Syndiospecific Propylene Polymerization Using C_1-Symmetric *ansa*-Metallocene Catalysts: Substituent and Bridge Effects

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ABSTRACT: A series of syndiospecific C_1-symmetric *ansa*-metallocenes ([Me_2X(Cp)(2-R_1-3-R_2-Ind)]$ZrCl_2$, X = C, Si; R_1 = H, Me; R_2 = Me, Et, CH_2SiMe_3) have been synthesized, and their catalytic behavior in the polymerization of propylene has been studied. Upon activation with MAO, these carbon- or silicon-bridged cyclopentadienyl/indenyl systems afford polypropylene with various degrees of syndiotacticity ([*rrrr*] = 28−66%), as a function of the substituent size, substitution pattern, and bridging moiety. The silicon-bridged systems produced PP samples of higher molecular weight, lower syndiotacticities, and comparable productivities with respect to their carbon-bridged analogues. Statistical modeling of the experimental pentad distributions suggests that site epimerization is the major cause of stereoerrors within both sets, while a decreased site stereospecificity can be implied for the silicon-bridged systems.

Introduction

Developments over the past 2 decades in the application of well-defined organometallic and coordination compounds for the catalytic polymerization of olefins have led to new insights into the mechanism of olefin polymerization[1,2] and have provided access to a variety of new polymer microstructures, including highly syndiotactic polypropylene,[3−5] alternating ethylene/propylene copolymers,[6−9] hyperbranched polyethylene,[10,11] and syndiotactic polystyrene.[12,13]

The advent of metallocene catalysts for the synthesis of syndiotactic polypropylene was a pioneering development that provided new insights into the mechanism of olefin enchainment as well as on the correlation of microstructure to the conformational and physical properties of polypropylene. Analysis of the stereospecificity of these catalysts[3−5] has provided compelling experimental support for Cossee's mechanism of enchainment first proposed in 1960.[14,15] In addition, the advent of these metallocene catalysts for the first time provided sufficient quantities of highly regular sPP to investigate the physical properties of this material.[16−20] New insights into the structure/property relationships of both isotactic and syndiotactic polypropylene[21,22] have stimulated the search for new synthetic methods to prepare polypropylenes of intermediate tacticity[2] to investigate the role of both regio- and stereoerrors on the properties of these materials.[18,22−24]

We have recently reported a class of C_1-symmetric *ansa*-metallocenes (**3**−**5**) that catalyze the polymerization of propylene to give syndiotactic polypropylenes of intermediate tacticity (Figure 1).[25] These systems generate polypropylenes of lower tacticity than those of the well-established C_s-symmetric catalysts derived from bridged cyclopentadienyl/fluorenyl metallocenes (e.g., **1a,b**)[26] as well as the doubly bridged substituted bis(cyclopentadienyl) systems developed by Bercaw (**2a,b**).[27] In this contribution, we report a systematic investigation of the factors responsible for the syndiospecificity of C_1-symmetric, bridged cyclopentadienyl/indenyl metallocenes in an effort to provide novel low-tacticity sPPs as well as to investigate the mechanistic events involved in enantiomorphic site-controlled syndiospecific polymerization.

Results

The syntheses of complexes **14**,[28,29] **15**,[30] and **16**[31] have been previously reported; we employed a modified synthetic strategy for the series of ligand precursors **6**−**13** and metallocenes **14**−**21**. Substituted indenes were deprotonated and reacted with 6,6-dimethylfulvene to yield the ligand precursors to carbon-bridged systems (**14**−**17**). Treatment of the lithiated indenes with Me_2SiCl_2 followed by NaCp afforded the precursors to dimethylsilyl-bridged metallocenes (**18**−**21**). These one-pot syntheses procedures yielded compounds **6**−**13** in moderate to good yields. Compounds **6**−**9** were isolated as mixtures of 1,3- and 1,4-cyclopentadienyl isomers; a larger number of isomers are obtained in the case of the dimethylsilane derivatives **11**−**13** due to silatropic shift on the Cp ring. Scheme 1 outlines the synthetic route to compounds **6**−**13** (only major isomers are shown).

Suspension of the dilithio salt of ligand precursors (**6**−**13**) and $ZrCl_4$ in dry toluene afforded the C_1-symmetric carbon-bridged (**14**−**17**) and silicon-bridged (**18**−**21**) *ansa*-zirconocene dichlorides in low to moderate yields, comparable in most cases with those previously reported for metallocenes (**3**−**5**) which were synthesized using diethyl ether as the reaction solvent.[25] Complexes **14**−**21** are microcrystalline yellow/orange solids, obtained in analytical purity after a series of recrystallization steps (Scheme 2).

Table 1 summarizes the polymerization data for complexes **14**−**21**. (Selected polymerization results with the previously reported complexes **3**−**5** have been included for comparison.) Upon activation with MAO ([Al]/[Zr] = 1000:1), metallocenes **15**−**21** polymerize propylene to yield polypropylenes with various degrees of syndiotacticity. Under our experimental conditions (20 °C, liquid propylene), [Me_2C(Cp)(2-Me-Ind)]$ZrCl_2$ (**14**) produces low molecular weight colorless oils. In contrast, complex **15** (bearing the methyl substituent in position 3) affords a tacky solid for which the pentad distribution reveals a moderate but clear syndiotacticity ([*rrrr*] = 42%). This value falls at the lower end of the syndiotacticities found among the monosubstituted complexes **15**, **3**, and **4**; for this series of metallocenes, the syndiospecificity appears to increase from [*rrrr*] =

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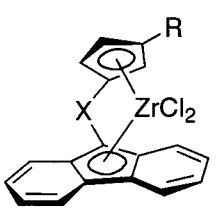
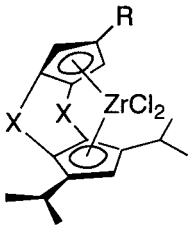
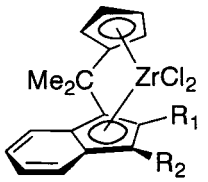






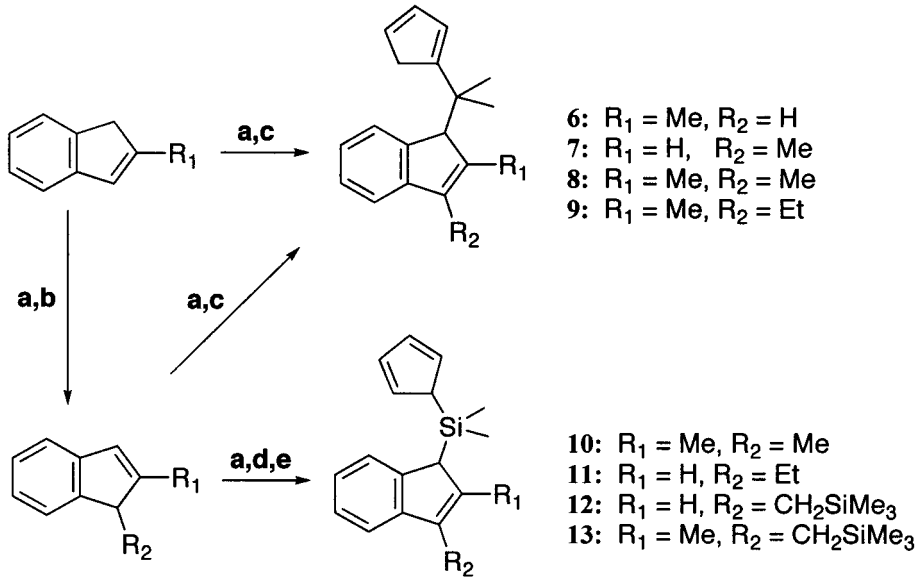
1a: X = Me_2C, R = H
1b: X = Me_2Si, R = H
1c: X = Me_2C, R = Me
1d: X = Me_2C, R = ^{t}Bu

X = Me_2Si
2a: R = H
2b: R = ^{i}Pr
2c: R = (1R,2S,5R)-menthyl

3: R_1 = H, R_2 = Et
4: R_1 = H, R_2 = CH_2SiMe_3
5: R_1 = Me, R_2 = CH_2SiMe_3

Figure 1. Structure of complexes **1**−**5** employed in the syndiospecific (**1a,b**, **2a,b**, **3**−**5**) and hemiisospecific (**1c,d**, **2c**) polymerization of propylene.

