, Ti-CH_3); −0.37 (bq, 3H, Ti-CH_3); 0.90 (bs, 3H, Si-CH_3); 0.97 (bs, 3H, Si-CH_3); 1.46 (s, 9H, *t*-Bu); 7.07−7.76 (m, 12H, Ar); 7.95 (dm, 1H, J = 8.22 Hz, Ar). Anal. Calcd for $C_{29}H_{34}N_2SiTi$: C, 71.59; H, 7.04; N, 5.76. Found: C, 71.41; H, 7.01; N, 5.71.

Dimethylsilyl(*tert*-butylamido)(*N*-methyl-2-methyl-1,8-dihydroindeno[2,1-*b*]pyrrol-8-yl)dimethyl Titanium (5).

***N*-Methyl-2-methyl-1,8-dihydroindeno[2,1-*b*]pyrrole.** This compound was prepared according to the protocol described in ref 11.

2-Me-3-carbomethoxydihydroindeno[2,1-*b*]pyrrole (5a). A 9.2 g (50 mmol) sample of aminoindanone hydrochloride (prepared as reported by Gabriel et al. in *Chem. Ber.* **1986**, *29*, 2604−2606) and 23 mL (200 mmol) of methylacetoacetic ester were added to 100 mL of acetic acid. Then 13.6 g (100 mmol) of NaOAc trihydrate was added by small portions in 2 h. The resulting mixture was heated at 80 °C under stirring for 3 h. Then it was cooled to room temperature; the precipitate was filtered, washed twice with 100 mL of water and ethanol ether, and finally dried, thus obtaining 6.6 g of carbomethoxyindenopyrrole (yield = 58%). ^{1}H NMR ($CDCl_3$): 8.40 (bs, 1H); 7.97 (d, 1H); 7.37(d, 1H); 7.30 (t, 1H); 7.10 (td, 1H); 3.95 (s, 3H); 3.53 (s, 2H); 2.62 (s, 3H).

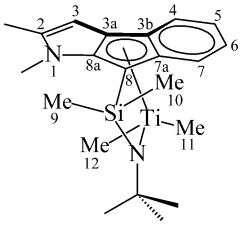
***N*-Methyl-2-Me-3-carbomethoxydihydroindeno[2,1-*b*]-pyrrol (5b).** A 6.5 g (29 mmol) sample of **5a**, prepared as reported above, 3.6 mL (60 mmol) of methyl iodide, 30 mL of water, 30 mL of benzene, 10 g of NaOH, and l00 mg of n-$C_{16}H_{33}NMe_3Br$ were placed into a bulb, and the mixture was heated at 40 °C, under vigorous stirring, for 3 h. Then the reaction mixture was cooled to room temperature, the organic phase was separated, the solvent was evaporated, and the residue was recrystallized from a hexane/benzene mixture, thus obtaining 4.5 g of *N*-methylcarbomethoxyindenopyrrole (yield = 64%). ^{1}H NMR ($CDCl_3$): 7.97 (d, 1H); 7.37 (d, 1H); 7.23 (t, 1H); 7.08 (td, 1H); 3.95 (s, 3H); 3.53 (s, 3H); 3.47 (s, 2H); 2.52 (s, 3H).

***N*-Methyl-2-Me-dihydroindeno[2,1-*b*]pyrrol-3-carbonic Acid (5c).** A 5.54 g (20 mmol) sample of **5b**, prepared as reported above, 25 mL of methanol, and 25 mL of KOH 37% were placed into a bulb, and the resulting mixture was refluxed until the solid dissolves. The resulting solution was cooled to room temperature, washed twice with 50 mL of benzene, and neutralized with hydrochloric acid. The precipitate was filtered, washed with water, and dried, thus obtaining 3.6 g of *N*-methylindenopyrrolecarbonic acid (yield = 85%). ^{1}H NMR (DMSO-d_6): 7.92 (d, 1H); 7.38 (d, 1H); 7.22 (t, 1H); 7.03 (t, 1H); 3.56 (s, 2H); 3.52 (s, 3H); 2.53 (s, 3H). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.92; H, 5.69; N, 6.24.

***N*-Methyl-2-methyl-l,8-dihydroindeno[2,l-*b*]pyrrole (5d).** A 3.6 g (17 mmol) sample of the obtained compound **5c** and 40 mL of diglyme were placed into a bulb. The resulting suspension was heated at 160 °C and kept at this temperature for 2 h. The reaction mixture was then cooled to room temperature; the crystalline precipitate was filtered, washed with ethanol, and finally dried, thus obtaining 2.27 g of *N*-methyl-2-methyl-l,8-dihydroindeno[2,l-*b*]pyrrole (yield = 79%). ^{1}H NMR ($CDCl_3$): 7.34 (m, 2H); 7.20 (t, 1H); 6.98 (t, 1H); 6.07 (s, 1H); 3.52 (s, 3H); 3.48 (s, 2H); 2.28 (s, 3H). Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.19; H, 7.23; N, 7.58.

8-[Dimethylsilyl(*tert*-butylamino)]*N*-methyl-2-methyl-1,8-dihydroindeno[2,1-*b*]pyrrole. A suspension of 3.00 g (0.0164 mol) of *N*-methyl-2-methyl-1,8-dihydroindeno[2,1-*b*]-pyrrole (**5d**) in 60 mL of ether was treated at −20 °C dropwise with 17.0 mL (0.0279 mol) of *n*-BuLi 1.6 M in hexane under stirring. The mixture was stirred for an additional 5 h at room temperature. The resulting reaction mixture was quickly treated at −70 °C with 5.00 mL (0.0419 mol) of dimethyldichlorosilane in 10 mL of ether, then it was allowed to warm to room temperature and was stirred overnight. The solution was separated from LiCl and evaporated. The solid residue (4.1 g) was dried in a vacuum. Then it was dissolved in 70 mL of Et_2O, treated at −70 °C with 17 mL (0.162 mol) of *tert*-butylamine in 10 mL of ether, and finally allowed to warm to room temperature and stirred overnight. The solution was separated from the *tert*-butylamine hydrochloride and evaporated. The residue was treated with 100 mL of hexane, and the solution was isolated and evaporated. Yield: 3.98 g (78%) of crude product as a brown oil. ^{1}H NMR (C_7D_8, δ, ppm): 7.48 (d, 1H); 7.44 (d, 1H); 7.23 (t, 1H); 7.05 (t, 1H); 6.18 (s, 1H); 3.12 (s, 3H); 2.15 (s, 3H); 1.02 (s, 9H); −0.11 (s, 3H); −0.12 (s, 3H). Anal. Calcd for $C_{19}H_{28}N_2Si$: C, 73.02; H, 9.03; N, 8.96. Found: C, 72.89; H, 9.01; N, 8.98.

Dimethylsilyl(*tert*-butylamido)(*N*-methyl-2-methyl-1,8-dihydroindeno[2,1-*b*]pyrrol-8-yl)dimethyl Titanium (5). A solution of MeLi 1.2 M in ether (50 mL, 57.4 mmol) was