Scheme 1



6: R_1 = Me, R_2 = H
7: R_1 = H, R_2 = Me
8: R_1 = Me, R_2 = Me
9: R_1 = Me, R_2 = Et

10: R_1 = Me, R_2 = Me
11: R_1 = H, R_2 = Et
12: R_1 = H, R_2 = CH_2SiMe_3
13: R_1 = Me, R_2 = CH_2SiMe_3

a ^{n}BuLi
b R_2X
c 6,6-dimethylfulvene
d Me_2SiCl_2
e NaCp

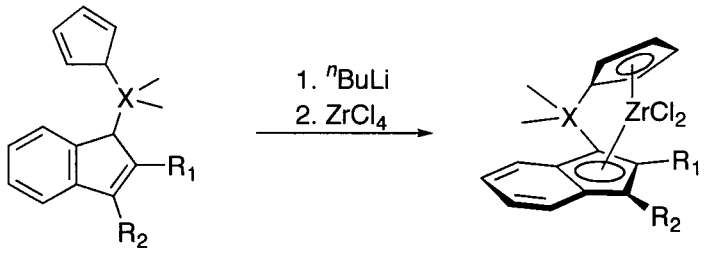
42% to 66% with increasing size of the 3-substituent (Table 1, entries 2 vs 9 vs 10).

The productivities of catalyst systems derived from **14**−**21** were of the same order of magnitude (1100−6700 kg of PP/mol h), but those of the monosubstituted C-bridged systems (**3**−**4** **14**−**15**) fall at the lower end of the range. The same trend was also found for the molecular weights: polymers produced with complexes **14**, **15**, and **3** produce PP with number-average molecular weights under 10 kg/mol. In the case of complex **4** slightly higher molecular weights and productivities were observed.

Comparison of the 3-methyl-substituted complex **15** with the 2,3-dimethyl-substituted metallocene **16** revealed a significant increase in the concentration of the syndiotactic pentads (from 42 to 66%) upon introduction of the 2-methyl substituent. A similar increase was observed in complexes **4** and **5** ([*rrrr*] = 66 and 74%, respectively) and is further supported by the higher [*rrrr*] shown by **17** (66%) when compared with [Me_2C-(Cp)(3-Et-Ind)]$ZrCl_2$ (**3**), which produces PPs with [*rrrr*] = 49%. Nevertheless, the generation of syndiotactic polypropylene with this class of metallocenes appears to require a substituent larger than hydrogen in the 3-position as metallocene **14**, lacking a substituent at this position, yields polypropylenes with no syndiotactic bias (Table 1, entry 1).

The nature of the bridging group influences the polymerization behavior: relative to the carbon-bridged analogues, the silicon-bridged metallocenes yield polymers of higher molecular weights (33 400−105 000 vs 6500−30 900 g/mol) but lower syndiotacticity. Nevertheless, within the silicon series, the influence of ligand substitution pattern is similar to that observed with the carbon-bridged series. The tacticity increases with increasing size of the 3-substituent (e.g., [*rrrr*] = 28% for **19**, [*rrrr*] = 36% for **20**) and also increases for the 2,3-disubstituted metallocenes relative to the 3-substituted metallocenes ([*rrrr*] = 43 and 41% for **18** and **21**, respectively). Furthermore, the increase observed in

Scheme 2



6: X = C, R_1 = Me, R_2 = H
7: X = C, R_1 = H, R_2 = Me
8: X = C, R_1 = Me, R_2 = Me
9: X = C, R_1 = Me, R_2 = Et
10: X = Si, R_1 = Me, R_2 = Me
11: X = Si, R_1 = H, R_2 = Et
12: X = Si, R_1 = H, R_2 = CH_2SiMe_3
13: X = Si, R_1 = Me, R_2 = CH_2SiMe_3

14: X = C, R_1 = Me, R_2 = H
15: X = C, R_1 = H, R_2 = Me
16: X = C, R_1 = Me, R_2 = Me
17: X = C, R_1 = Me, R_2 = Et
18: X = Si, R_1 = Me, R_2 = Me
19: X = Si, R_1 = H, R_2 = Et
20: X = Si, R_1 = H, R_2 = CH_2SiMe_3
21: X = Si, R_1 = Me, R_2 = CH_2SiMe_3

Table 1. Representative Polymerization Data for Systems 14−21/MAO[a]

complex	X	R_1	R_2	A (kg PP/mol h)	[*r*][b] (%)	[*rrrr*][b] (%)	M_w[c] (g/mol)	M_w/M_n[c]
14	C	Me	H	1100	50	11	4 400[e]	
15	C	H	Me	1750	80	42	6 500	2.1
16	C	Me	Me	3700	87	66	16 700	2.4
17	C	Me	Et	3500	87	64	15 900	2.2
18	Si	Me	Me	5600	77	43	65 400	2.1
19	Si	H	Et	3200	70	28	33 400	2.2
20	Si	H	CH_2SiMe_3	6700	75	36	49 400	2.0
21	Si	Me	CH_2SiMe_3	3500	74	41	105 000	2.2
3[f]	C	H	Et	1200	82	49	4 200[e]	
4[f]	C	H	CH_2SiMe_3	4300	89	66	12 000	1.3
5[f]	C	Me	CH_2SiMe_3	9900	91	74	30 900	2.1

[a] MAO as cocatalyst, [Al]:[M] = 1000:1; [M] = 2.5×10^{-5}; t = 20 min; T_p = 20 °C; liquid propylene. [b] By ^{13}C NMR. [c] By GPC. [d] By DSC. [e] M_n, determined by end group analysis from ^1H NMR data. [f] Ref 25, appended for comparison.

molecular weights parallels the increase in size and degree of substitution among complexes **18**−**21**. In contrast, the productivities were not so strongly influenced by the nature of the bridging group (Table 1).

Discussion

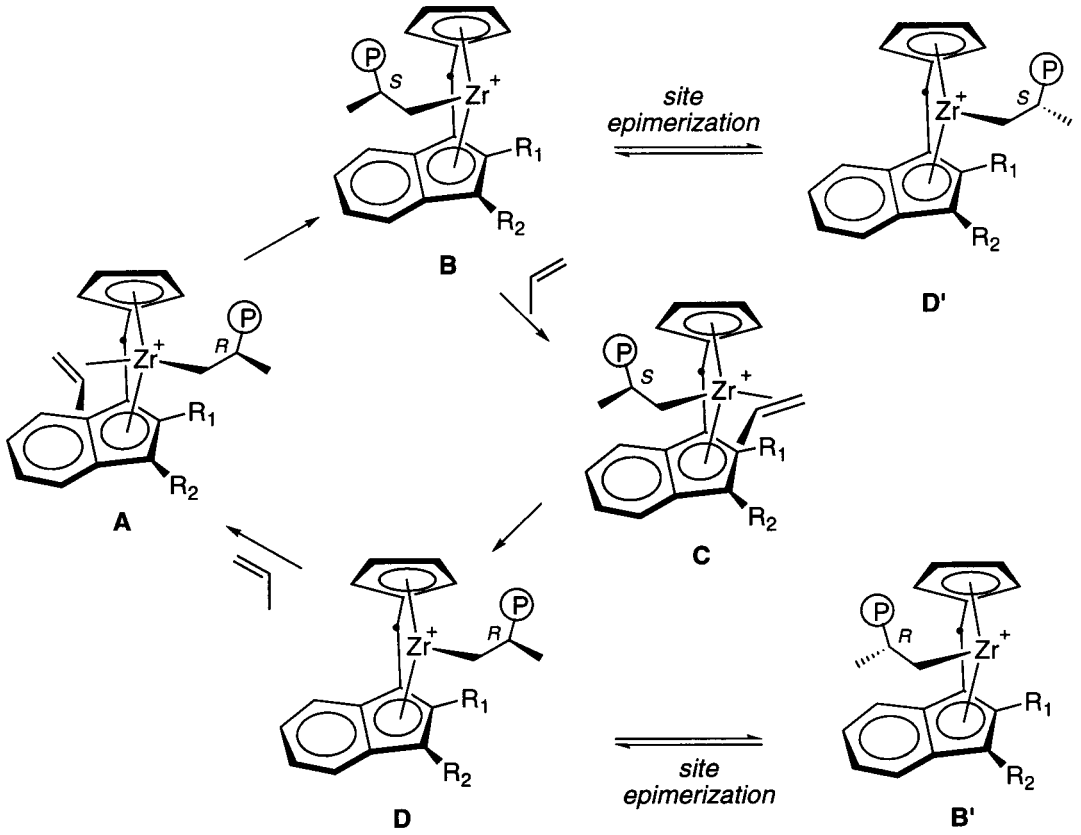
Until very recently, the synthesis of syndiotactic polypropylene (sPP) employing homogeneous catalytic systems was restricted to a group of C_s-symmetric catalyst structures.[2] Among these, the bridged cyclopentadienyl/fluorenyl systems developed by Ewen and Razavi (e.g., **1a**),[3,32,33] have been fundamental for the understanding of the processes involved in syndiospecific polymerization. A number of variants of this parent structure have proven useful for the synthesis of sPP (e.g., **1b**).[34−41] The doubly bridged bis(cyclopentadienyl) systems developed by Bercaw (e.g., **2a**)[27] have been shown to polymerize propylene in a syndiospecific manner. The existence of two enantiotopic coordination sites which select for the opposite enantiofaces of propylene coupled with the alternate insertion of propylene at the two sites ensures syndiospecific insertion in C_s-symmetric systems.[2,3,27,42−44] Several studies [27,37,40,45,46] have demonstrated that a decrease in symmetry on the parent C_s systems has a detrimental effect on their syndiospecificity.[5] Introduction of a methyl group in position 3 of the Cp ring of complex **1a** to give metallocene **1c** leads to the formation of hemi-isotactic polypropylene, whereas introduction of a *tert*-butyl substituent to give **1d** yields isotactic polypropylene (Figure 1).[2]