added at −40 °C under stirring to a solution of 3.98 g (12.8 mmol) of 8-[dimethylsilyl(*tert*-butylamino)]*N*-methyl-2-methyl-1,8-dihydroindeno[2,1-*b*]pyrrole (**2b**) in 55 mL of ether. The reaction mixture was stirred at room temperature for 2 h and then under reflux for 4 h. The resulting mixture was cooled to −60 °C, and a solution of 1.39 mL (12.8 mmol) of $TiCl_4$ in 55 mL of hexane was added. At the end of the addition the reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting mixture was evaporated and the residue extracted with hexane (3 × 50 mL). The hexane solution was concentrated to a volume of 10 mL and kept within 10 h at room temperature. The crystalline product was separated from the mother solution, washed twice with cold pentane, and dried. Yield: 1.93 g (39%) of dark red crystals. ^{1}H NMR (CD_2Cl_2, δ, ppm): −0.46 (bq, 3H, Ti-CH_3-(11)); −0.19 (bq, 3H, Ti-CH_3(12)); 0.74 (bq, 3H, Si-CH_3(9)); 0.83 (bq, 3H, Si-CH_3(10)); 1.46 (s, 9H, *t*-Bu); 2.45 (d, 3H, 2-CH_3, J = 0.98 Hz); 3.49 (s, 3H, *N*-CH_3); 6.37 (q, 1H, H3, J = 0.98 Hz); 7.07 (ddd, 1H, J = 8.71, 6.85, 1.27 Hz, H6); 7.34 (ddd, 1H, J = 8.71, 6.85, 0.98 Hz, H5); 7.66 (dt, 1H, J = 8.71, 0.98 Hz, H7); 7.73 (ddd, 1H, J = 8.71, 1.27, 0.98 Hz, H4). ^{13}C NMR (CD_2Cl_2, δ, ppm): 6.86 (Si-CH_3(10)); 7.36 (Si-CH_3(9)); 13.79 (2-CH_3); 33.66 (*N*-CH_3); 34.57 (*t*-Bu); 52.14 (Ti-CH_3(12)); 53.93 (Ti-CH_3-(11)); 57.94 (*C*-*t*-Bu); 69.66 (*C*8); 98.62 (*C*-H3); 123.33 and 123.43 (*C*-3a and *C*-3b); 123.91, 123.95, and 123.99 (*C*-H6, *C*-H5, and *C*-H4); 128.00 (*C*-H7); 134.77 (*C*-7a); 140.40 (*C*-8a); 143.15 (*C*-2). $^1J_{CH}$ (TiCH_3, Hz) [av]: 120.0. Anal. Calcd for $C_{21}H_{32}N_2SiTi$: C, 64.93; H, 8.30. Found: C, 64.10; H, 8.1.

Dimethylsilyl(*tert*-butylamido)(2-methyl-8*H*-indeno-[2,1-*b*]thiophen-8-yl) Dimethyl Titanium (6). 2-Methyl-4-phenylthiophene (6a). A solution of PhMgBr (prepared from 1.65 g of Mg (67.8 mmol) and 10.64 g of PhBr (67.8 mmol) in 40 mL of ether) was added at reflux under stirring to a mixture of 10.0 g (56.5 mmol) of 4-bromo-2-methylthiophene and 0.62 g (1.2 mmol) of $NiCl_2$(dppp) in 50 mL of ether. The reaction mixture was refluxed for an additional 3 h and then stirred overnight. The resulting mixture was treated with a 10% aqueous NH_4Cl solution, and the organic layer was separated, washed with 10% aqueous NH_4Cl, and then dried by anhydrous Na_2SO_4. The solvent was evaporated and the residue was recrystallized from methanol. Yield: 6.8 g (70%) of colorless crystals. ^{1}H NMR ($CDCl_3$, 30 °C, δ, ppm): 7.65 (d, 2H); 7.47 (d, 2H); 7.37 (t, 1H); 7.28 (m, 1H); 6.65 (s, 1H).

2-Methyl-8*H*-indeno[2,1-*b*]thiophen-8-one (6b). A solution of 12.88 g (74 mmol) of 2-methyl-4-phenylthiophene and 23.4 mL (0.16 mol) of TMEDA in 200 mL of ether was treated at −40 °C under stirring with 100 mL (0.16 mol) of *n*-BuLi 1.6 M in hexane. The reaction mixture was allowed to warm to room temperature and stirred for 3 h (a white precipitate was formed). The reaction mixture was then cooled to −40 °C and treated with 8.76 g (75 mmol) of ethyl *N*,*N*-dimethylcarbamate in 25 mL of ether. At the end of the addition it was