C_1-symmetric metallocenes containing bridged indenyl and cyclopentadienyl ligands are, as a class, not very active for propylene polymerization.[2,30,47−50] Nevertheless, some of these metallocenes yield polypropylenes of intermediate to low *isotacticity* with interesting elastomeric properties. The range of isotacticities observed for polypropylenes obtained from these metallocenes has been interpreted in terms of the insertion of propylene into a stereoselective and nonstereoselective site in competition with the migration of the polymer chain from one site to the other.[51]

Prior to our investigations on systems **3**−**5**,[25] there were conflicting reports in the literature on the stereoselectivity of (3-R-indenyl)(Cp) zirconocenes. Chien had reported that the methyl-substituted metallocene **15** yielded hemi-isotactic polypropylene (hitPP), whereas a patent report by Miya indicated that the dimethyl-substituted complex **16** affords syndiotactic PP ([*rr*] = 68% at 30 °C, toluene solution).[31] Furthermore, Resconi had reported that the carbocyclic-substituted complexes **22** and **23** also yield syndiotactic PP with a [*rrrr*] content of 71 and 67%, respectively.[2] On the basis of these reports, we were prompted to revisit the polymerization of propylene with **15** and **16** as part of a systematic investigation on the role that substituents in the 2- and 3-position have on the stereospecificity of this class of metallocenes.

Under the conditions studied by Chien and co-workers (40 °C, toluene solution, [Zr] = 50 μM, $P_{propylene}$ = 15 psig) complex **15** was reported to yield hitPP, suggesting a very poor contribution of the methyl substitution to

Scheme 3



the stereospecificity of the complex (compared to the parent unsubstituted Cp/Ind).[38,47,48] Under our experimental conditions (liquid monomer, 20 °C) metallocene **15** produces polypropylene with a [*rrrr*] of 42%, revealing a mostly syndiospecific monomer enchainment. Although slightly lower than the analogous catalysts derived from complexes **3** and **4**, this observation suggests that *a substituent as small as a methyl group placed in position 3 of the indenyl ring is enough for a stereoselective propagation mechanism* in the case of **15**. This observation and the results of Miya and Resconi suggest that while unsubstituted bridged Cp-indenyl-metallocenes generate polypropylenes of low to intermediate isotacticity, those of the class represented by metallocenes **3**−**5** and **14**−**21** generate polypropylenes of intermediate *syndiotacticity* when the substituent in the 3-position of the indene is larger than hydrogen (Table 1).

The stereoselectivities of metallocenes **3**−**5** and **14**−**21** are most readily accommodated in the framework of a mechanism for stereocontrol where the introduction of a substituent at 3-position of the indene renders both sites of the metallocene stereoselective, but selective for opposite enantiofaces of propylene (Scheme 3). According to this mechanism, the source of stereoerrors leading to intermediate tacticity can be ascribed to several possible sources, namely, (1) low to intermediate enantioface selectivity at either or both of the two insertion sites, (2) isomerization of the polymer chain from one coordination site to the other in competition with olefin insertion (also referred to as *site epimerization* or *backskip*), or (3) epimerization of stereocenters in the polymer chain by β-hydrogen elimination/reinsertion (*chain epimerization*).

One of the consistent trends that we have observed for this class of metallocene catalysts is that for a variety of substituents R_2 at the 3-position introduction of a methyl group at the 2-position (R_1 = Me) increases both the molecular weight and the syndiotacticity of the resulting polypropylenes (compare **4** vs **5**,[25] **15** vs **16**, and **20** vs **21**, Table 1). The increase in the molecular weight upon introduction of a 2-methyl substituent has been observed for isospecific C_2-symmetric bis(indenyl)-metallocenes.[2,52,53] Several reports have also indicated that the stereoselectivity of bis(indenyl)metallocenes can be increased by the introduction of a 2-alkyl substituent,[2,42,52,54] but the magnitude of the increase for these syndiospecific metallocenes can be quite large (**15** [*rrrr*] = 42%; **16** [*rrrr*] = 66%). We have previously proposed, on the basis of the concentration dependence of the stereochemistry for metallocenes **4** and **5**, that the role of the 2-substituent is to decrease the tendency of these catalysts to undergo site epimerization (**B** to **D** isomerization, Scheme 3) prior to monomer insertion.[25,55]

The role of the 2-methyl substituent appears to enhance the stereoselectivity of the 3-indenyl-substituted metallocenes but has little influence on stereodifferentiation by itself. For example, the 2-methyl-substituted metallocene **14**, lacking a substituent in the 3-indenyl position, yields a low molecular weight, largely atactic polypropylene with a syndiotactic pentad content [*rrrr*] = 11%; this microstructure is in fact similar to that reported for the unsubstituted analogue [Me_2C(Cp)-(Ind)]$ZrCl_2$ (R_1, R_2 = H).[56]

We had previously observed that the size of the 3-indenyl substituent appeared to have an influence on the stereoselectivity of this class of metallocenes: metallocene **3** afforded a polypropylene with [*rrrr*] = 49%, whereas metallocene **4** yielded a more syndiotactic polypropylene with [*rrrr*] = 66%.[25] Analysis of the stereoselectivities of the entire series **3**−**5** and **14**−**21** reveals that this is not a consistent trend. The micro-

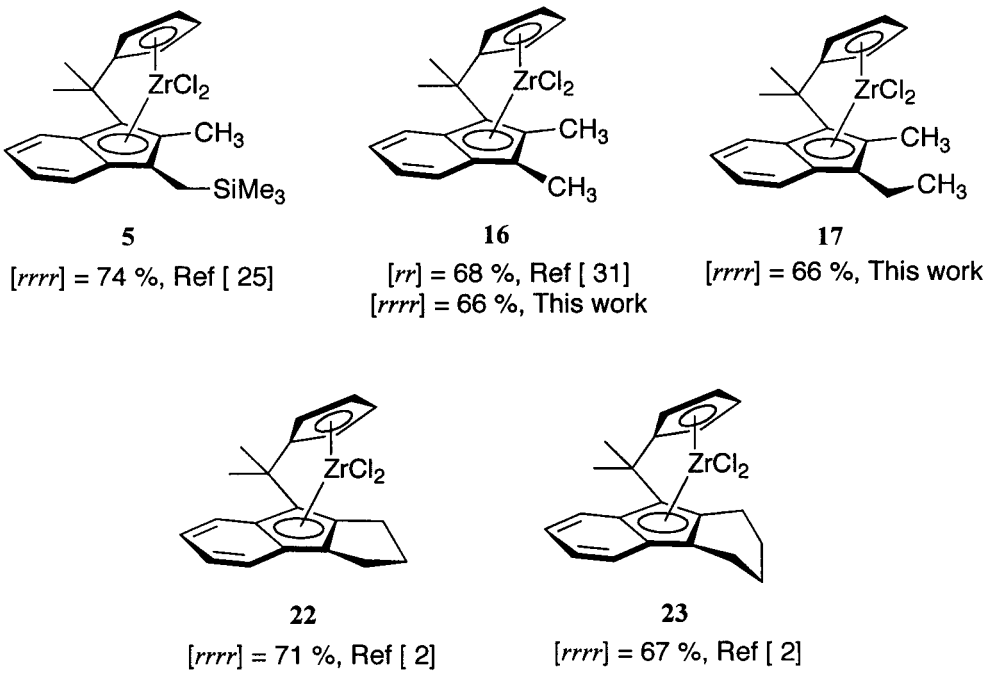


Figure 2. Structures of syndiospecific 2,3-disubstituted Ind/Cp complexes.

Table 2. Experimental Pentad Distributions for C-Bridged Systems 14−17

	line intensities								
complex	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*mmrm* + *rmrr*	*rmrm*	*rrrr*	*rrrm*	*mrrm*
14	11.1	13.8	5.4	21.7	11.1	4.1	11.1	11.9	9.7
15	0.1	1.3	2.2	5.8	17.6	4.0	41.8	21.3	6.0
16		0.8	2.2	4.7	8.8	1.6	65.5	14.2	2.2
17		0.7	2.3	4.8	9.0	0.9	63.5	16.0	3.0

Table 3. Experimental Pentad Distributions for Si-Bridged Systems 18−21

	line intensities								
complex	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*mmrm* + *rmrr*	*rmrm*	*rrrr*	*rrrm*	*mrrm*
18	1.2	3.7	3.6	10.5	13.7	3.4	43.3	17.3	3.3
19	2.7	5.8	3.9	11.8	17.9	4.9	28.4	18.6	6.0
20	1.0	3.5	3.5	9.3	17.8	4.9	35.6	19.3	5.0
21	3.0	4.0	4.1	9.6	12.3	3.7	41.4	17.1	4.7

structures of the polypropylenes obtained from the methyl-substituted **15** and the ethyl-substituted **3** are comparable (Table 1), as are those from **16**/**17** and **18**/**21.** Furthermore, as shown in Figure 2, the polypropylene tacticities derived from a variety of 2,3-disubstituted indenylmetallocenes (**5 16 17**, **22**, and **23)** are comparable, with the exception that the 3-CH_2SiMe_3-substituted **5** ([*rrrr*] = 74%) yields a slightly higher syndiotacticity than other members of the series.

In addition to the nature of the substituents in the 2- and 3-positions, the nature of the bridging group also influences the polymerization behavior of these metallocenes. The molecular weights obtained from the silicon-bridged metallocenes are consistently higher than those obtained from the carbon-bridged analogues (Table 1). Similar effects have been observed with other *ansa*-metallocenes.[9,57,58] The stereoselectivities of the silicon-bridged metallocenes are also consistently lower than their carbon-bridged congeners (Table 1). The observed [*rrrr*] values for the monosubstituted complexes **19** and **20** are 28 and 36%, respectively, significantly lower than complexes **3** and **4** (49 and 66%). The experimental pentad distributions for polymers synthesized using complexes **18**−**21** (Table 3) show the presence of *mmmm* pentads of measurable intensity, essentially absent from those synthesized using **3**−**5**. Similar trends have been observed for the syndiospecific metallocenes $Me_2C(Cp)(Flu)$ (**1a)** and $Me_2Si(Cp)(Flu)$ (**1b)** at 67 °C ([*rrrr*] = 85 and 51%, respectively),[34,58,59] where the silicon-bridged metallocenes are less stereoselective than their carbon-bridged analogues. The lower stereospecificity of the silicon-bridged metallocenes is likely due to a combination of a lower degree of enantioface discrimination of the two sites[2,59] along with a higher tendency of the silicon-bridged metallocenes to undergo site epimerization.[9]

To provide further insight into the origin of stereoerrors with these metallocenes, we have applied the statistical modeling of the observed pentad distributions using Farina's model[60−62] in order to assess the relative contribution of enantioface selectivity and site epimerization. Farina's model expresses all possible pentads as functions of four probability parameters, namely *a*, *b*, *c*, and *d*, assigned to events occurring during the propagation steps of the polymerization mechanism. Parameter *a* describes the probability of generating a stereogenic center of *a given configuration at a given site*, while *b* represents the probability of generating a stereogenic center of the *same configuration at the complementary propagation site*. Parameters *c* and *d* represent the probability of consecutive insertions at each of the two sites. For the purposes of the statistical

Table 4. Statistical Parameters for Complexes 15−17[a]

complex	*a*	*c*	Af × 10^2	ref
15	0.968	0.165	9.03	this work
16	0.966	0.061	3.36	this work
17	0.963	0.066	5.20	this work
3[b]	0.985	0.149	4.43	25
4[b]	0.984	0.083	2.99	25
5[b]	0.969	0.037	1.23	25
22[b]	0.963	0.039	0.09[c]	2
23[b]	0.955	0.045	0.11[c]	2

[a] For a complete model description, see refs 60−62. [b] Appended for comparison. [c] Although not calculated in ref 2, our modeling of the pentad distributions afforded the same values of *a* and *c* for both complexes and Af values of 0.09 and 0.11, respectively.

Table 5. Statistical Parameters for Complexes 18−21[a]

complex	*a*	*c*	Af × 10^2
18	0.910	0.093	4.50
19	0.866	0.143	8.61
20	0.922	0.154	5.85
21	0.896	0.082	10.21

[a] For a complete model description, see refs 60−62.

analysis, we have assumed that the stereoselectivities and the probability of multiple insertions at the two sites are identical ($a = 1 - b$ and $c = d$). This is clearly an oversimplification, given that the coordination sites of the metallocenes of this series are not enantiotopic; nevertheless, this level of analysis keeps the number of adjustable parameters of the model to a minimum while providing a rough estimate of the relative contribution of enantioface selectivity and site epimerization.

The results of our modeling using the average site specificity (*a*) and the average probability of backskip (*c*) are given in Tables 4 and 5; we have included the analysis of the reported pentad distributions of **3**, **5**, **22**, and **23** for comparison (Table 4). The results of this analysis for the carbon-bridged metallocenes (Table 4) suggest that the average stereoselectivities of the sites are rather high ($a = 0.955-0.985$), implicating that site epimerization or "backskip" is the predominant contributor to the low stereospecificity of these metallocenes, as suggested by the probabilities of multiple insertions at the sites of 0.039−0.149. Moreover, the higher value of $c = 0.149$ calculated for **3** relative to that calculated for **17** ($c = 0.066$) suggests that the higher stereospecificity observed with the 2-methyl-substituted metallocenes **17** might be ascribed predominantly to a lower tendency of **17** to undergo site epimerization, as previously proposed for **4** vs **5**.[25] This is also consistent with the higher value of $c = 0.165$ calculated for **15** relative to that of **16** ($c = 0.061$). The magnitude of the Hamilton's agreement factor (Af) used as a correlation between the experimental and the modeled pentad distribution suggests that, despite the simplifying assumptions, the model provides an adequate representation of the stereospecific behavior of this family of complexes.

In comparison to our findings in the case of the C-bridged systems, the pentad distributions of PP samples synthesized using catalysts derived from the Si-bridged metallocenes **18**−**21** are less accurately described by Farina's model. The variable and higher values calculated for agreement factors (Af) indicate that the lower stereospecificity of these complexes may be due to several competing factors which are not readily accommodated in the simplified model. Nevertheless, the lower calculated average stereoselectivities ($a = 0.866-0.922$) and the slightly higher estimated probabilities of multiple insertions at the two sites ($c = 0.082-0.154$) imply that both factors are likely responsible for the lower stereospecificity of the silicon-bridged metallocenes relative to the carbon-bridged analogues.

Conclusions

Systematic investigations of the stereoselectivity of metallocenes **3**−**5** and **14**−**23** reveal that *ansa*-(3-R-indenyl)(Cp) zirconocenes generate syndiotactic polypropylenes of low to intermediate tacticity. The microstructure of the polypropylenes produced depends on both the substitution pattern of the indenyl ligand and the nature of the bridging group. Carbon-bridged metallocenes yield more highly syndiotactic polypropylenes than the silicon-bridged congeners, and substitution of the indenyl ligand at both the 2- and 3-indenyl positions leads to higher syndiotacticities that monosubstitution at the 3-indenyl position. While the origin of the low stereospecificity cannot be unambiguously established, several lines of evidence point to the epimerization of the catalyst site as one of the major contributors to stereoerrors in these polypropylenes.

Experimental Section

General Considerations. All operations involving air-sensitive reagents and materials were carried out under a nitrogen atmosphere using standard Schlenk, vacuum, or drybox techniques. Solvents were dried and distilled under nitrogen prior to use or purified by passing through towers containing Q5 and alumina. Indene (Aldrich, tech.) was distilled in vacuo prior to use. 1,3-Cyclopentadiene was cracked following a standard procedure, while sodium cyclopentadienylsodium (NaCp) and indenyllithium (LiInd) were synthesized following a procedure published elsewhere. Ethyl bromide was washed with concentrated H_2SO_4, water, $NaHCO_3$, and water (2 times), dried over $CaCl_2$, and vacuum transferred from P_2O_5, while reagent-grade methyl iodide was passed through activated basic alumina and stored over Cu^0. Synthesis and characterization data for 3-trimethylsilylmethylindene, 3-ethylindene, and 2-methyl-3-(trimethylsilylmethyl)-indene have been reported previously.[25] Bromomethyltrimethylsilane (Gelest), *n*-BuLi (1.48 M solution in hexanes), 6,6-dimethylfulvene, 2-methylindene, dichlorodimethylsilane (Aldrich), and $ZrCl_4$ (99.9+%) (Aldrich) were used as received. NMR spectra were recorded using a Varian GX-400 NMR spectrometer and referenced against TMS or the residual protons of the deuterated solvents (^{1}H NMR: $CDCl_3 = 7.26$ ppm, $CD_2Cl_2 = 5.36$ ppm, $C_6D_6 = 7.16$ ppm; ^{13}C NMR: $CDCl_3 = 77.0$ ppm). Elemental analysis was obtained from E+R Microanalytical Laboratory, Inc., Parsippany, NJ.