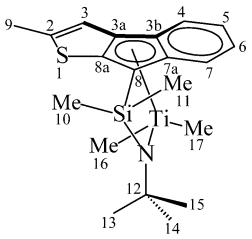
allowed to warm to room temperature and stirred overnight. The resulting reaction mixture was treated with a 10% aqueous NH_4Cl solution, and the organic layer was separated, washed with 10% aqueous NH_4Cl, and then dried by anhydrous Na_2SO_4. The solvent was removed, and the residue was washed with methanol. Yield: 6.8 g (46%) of red crystals. ^{1}H NMR ($CDCl_3$, 30 °C, δ, ppm): 7.44 (d, 1H); 7.29 (t, 1H); 7.14 (t, 1H); 7.07 (d, 1H); 6.79 (m, 1H); 2.55 (s, 3H).

2-Methyl-8*H*-indeno[2,1-*b*]thiophene (6c). A mixture of 6.83 g (0.034 mol) of 2-methyl-8*H*-indeno[2,1-*b*]thiophen-8-one and 9.1 mL (0.182 mol) of hydrazine monohydrate in 91 mL of diethylene glycol was stirred at 80 °C for 40 min and then was refluxed for 1 h. The reaction mixture was then cooled to room temperature, treated with a solution of 9.5 g (0.169 mol) of KOH in 34 mL of water, and finally refluxed for 2 h. The resulting mixture was poured into 600 mL of water, and the precipitate was filtered, washed five times with 200 mL of water, and dried. Yield: 5.8 g (92%). ^{1}H NMR ($CDCl_3$, 30 °C, δ, ppm): 7.53 (d, 1H); 7.51 (d, 1H); 7.37 (t, 1H); 7.23 (t, 1H); 7.01 (m, 1H); 3.81 (s, 2H); 2.61 (s, 3H). Anal. Calcd for $C_{12}H_{10}S$: C, 77.38; H, 5.41. Found: C, 77.36; H, 5.40.

Chloro(dimethyl)(2-methyl-8*H*-indeno[2,1-*b*]thiophen-8-yl)silane. A suspension of 1.86 g (0.01 mol) of 2-methyl-8*H*-indeno[2,1-*b*]thiophene in 25 mL of ether was treated dropwise at −40 °C under stirring with 6.25 mL (0.01 mol) of *n*-BuLi 1.6 M in hexane. The reaction mixture was stirred for an additional 3 h. Then it was treated at −70 °C with 1.20 mL (0.01 mol) of dimethyldichlorosilane in 5 mL of ether. At the end of the addition the mixture was allowed to warm to room temperature and stirred overnight. The solution was isolated and concentrated to give 2.47 g (89%) of the crude product, which was used in the next step without further purification. ^{1}H NMR (C_6D_6, 30 °C, δ, ppm): 7.57 (m, 2H); 7.33 (t, 1H); 7.18 (t, 1H); 6.85 (m, 1H); 3.78 (s, 1H), 2.32 (s, 3H); 0.10 (s, 3H); 0.08 (s, 3H). Anal. Calcd for $C_{14}H_{15}ClSSi$: C, 60.30; H, 5.42. Found: C, 60.37; H, 5.40.

8-[Dimethylsilyl(*tert*-butylamino)](2-methyl-8*H*-indeno-[2,1-*b*]thiophene. A solution of 0.93 mL (8.9 mmol) of *tert*-butylamine in 30 mL of ether was treated dropwise at −30 °C with 5.55 mL (8.9 mmol) of *n*-BuLi 1.6 M in hexane. The reaction mixture was stirred at room temperature for 3 h, and the resulting suspension was treated at −70 °C with a solution of 2.47 g (8.8 mmol) of chloro(dimethyl)(2-methyl-8*H*-indeno-[2,1-*b*]thiophen-8-yl)silane in 10 mL of ether. The resulting mixture was allowed to warm to room temperature and stirred overnight. The solution was separated from LiCl and evaporated. The residue was treated with 60 mL of hexane, and the solution was isolated and evaporated. Yield: 1.98 g (71%) of crude product as a red oil. ^{1}H NMR (C_6D_6, 30 °C, δ, ppm): 7.67 (d, 1H); 7.62 (d, 1H); 7.39 (t, 1H); 7.27 (t, 1H); 6.96 (m, 1H); 3.81 (s, 1H); 2.40 (s, 3H); 1.18 (s, 9H); 0.19 (s, 3H); −0.14 (s, 3H). Anal. Calcd for $C_{18}H_{25}NSSi$: C, 68.51; H, 7.99; N, 4.44. Found: C, 68.48; H, 7.90; N, 4.39.

Dimethylsilyl(*tert*-butylamido)(2-methyl-8*H*-indeno-[2,1-*b*]thiophen-8-yl)dimethyl Titanium (6). A solution of



MeLi 1.2 M in ether (26 mL, 31.2 mmol) was added at −40 °C under stirring to a solution of 2.43 g (6.2 mmol) of 8-[dimethylsilyl(*tert*-butylamino)](2-methyl-8*H*-indeno[2,1-*b*]thiophene in 30 mL of ether. The reaction mixture was stirred under reflux for 3 h. Then it was cooled to −60 °C, and a solution of 0.68 mL (6.2 mmol) of $TiCl_4$ in 30 mL of hexane was added. At the end of the addition the reaction mixture was allowed to warm to room temperature and stirred overnight. Then the solvents were evaporated and the residue was extracted with hexane (3 × 50 mL). The hexane solution was concentrated to a final volume of 10 mL and kept within 10 h at room temperature. The crystalline product was separated from the mother solution, washed twice with cold pentane, and dried. Yield: 0.48 g (20%) of dark red crystals. ^{1}H NMR (CD_2Cl_2, δ, ppm): −0.41 (bs, 3H, Ti-CH_3(17)); 0.01 (bs, 3H, Ti-CH_3(16)); 0.67 (bs, 3H, Si-CH_3(10)); 0.79 (bs, 3H, Si-CH_3(11)); 1.49 (s, 9H, *t*-Bu); 2.66 (s, 3H, 2-CH_3); 7.19 (s, 1H, H3); 7.14 (t, 1H, J = 7.43 Hz, H6); 7.36 (t, 1H, J = 7.43 Hz, H5); 7.56 (d, 1H, J = 8.41 Hz, H7); 7.86 (d, 1H, J = 8.41 Hz, H4). ^{13}C NMR (CD_2Cl_2, δ, ppm): 4.11 (Si-*C*H_3(10)); 4.57 (Si-*C*H_3(11)); 16.88 (2-*C*H_3); 34.40 (*t*-Bu); 55.59 (Ti-*C*H_3(17)); 56.51 (Ti-*C*H_3(16)); 58.60 (*C*-*t*-Bu); 79.50 (*C*8); 116.59 (*C*-H3); 123.73 (*C*-H4); 124.97 (*C*-H5); 125.13 (*C*-H6); 126.39 (*C*-3b); 128.28 (*C*-H7); 135.82 (*C*-3a); 136.03 (*C*-7a); 141.59 (*C*-8a); 147.28 (*C*-2). $^1J_{CH}$ (Ti*CH*$_3$, Hz) [av]: 120.8. Anal. Calcd for $C_{20}H_{29}NSSiTi$: C, 61.36; H, 7.47. Found: C, 60.05; H, 7.3.

X-ray Diffraction Structural Analysis. (a) Collection and Reduction of X-ray Diffraction Data. Suitable crystals of **2** and **6** were mounted in air on a glass fiber tip onto a goniometer head. Single-crystal X-ray diffraction data were collected on a Siemens SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature (295(2) K). Unit cell parameters were initially obtained from the reflections taken from 45 frames collected in three different ω regions and eventually refined against about 1000 reflections. A full sphere of reciprocal space was scanned by 0.3° ω steps, collecting 1800 frames each at 30 s exposure. Intensity decay was monitored by recollecting the initial 50 frames at the end of data collection and analyzing the duplicate reflections. The collected frames were processed for integration; an empirical absorption correction was made on the basis of the symmetry-equivalent reflection intensities (SADABS).[39] Crystal data and data collection parameters are summarized in Table 6.