Synthesis of 2-Methylindenyllithium (24). 2-Methylindene (4.97 g, 38.2 mmol) was dissolved in diethyl ether (20 mL) and cooled to 0 °C. *n*-BuLi (37.8 mmol) was added dropwise causing a bright yellow coloration of the solution, followed by the precipitation of an off-white solid. Addition of an extra 20 mL diethyl ether did not dissolve the formed solids, and the suspension became impossible to stir. After standing overnight, cannula filtration afforded an off-white solid, which was washed several times with pentane until a colorless filtrate was obtained. The solid was dried in vacuo. Yield 4.70 g (94%). The obtained salt was stored in the drybox and used in subsequent steps without further purification.

Synthesis of 2,3-Dimethylindene (25). A solution of *n*-BuLi (48.2 mmol) in hexanes was added dropwise to a cold (0 °C) solution of 2-methylindene (6.54 g, 50.3 mmol) in 80 mL of THF. The resulting dark yellow solution was stirred overnight, transferred to an addition funnel, and added dropwise to a cold (0 °C) solution of methyl iodide (4.0 mL, ca. 64 mmol) in THF (50 mL). The resulting mixture was stirred overnight at room temperature, and deionized water (100 mL)

was added to the crude mixture. The organic layer was washed with water (3 × 25 mL); the aqueous layers were collected and extracted with pentane (3 × 40 mL). The organics were combined and dried with $MgSO_4$, and the solvents were removed in vacuo to yield a dark yellow liquid, which was flushed through silica gel using pentane as eluent. The purity of the product (obtained as a 3:2 mixture of two isomers: 2,3-dimethylindene **25** and 1,2-dimethylindene **26**) was determined appropriate for the subsequent steps by inspection of its GC and ^{1}H NMR data. Yield: 6.80 g (94%). ^{1}H NMR (δ, $CDCl_3$): 7.47 (m, 1+1H, ArC*H* **25** + **26**), 7.25 (m, 2+2H, ArC*H* **25** + **26**), 7.13 (m, 1+1H, ArC*H* **25** + **26**), 6.43 (s, 1H, IndC*H* **25**), 3.30 (s, 2H, IndCH_2 **26**), 3.24 (q, 1H, IndC*H*-CH_3 **25**), 2.10, 2.07 (s+s+s, 3+3+3H Ind-CH_3 **26 26 25**), 1.33 (m, 3H, IndCH-CH_3 **25**). EI-LRMS (*m*/*z*): 144 (M^+, 60%), 129 ($C_{10}H_9^+$, 100%).

Synthesis of 3-Ethyl-2-methylindene (27). A solution of ethyl bromide (2.65 g, 35.5 mmol) in diethyl ether (25 mL) was added dropwise to a suspension of 2-methylindenyllithium (4.05 g, 29.8 mmol) in diethyl ether (40 mL). After the addition of ca. half of the ethyl bromide solution, the 2-methylindenyllithium suspension became a translucent orange solution. Upon completion of the addition, the resulting mixture was stirred for ca. 3 h, and an extra 0.5 mL (ca. 6.7 mmol) of ethyl bromide was added to the orange solution, which was stirred overnight at room temperature. Removal of the solvents in vacuo yielded a yellow oil, which was dissolved in pentane (50 mL) and washed with water (3 × 25 mL). The aqueous rinses were combined and extracted with pentane (3 × 25 mL), while the organics were combined and dried over $MgSO_4$. Removal of the solvent in vacuo yielded 3.96 g (85%) of a bright yellow oil of adequate purity (GC and NMR) for the subsequent steps. ^{1}H NMR (δ, $CDCl_3$): 7.41 (d, 1H, ArC*H*), 7.28 (d+t, 1+1H, ArC*H*), 7.17 (t, 1H, ArC*H*), 6.54 (s, 1H, IndC*H*), 3.47 (AB*M*X_3, 1H, IndC*H*−Et), 2.11 (s, 3H, Ind-CH_3), 2.05 (*AB*MX_3, J_{AB} = 84 Hz, Ind-CH_2-CH_3), 0.66 (t, 3H, CH_2−CH_3). ^{13}C NMR (δ, $CDCl_3$): 148.9, 146.9, 145.3: (IndC_q), 126.9, 126.2, 123.4, 122.5: (Ar*C*H), 119.6 (Ind*C*H), 52.8 (Ind*C*H-Et), 22.3 (Ind-*C*H_3), 15.0 (CH_2-CH_3), 8.4 (CH_2-*C*H_3). EI-LRMS (*m*/*z*): 158 (M^+, 66%), 143 ($C_{11}H_{11}^+$, 100%), 128 ($C_{10}H_8^+$, 80%).

Synthesis of 2-(Cyclopentadienyl)-2-(2-methylindenyl-)propane (6). *n*-Butyllithium (16.2 mmol) in hexanes was added dropwise to a cold (0 °C) solution of 2-methylindene (2.06 mL, 15.4 mmol) in ca. 30 mL of THF. The resulting dark yellow solution was stirred overnight, transferred to an addition funnel, and slowly added to a chilled (−78 °C) solution of 6,6-dimethylfulvene (1.85 mL, 15.4 mmol) in THF (30 mL). The reaction was allowed to warm to room temperature and stirred for an additional 12 h. The resulting mixture was poured over ice cold 1 M NH_4Cl and diluted with pentane (50 mL). The organics were washed with water (3 × 50 mL) while the aqueous layers were extracted with pentane (3 × 30 mL). The organics were combined and dried over $MgSO_4$, and the solvents were removed in vacuo, yielding a yellow liquid. The product was further purified by flash column chromatography (silica gel, 2% diethyl ether in pentane), yielding 1.98 g (55%) of **6**, isolated as a mixture of two (1,3-Cp and 1,4-Cp) isomers in a (3:2 ratio). ^{1}H NMR (δ, $CDCl_3$): 7.18 (m, ArC*H*), 7.11 (d, ArC*H*), 6.94−7.02 (m, ArC*H*), 6.81 (m, 1H, CpC*H* maj), 6.55 (m, 1H, CpC*H* min), 6.48 (m, 1H, CpC*H* min), 6.46 (s, 1H, IndC*H* min), 6.45 (s, 1H, IndC*H* maj), 6.38 (m, 1H, CpC*H* min), 6.18 (s, 1H, CpC*H* min), 5.97 (t, 1H, CpC*H* maj), 3.54 (s, 1H, IndC*H*-CMe_2 maj), 3.51 (s, 1H, IndC*H*-CMe_2 min), 3.07 (d, 2H, CpCH_2 min), 3.02 (t, 2H, CpCH_2 maj), 1.95 (s, 3H, Ind-CH_3 min), 1.92 (s, 3H, Ind-CH_3 maj), 1.24 (s, 3H, CMe_2 maj), 1.21 (s, 3H, CMe_2 min), 1.14 (s, 3H, CMe_2 min), 1.08 (s, 3H, CMe_2 maj). ^{13}C NMR (δ, $CDCl_3$): 148.7, 148.5, 145.5, 145.3 (C_q), 134.0, 133.1, 130.7, 129.6, 129.5, 129.4, 126.5, 126.4, 126.3, 125.6, 125.0, 124.8, 123.9, 123.0, 122.9, 119.4, 119.3 (Ar*C*H, Cp*C*H), 62.0, 60.2 (Ind*C*H-CMe_2), 40.8, 40.5 (CpCH_2), 39.2, 38.1 (*C*Me_2), 27.2, 26.5, 25.6, 23.9 (CMe_2), 18.4, 18.3 (Ind-*C*H_3). EI-LRMS (*m*/*z*): 236 (M^+, 17%), 128 ($C_{10}H_8^+$, 19%), 107 ($C_8H_{11}^+$, 100%).