(b) Structure Solution and Refinement. The structures were solved by direct methods[40] and subsequent Fourier synthesis; they were refined by full-matrix least-squares on F^2 using reflections with $I > 2\sigma(I)$.[41] Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the internal library of SHELX97. Weights were assigned to individual observations according to the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; a and b were chosen to give a flat analysis of variance in terms of F_o^2. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were placed in idealized position and refined riding on their parent atom with an isotropic displacement parameter 1.2 times that of the pertinent carbon atom. For compound **2** the hydrogen atoms of the C(20) methyl group have been modeled as disordered over two positions (with occupation factors of 0.64 and 0.36) rotated from each other by 60°. Final difference electron density map showed no features of chemical significance, with the largest peaks lying close to the metal atoms. Final conventional agreement indexes and other structure refinement parameters are listed in Table 6.

Polymerizations. Propylene Polymerization in Liquid Monomer. A 2 mmol portion of Al(*i*-Bu)$_3$ (as 1 M hexane solution) and 600 g of propylene were charged, at room temperature, in a 2 L jacketed stainless steel autoclave, equipped

(39) Sheldrick, G. M. *SADABS*; Universität Göttingen: Germany, 1996.

(40) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(41) Sheldrick, G. M. *SHELX97*; Universität Göttingen: Germany, 1997.

Table 8. Pentad Fractions for a Syndiospecific Bernoullian Model in the Presence of Site Isomerization[a]

pentad	E_0	E_1	E_2	E_3	E_4
mmmm	p3	4p3	3p4 + 3p3	2p4 + 2p3	p5
mmmr	2p3	2(2p4 + 2p3)	2(p4 + 5p3)	2(p5 + p4 + 2p3)	2p4
rmmr	p4	4p3	p5 + 2p4 + 3p3	2(p4 + p3)	p3
mmrr	2p4	2(p4 + 3p3)	2(p5 + p4 + 4p3)	2(p4 + 3p3)	2p4
xmrx[c]	4p3	2(p5 + 3p4 + 4p3)	2(4p4 + 8p3)	2(p5 + 3p4 + 4p3)	4p3
rmrm	2p3	2(p4 + 3p3)	2(p5 + 3p4 + 2p3)	2(p4 + 3p3)	2p3
rrrr	p5	2(p4 + p3)	3p4 + 3p3	4p3	p3
rrrm	2p4	2(p5 + p4 + 2p3)	2(p4 + 5p3)	2(2p4 + 2p3)	2p3
mrrm	p3	2(p4 + p3)	p5 + 2p4 + 3p3	4p3	p4

[a] $p5 = a^5 + (1 - a)^5$, $p4 = a^4(1 - a) + a(1 - a)^4$, and $p3 = a^3(1 - a)^2 + a^2(1 - a)^3$. [b] Total energy for all pentads is $E_0(1 - p_{bs})^4 + E_1(1 - p_{bs})^3 p_{bs} + E_2(1 - p_{bs})^2 p_{bs}^2 + E_3(1 - p_{bs}) p_{bs}^3 + E_4 p_{bs}^4$. p_{bs} is the probability of site isomerization (see text). [c] $xmrx = mmrm + rmrr$.

with a magnetically driven stirrer and a 35 mL stainless steel vial, connected to a thermostat for temperature control, previously purified by washing with an Al(*i*-Bu)$_3$ solution in hexane and dried at 50 °C in a stream of propylene. The autoclave was then thermostated at 2 °C below the polymerization temperature, and the catalyst system, prepared by dissolving the Ti complex in the required amount of MAO/toluene solution and aging 10 min at room temperature, was injected in the autoclave by means of nitrogen pressure through the stainless steel vial. The temperature was rapidly raised to the polymerization temperature, and the polymerization was carried out at constant temperature. After quenching with CO, venting the unreacted monomer, and cooling the reactor to room temperature, the polymer was dried under reduced pressure, at 60 °C.

Propylene Polymerization in Solution. Toluene (95 mL) and Al(*i*-Bu)$_3$ (0.5 mmol as toluene solution) were introduced into a 260 mL Büchi glass autoclave equipped with magnetic stirrer, thermocouple, and feeding line for the monomer, previously purged with propylene, and warmed to the polymerization temperature in a thermostatic bath. The catalytic system was separately prepared in 5 mL of toluene by mixing the desired amounts of metallocene and cocatalyst. After about 30 s of stirring at room temperature, the solution was introduced into the autoclave under monomer flow. The reactor was closed and pressurized; the pressure was kept constant by feeding in propylene. The polymerization was stopped by degassing the reactor and by adding 2 mL of methanol. The polymer was precipitated with 200 mL of acidified methanol, filtered, washed with methanol, and dried overnight at 60 °C under reduced pressure.

Polymer Analysis. Viscosity Measurements. The intrinsic viscosity (IV) was measured in tetrahydronaphthalene (THN) at 135 °C. The weight average molecular weights of *am*-PP were obtained from their intrinsic viscosity values and the Mark−Houwink−Sakurada parameters derived by Pearson and Fetters: $[\eta] = 1.85 \times 10^{-4} \times (\bar{M}_w)^{0.737}$.[42] The average degree of polymerization, $\bar{P}_n$, is estimated from $\bar{M}_w$ by assuming $\bar{M}_w/\bar{M}_n = 2$.

^{13}C NMR Analysis. Carbon spectra of polymers were recorded on a Bruker DPX-400 spectrometer operating at 100.61 MHz in the Fourier transform mode, at 120 °C. The samples were prepared by dissolution of 40 mg of polymer in 0.5 mL of 1,1,2,2-tetrachloroethane-d_2 at 120 °C. The peak of the *mmmm* pentad (21.8 ppm) was used as internal reference. Each carbon spectrum was acquired with a 90° pulse, 12 s of delay between pulses, and CPD (waltz 16) to remove ^{1}H−^{13}C coupling. About 3000 transients were stored in 32 K data points using a spectral window of 60 ppm.

Statistical modeling of pentad distributions of these *sam*-PP was satisfactorily done using a model based on enantiomorphic site control. In this case, the probability of insertion of a monomer with a given enantioface at site 1 is equal to the probability of insertion of a monomer with the opposite enantioface at site 2. This probability is indicated with the parameter *a*. The resulting expressions for pentad distribution for the syndiotactic Bernoullian model are reported in ref 3.

The pentad fraction distribution is symmetric with respect to $a = 0.5$, as we obtain the same values using $a = p$ or $a = 1 - p$ ($0 \le p \le 1$). It would be easy to show that this model satisfies the ratio [*rmmr*]:[*mmrr*]:[*rrrm*] = 1:2:2 as experimentally observed for syndiotactic polymers obtained with "site-controlled" catalysts. The presence of isolated *m* dyads in ^{13}C NMR spectra (*rrmr* pentad) of these polymers is attributable to an isomerization of the site due to a "skipped" monomer insertion during chain growth. This fact can be included in the model considering the probability of site isomerization, p_{bs}, in the expressions for pentad distribution shown in Table 8.

The best fit between the experimental and calculated areas is searched through a least-squares method, minimizing the function $f = \sum_i (A_i^{exp} - A_i^{calc})^2$, where the sum is extended over all the pentads, A_i^{exp} are the experimental areas, and A_i^{calc} are the calculated ones.

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Supporting Information Available: 2D NMR spectra of the complexes **1**, **5**, **2**, **3**, **4**, and **6** and the pertinent crystallographic information for **2** and **6** (CIF), and a list of computed coordinates and energy for **1**, **3**, and **5**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) Pearson, D.; Fetters, L.; Younghouse, L.; Mays, J. *Macromolecules* **1988**, *21*, 478.