Synthesis of 2-(Cyclopentadienyl)-2-(3-methylindenyl) propane (7). A solution of indenyllithium (2.00 g, 16.4 mmol) in 60 mL of THF was added dropwise to methyl iodide (1.1 mL, ca. 17 mmol) in THF at 0 °C over a period of 3 h. The resulting mixture was allowed to warm to room temperature overnight. The reaction was quenched by addition of 1 M NH_4-Cl, and the product was extracted with pentane. The organic layer was washed with water (3 × 30 mL) while the aqueous layer was further extracted with pentane (3 × 30 mL). The organics were combined and dried over $MgSO_4$, and the solvents were removed in vacuo to yield a yellow/orange oil, which was immediately flashed through a silica gel column using pentane as eluent. Removal of the solvent yielded a yellow liquid as a mixture of two isomers (GC) in essentially quantitative yield (2.07 g, 15.4 mmol, 97%). The product was redissolved in THF (30 mL) and cooled to 0 °C, prior to the addition of *n*-BuLi (16.2 mmol) in hexanes. The resulting orange solution was stirred overnight, transferred to an addition funnel, and slowly added to a chilled (−78 °C) solution of 6,6-dimethylfulvene (1.85 mL, 15.4 mmol) in THF (30 mL). The reaction was allowed to warm to room temperature and stirred for an additional 12 h. The resulting mixture was poured over ice cold 1 M NH_4Cl and diluted with pentane (50 mL). The organics were washed with water (3 × 50 mL) while the aqueous layers were extracted with pentane (3 × 30 mL). The organics were combined and dried over $MgSO_4$, and the solvents were removed in vacuo, yielding a dark orange oil. Fractional distillation (bp 99 °C at 75 mTorr) afforded 2.32 g (64%) of **7** as a bright yellow liquid (mixture of two isomers, 1,3-Cp and 1,4-Cp in a 3:2 ratio), which solidified overnight at −15 °C. ^{1}H NMR (δ, $CDCl_3$): 7.22−7.26 (m, ArC*H*), 7.00−7.07 (m, ArC*H*), 6.95 (d, 1H, ArC*H*), 6.84 (d, 1H, ArC*H*), 6.80 (m, 1H, CpC*H* maj), 6.54 (m, 1H, CpC*H* maj), 6.49 (m, 1H, CpC*H* min), 6.38 (m, 1H, CpC*H* min), 6.20 (s, 1H, CpC*H* min), 6.12 (m, 1+1H, IndC*H* maj+min), 5.99 (t, 1H, CpC*H* maj), 3.62 (s, 1H, IndC*H*-CMe_2 maj), 3.57 (s, 1H, IndC*H*-CMe_2 min), 3.10 (t, 2H, CpCH_2 min), 3.06 (s, 2H, CpCH_2 maj), 2.12 (m, 3+3H, Ind−CH_3 maj+min), 1.28 (s, 3H, CMe_2 min), 1.23 (s, 3H, CMe_2 maj), 0.97 (s, 3H, CMe_2 maj), 0.95 (s, 3H, CMe_2 min). ^{13}C NMR (δ, $CDCl_3$): 146.5, 145.8, 139.5, 139.4 (C_q), 133.9, 132.9, 132.0, 130.7, 126.3, 126.2, 125.7, 124.3, 124.2, 124.1, 124.0, 118.6, 118.5 (Ar*C*H, Cp*C*H), 59.3, 57.4 (Ind*C*H−CMe_2), 40.9, 40.5 (Cp*C*H_2), 39.1, 38.0 (*C*Me_2), 28.7, 27.0, 23.4, 22.8 (C*Me*$_2$), 13.0 (Ind−*C*H_3 maj+min). EI-LRMS (*m*/*z*): 236 (M^+, 17%), 128 ($C_{10}H_8^+$, 19%), 107 ($C_8H_{11}^+$, 100%).

Synthesis of 2-(Cyclopentadienyl)-2-(2,3-dimethylindenyl)propane (8). A 3:2 mixture of 2,3- and 1,2-dimethylindene (2.40 g, 16.6 mmol) was dissolved in THF (30 mL) and cooled to 0 °C. *n*-Butyllithium (16.6 mmol) was added dropwise to the cold solution, and an orange color developed immediately. After 10 h of stirring at room temperature, the orange solution was transferred to an addition funnel and slowly added to a chilled (−78 °C) solution of 6,6-dimethylfulvene in THF (50 mL). The resulting yellow solution was allowed to warm to room temperature in the cold bath and stirred at room temperature for 24 h. The mixture was poured over ice cold 1 M NH_4Cl solution (100 mL). The aqueous layer was extracted with pentane (3 × 20 mL), and the combined organic extracts were washed with water (3 × 25 mL) and dried over $MgSO_4$. Evaporation of the solvents and drying in vacuo yielded an orange liquid. Fractional distillation afforded 2.16 g (52%) of **8** (bp 108−110 °C at 60−65 mTorr) as a mixture of six isomers. Spectral data for the two major components: ^{1}H NMR (δ, $CDCl_3$): 7.0−7.4 (ArC*H*), 6.94 (1H, CpC*H* maj), 6.67 (1H, CpC*H* maj), 6.61 (1H, CpC*H* min), 6.49 (1H, CpC*H* min), 6.27 (1H, CpC*H* maj), 3.61 (s, 1H, IndC*H*-CMe_2 maj), 3.57 (s, 1H, IndC*H*−CMe_2 min), 3.20 (t, 2H, CpCH_2 min), 3.12 (s, 2H, CpCH_2 maj), 2.11 (m, 3+3H, Ind-3-CH_3 maj+min), 1.98 (s, 3H, Ind-2-CH_3 min), 1.94 (s, 3H, Ind-2-CH_3 maj), 1.32 (s, 3H, CMe_2 maj), 1.27 (s, 3H, CMe_2 min), 1.24 (s, 3H, CMe_2 min), 1.18 (s, 3H, CMe_2 maj). ^{13}C NMR (δ, $CDCl_3$): 158.8, 156.3, 147.3, 147.1, 144.7, 140.8, 140.5, 137.6 (C_q), 133.8, 133.2, 132.1, 130.5, 126.2, 125.4, 124.5, 124.3, 123.9, 123.7, 123.1, 122.1, 117.4 (Ar*C*H, Cp*C*H), 62.0, 60.1 (Ind*C*H-CMe_2), 40.7, 40.5 (Cp*C*H_2), 39.5, 38.3 (*C*Me_2), 26.9, 26.3, 25.9, 24.0 (C*Me*$_2$), 15.1 (Ind-2-*C*H_3 maj+min), 10.1 (Ind-3-*C*H_3 maj+min). EI-LRMS (*m*/*z*): 250 (M^+, 11%), 107 ($C_8H_{11}^+$, 100%).

Synthesis of 2-(Cyclopentadienyl)-2-(3-ethyl-2-methylindenyl)propane (9). A solution of *n*-BuLi (27.0 mmol) in hexanes was added dropwise to a cold (0 °C) solution of 3-ethyl-2-methylindene (3.89 g, 24.6 mmol) in THF (40 mL). The resulting dark red solution was stirred for 5 h, transferred to an addition funnel, and added dropwise to a chilled (−78 °C) solution of 6,6-dimethylfulvene in 20 mL of THF. The reaction was allowed to warm to room temperature in the dry ice/acetone bath and stirred for an additional 6 h at room temperature (ca. 10 h). The mixture was poured over ice cold 1 M NH_4Cl solution (100 mL) and diluted with pentane (100 mL). The aqueous layer was extracted with additional portions of pentane (3 × 20 mL), and the combined organic extracts were washed with water (3 × 25 mL) and dried over $MgSO_4$. Evaporation of the solvents and drying in vacuo yielded a dark orange oil. Fractional distillation afforded 4.10 g (63%) of **9** (bp 123−128 °C at 60 mTorr) as a mixture of six isomers (GC). Column chromatography (hexane, silica gel) affords the compound as a mixture of the two major components of the distillate. Spectral data for the two major components: ^{1}H NMR (δ, $CDCl_3$): 7.14−7.25 (ArC*H*, 2H maj + 2H min), 7.06−7.12 (ArC*H*, 1H, maj), 6.90−7.00 (ArC*H*, 1H maj + 2H min), 6.78 (1H, CpC*H* maj), 6.52 (1H, CpC*H* maj), 6.46 (1H, CpC*H* min), 6.37 (1H, CpC*H* min), 6.16 (1H, CpC*H* maj), 5.92 (1H, CpC*H* maj), 3.51 (s, 1H, IndC*H*-CMe_2 maj), 3.47 (s, 1H, IndC*H*-CMe_2 min), 3.04 (t, 2H, CpCH_2 min), 2.98 (s, 2H, CpCH_2 maj), 2.46 (m, 2+2H, Ind-CH_2-CH_3), 1.82 (s, 3H, Ind-2-CH_3 min), 1.80 (s, 3H, Ind-2-CH_3 maj), 1.18, 1.14, 1.10, 1.09, 1.07, 1.04 (6s, CMe_2, Ind-CH_2-CH_3). ^{13}C NMR (δ, $CDCl_3$): 158.7, 156.2, 146.3, 146.1, 145.0, 140.4, 140.2, 140.1, 140.0 (C_q), 133.7, 133.2, 132.1, 130.5, 126.2, 125.3, 124.7, 124.5, 123.7, 122.9, 122.7, 117.5, 117.4 (Ar*C*H, Cp*C*H), 61.8, 60.0 (Ind*C*H-CMe_2), 40.7, 40.5 (CpCH_2), 39.5, 38.3 (CMe_2), 27.0, 26.4, 25.8, 24.0 (CMe_2), 18.2 (Ind-CH_2-CH_3 maj+min), 14.9 (Ind-2-CH_3 maj+min), 10.1 (Ind-CH_2-CH_3 maj+min). EI-LRMS (*m*/*z*): 264 (M^+, 12%), 107 ($C_8H_{11}^+$, 100%).

Synthesis of 2-(Cyclopentadienyl)-2-(2,3-dimethylindenyl)dimethylsilane (10). A 3:2 mixture of 2,3- and 1,2-dimethylindene (4.00 g, 27.7 mmol) was dissolved in THF (40 mL) and cooled to 0 °C. *n*-Butyllithium (27.7 mmol) was added dropwise to the cold solution, and a bright orange color developed immediately. The mixture was allowed to warm to room temperature, stirred for an additional 18 h, and transferred to an addition funnel, prior to its slow addition over a cold (0 °C) solution of Me_2SiCl_2 (10 mL, ca. 83 mmol) in THF (50 mL). The resulting yellow suspension was stirred overnight at room temperature, and the solvents and excess Me_2SiCl_2 were removed in vacuo, yielding a yellow oil and a fine white solid. THF (60 mL) was added to the crude product, and the suspension was cooled to 0 °C. NaCp (2.45 g, 27.8 mmol) in THF (50 mL) was added dropwise to the cold suspension, and the resulting light pink mixture was stirred for an additional 10 h at room temperature. The mixture was diluted with 100 mL of pentane prior to the addition of 100 mL of deionized water. The organic layer was separated and washed with water (3 × 20 mL) while the aqueous layers were extracted with pentane (3 × 25 mL). The organics were combined and dried over $MgSO_4$, and the solvents were removed in vacuo, yielding an orange oil. The product was further purified by fractional distillation (bp 95−114 °C at 48−60 mTorr), which afforded 4.50 g (61%) of a yellow oil. Spectroscopic data for the major isomer: ^{1}H NMR (δ, $CDCl_3$): 7.45 (d, ArC*H*), 7.22−7.02 (m, ArC*H*), 6.59 (b, CpC*H*), 6.40 (b, CpC*H*), 6.20 (b, CpC*H*), 3.40 (s, IndC*H*-Si), 2.18 (s, Ind-CH_3), 2.15 (s, Ind-CH_3), −0.11 (s, Si(CH_3)$_2$), −0.18 (s, Si(CH_3)$_2$). ^{13}C NMR (δ, $CDCl_3$): 146.3, 143.7, 139.5, 132.8, 131.5, 130.7, 125.0, 122.8, 122.7, 118.2 (Cp*C*H, Ar*C*H), 48.9 (Ind*C*H-Si), 15.0 (Ind-2-*C*H_3), 10.2 (Ind-3-*C*H_3), −3.2 (Si(*C*H_3)$_2$), −5.0 (Si(*C*H_3)$_2$). EI-LRMS (*m*/*z*): 266 (M^+, 19%), 123 ($C_7H_{11}Si^+$, 100%).

Synthesis of (Cyclopentadienyl)(3-ethylindenyl)dimethylsilane (11). A solution of 3-ethylindene[25] (5.12 g, 35.4 mmol) in 40 mL of diethyl ether was cooled to 0 °C prior to the dropwise addition of *n*-BuLi (35.3 mmol), which caused the immediate precipitation of a white solid. The bright yellow suspension was allowed to warm to room temperature and stirred for an additional 12 h. After this time, the precipitated salt was redissolved by the addition of ca. 20 mL of THF, and the resulting orange solution was transferred to an addition funnel adapted to a flask containing a solution of Me_2SiCl_2 (17.2 mL, ca. 142 mmol) in 80 mL of diethyl ether. An extra 40 mL of THF was added to the Me_2SiCl_2 solution, and the ethylindenyllithium solution was added dropwise over a period of 3 h, which caused the immediate precipitation of a fine solid. The resulting solution was stirred at room temperature for ca. 16 h prior to the removal of the solvents and the excess Me_2SiCl_2 in vacuo, which yielded a mixture consisting of a yellow oil and a fine white solid. THF (80 mL) was added to the flask, the mixture was cooled to 0 °C, and a solution of NaCp (3.16 g, 35.8 mmol) in THF was added dropwise over a period of 2 h. The mixture was allowed to warm to room temperature and stirred for an additional 12 h. The reaction was quenched by addition of 100 mL of deionized water, and the organics were diluted with 100 mL of pentane. The organic layer was separated and washed with pentane (3 × 40 mL), and the aqueous layers were combined and extracted with pentane (3 × 50 mL). The organics were combined and dried over $MgSO_4$, and the solvents were removed in vacuo, yielding a dark orange oil. Fractional distillation (93−105 °C at 40−50 mTorr) afforded 4.89 g (52% from ethylindene) of **11** as a mixture of isomers. Spectral data for major isomer (overlapped signals with minor isomers in most cases): ^{1}H NMR (δ, $CDCl_3$): 7.45−7.52 (2d, 2H, ArC*H*), 7.30−7.35 (t, 1H, ArC*H*), 7.21−7.26 (m, 1H, ArC*H*), 6.10−6.80 (b, 4H, CpC*H*), 6.30 (s, 1H, Ind-C*H*), 3.50 (s, IndC*H*-Si), 2.78 (q, 2H, CH_2-CH_3), 1.36 (t, 3H, CH_2-CH_3), −0.09 (s, 3H, Si-CH_3), −0.23 (s, 3H, Si-CH_3). ^{13}C NMR (δ, $CDCl_3$): 144.2, 137.4, 132.8, 128.2, 124.9, 123.9, 123.4, 123.0, 119.2 (Cp*C*H, Ar*C*H), 60.4, 52.3, 44.3 37.7 ($CpCH_2$, Ind*C*H-Si), 20.8 (Ind-*C*H_2-CH_3), 13.0 (Ind-CH_2-*C*H_3), −4.8 (Si(*C*H_3)$_2$), −6.1 (Si(*C*H_3)$_2$). EI-LRMS (*m*/*z*): 266 (M^+, 18%), 123 ($C_7H_{11}Si^+$, 100%).

Synthesis of (Cyclopentadienyl)(3-(trimethylsilylmethyl)indenyl)dimethylsilane (12). A solution of *n*-BuLi in hexanes (42.1 mmol) was added dropwise to a cold (0 °C) solution of 1-(trimethylsilylmethyl)indene (8.12 g, 40.1 mmol) in pentane (50 mL). The bright yellow solution was allowed to warm to room temperature and stirred for an additional 16 h. THF (30 mL) was added to the viscous solution, and an orange color was developed immediately. The resulting solution was transferred to an addition funnel and added dropwise to a solution of Me_2SiCl_2 (19.5 mL, 160.4 mmol) in 80 mL of THF at 0 °C over 3 h. The mixture was stirred for an additional 6 h, and the solvents and excess Me_2SiCl_2 were removed in vacuo, yielding an orange oil and a light solid. The product was redissolved in ca. 50 mL of THF and cooled to 0 °C, prior to the dropwise addition of a solution of NaCp (3.71 g, 42.1 mmol) in 60 mL of THF. The mixture was allowed to warm to room temperature overnight and diluted with 100 mL of pentane prior to the addition of 100 mL of deionized water. The organic layer was separated and washed with water (3 × 40 mL), the aqueous layers were extracted with pentane (3 × 50 mL). The organics were combined and dried over $MgSO_4$, and the solvents were removed in vacuo, yielding 12.85 g of a dark orange oil. The product was further purified by fractional distillation (bp 115−120 °C at 55−65 mTorr), which afforded 7.81 g (60%) of a yellow/green oil. Spectral data for major isomer (overlapped signals with minor isomers in most cases): ^{1}H NMR (δ, $CDCl_3$): 7.00−7.50 (m, 4H, ArC*H*), 6.10−6.80 (4H, IndC*H*, CpC*H*), 3.45 (1H, IndC*H*-Si), 2.12 (s, CH_2-Si), 0.03 (s, 9H, Si(CH_3)$_3$), −0.06 (s, 3H, Si(CH_3)$_2$), −0.15 (s, 3H, Si(CH_3)$_2$). ^{13}C NMR (δ, $CDCl_3$): 145.4, 143.1, 139.4, 132.7, 130.7, 128.2, 127.4, 124.7, 123.6, 123.2, 122.7, 119.5 (Cp*C*H, Ar*C*H), 44.3 (Ind*C*H-Si), 17.6 (CH_2−Si), −1.2 (Si(*C*H_3)$_3$) −4.7 (Si(*C*H_3)$_2$), −6.1 (Si(*C*H_3)$_2$). EI-LRMS (*m*/*z*): 324 (M^+, 13%), 123 ($C_7H_{11}Si^+$, 100%).

Synthesis of (Cyclopentadienyl)(2-methyl-3-(trimethylsilylmethyl)indenyl)dimethylsilane (13). A solution of *n*-BuLi in hexanes (14.4 mmol) was added dropwise to a cold (0 °C) solution of 2-methyl-1-trimethylsilylmethylindene (2.82 g, 13.0 mmol) in diethyl ether (25 mL), and the resulting orange/gold solution was stirred for an additional 16 h at room

temperature. The solution was transferred to an addition funnel and added dropwise to a cold (0 °C) solution of Me_2SiCl_2 (3.2 mL, 26.5 mmol) in diethyl ether (ca. 30 mL). The reaction was allowed to warm to room temperature and stirred for an additional 6 h. Removal of the solvents and excess Me_2SiCl_2 yielded a yellow oil and a fine white solid. Diethyl ether (50 mL) was added to the mixture, which was cooled to 0 °C prior to the dropwise addition of a solution of NaCp (1.21 g, 13.7 mmol) in 60 mL of THF. The resulting pink mixture was stirred overnight, diluted with 50 mL of diethyl ether, and poured over 60 mL of ice cold 0.5 M NH_4Cl solution. The organic layer was separated and washed with water (4 × 20 mL), while the aqueous layers were combined and extracted with diethyl ether (3 × 20 mL). The organics were combined and dried over $MgSO_4$, and the solvents were removed in vacuo, yielding 4.24 g of a thick, dark orange oil. Column chromatography (silica gel, 1% diethyl ether in pentane) afforded 1.62 g (41%) of pure material (as a mixture of isomers). Spectral data for major isomer (overlapped signals with minor isomers in most cases): ^{1}H NMR (δ, $CDCl_3$): 7.41 (d, 1H, ArC*H*); 7.24 (d, 1H, ArC*H*), 7.05−7.20 (2t, 1+1H, ArC*H*), 6.20−6.80 (b, CpC*H*), 3.34 (s, 1H, IndCH-Si); 2.80 (dd, 2H, CH_2-Si), 2.13 (s, 3H, Ind-CH_3), 0.06 (s, 9H, CH_2-Si(CH_3)$_3$); −0.18 (s, 3H, Si(CH_3)$_2$), −0.22 (s, 3H, Si(CH_3)$_2$). ^{13}C NMR (δ, $CDCl_3$): 150.9, 143.1, 138.3, 133.0, 130.8, 124.8, 124.7, 122.6, 122.4, 122.1, 118.8 (Ar*C*H, Cp*C*H), 67.9 (Ind-*C*H), 48.8 (Ind*C*H-Si), 25.6, 22.3, 15.8, 15.4 (*C*H_2-Si, Ind-*C*H_3, more than 1 isomer), −0.6 (Si(*C*H_3)$_3$) −4.7 (Si(*C*H_3)$_2$), −5.7 (Si(*C*H_3)$_2$).

Synthesis of [Isopropylidene(cyclopentadienyl)(2-methylindenyl)]zirconium Dichloride (14).[28,29] To a solution of **6** (1.00 g, 4.25 mmol) in THF (35 mL) at 0 °C was added dropwise *n*-BuLi (8.9 mmol). The resulting bright yellow solution was allowed to warm to room temperature and stirred for an additional 16 h. The solvent was removed in vacuo to yield a bright yellow solid, which was mixed with solid $ZrCl_4$ (0.99 g, 4.25 mmol) in the drybox. The flask was cooled to 0 °C, and toluene (60 mL) was transferred via cannula. The resulting orange suspension was stirred for 24 h. Filtration through Celite afforded an orange solution which was evaporated to dryness to yield ca. 1 g of crude product. The obtained solid was redissolved in toluene and stored at −15 °C for 1 week. The yellow precipitate was isolated after cannula transfer of the mother liquor, washed with pentane (2 × 20 mL), and dried in vacuo. The filtrate was concentrated to $^1/_2$ of its volume and stored at −40 °C for 7 days, which afforded a second crop after filtration. A total of three crops were collected. Combined yield: 590 mg (35%). ^{1}H NMR (δ, $CDCl_3$): 7.73 (d, 9.0 Hz, 1H, Ar), 7.56 (d, 8.6 Hz, 1H, Ar), 7.31 (dd, 9.0, 8.6 Hz, 1H, Ar), 6.97 (dd, 8.8, 8.6 Hz, 1H, Ar), 6.63 (s, 1H, Ind-C*H*); 6.52, (m, 1H, Cp), 6.49 (m, 1H, Cp), 5.82 (m, 2H, Cp), 5.62 (m, 1H, Cp); 2.39 (s, 3H, Ind-CH_3), 2.26 (s, 3H, C(CH_3)$_2$), 2.13 (s, 3H, C(CH_3)$_2$). ^{13}C NMR (δ, $CDCl_3$): 129.2 (IndC_q), 125.9, 125.8, 125.3, 123.6 (Ar*C*H), 121.4, 121.3 (Cpβ*C*H), 119.5, 119.3 (1,2-IndC_q), 116.3 (Ind*C*H), 106.2, 102.6 (Cpα*C*H), 97.4 (CpC_q), 41.0 (*C*(CH$_3$)$_2$), 28.4, 27.7 (C(*C*H$_3$)$_2$), 20.8 (Ind-*C*H$_3$).

Synthesis of [Isopropylidene(cyclopentadienyl)(3-methylindenyl)]zirconium Dichloride (15).[30] To a solution of **7** (1.00 g, 4.25 mmol) in THF (35 mL) at 0 °C was added dropwise *n*-BuLi (8.9 mmol). The resulting dark orange solution was allowed to warm to room temperature and stirred for an additional 16 h. The solvent was removed in vacuo to yield a yellow/orange solid, which was mixed with solid $ZrCl_4$ (0.99 g, 4.25 mmol) in the drybox. The flask was cooled to 0 °C, and toluene (60 mL) was transferred via cannula. The resulting dark orange/brown suspension was stirred for 6 days at room temperature. After this time, the solvent was evaporated to dryness, and the remaining light orange solid was extracted with CH_2Cl_2. The solvent was removed in vacuo to yield an orange solid which was dried under vacuum and extracted with toluene. The toluene solution was decanted, concentrated, and stored at −40 °C for ca. 20 days, which yielded **15** as yellow/orange crystals. The solid was filtered, washed with pentane, and dried in vacuo. Two crops were collected. Combined yield: 409 mg (29%). ^{1}H NMR (δ, $CDCl_3$): 7.62 (d, 8.1 Hz, 1H, Ar), 7.51 (d, 8.7 Hz, 1H, Ar), 7.32 (dd, 8.5, 8.6 Hz, 1H, Ar), 7.00 (dd, 8.1, 8.6 Hz, 1H, Ar), 6.57, (m, 1H, Cp), 6.51 (m, 1H, Cp), 5.83 (m, 1H, Cp), 5.74 (s, 1H, Ind-C*H*); 5.52 (m, 1H, Cp); 2.42 (s, 3H, C(CH_3)$_2$), 2.19 (s, 3H, C(CH_3)$_2$) 1.91 (s, 3H, Ind-CH_3). ^{13}C NMR (δ, $CDCl_3$): 129.5 (IndC_q), 126.4, 125.6, 124.0, 123.3 (Ar*C*H), 120.6, 120.2 (Cpβ*C*H), 118.6 (IndC_q), 114.0 (Cpα*C*H), 105.4 (Ind*C*H), 103.9 (Cpα*C*H), 99.1 (CpC_q), 38.9 (*C*(CH$_3$)$_2$), 26.3, 25.6 (C(*C*H$_3$)$_2$), 12.4 (Ind-*C*H$_3$).

Synthesis of [Isopropylidene(cyclopentadienyl)(2,3-dimethylindenyl)]zirconium dichloride (16).[31] A solution of *n*-BuLi (8.41 mmol) in hexanes was added dropwise to a cold (0 °C) solution of **8** (1.00 g, 3.99 mmol) in 40 mL of THF. The resulting bright orange solution was allowed to warm to room temperature and stirred for an additional 12 h. Removal of the solvent in vacuo yielded a yellow solid, which was mixed with $ZrCl_4$ (910 mg, 3.91 mmol) in a drybox. Addition of toluene at 0 °C to the two solids caused the formation of a red suspension, which was stirred for 36 h at room temperature. Filtration through Celite afforded an orange solution, which was concentrated until turbidity appeared. The solution was stored at −40 °C, and a yellow powder precipitated, which was filtered, washed with pentane (2 × 20 mL), and dried under vacuum. Yield: 76 mg (6%). ^{1}H NMR (δ, $CDCl_3$): 7.73 (d, 9.0 Hz, 1H, Ar), 7.53 (d, 8.6 Hz, 1H, Ar), 7.31 (dd, 9.0, 8.6 Hz, 1H, Ar), 6.96 (dd, 8.8, 8.6 Hz, 1H, Ar), 6.58, (m, 1H, Cp), 6.47 (m, 1H, Cp), 5.83 (m, 1H, Cp), 5.62 (m, 1H, Cp), 2.36 (s, 3H, 3-CH_3-Ind), 2.28 (s, 3H, C(CH_3)$_2$), 2.17 (s, 3H, 2-CH_3-Ind), 2.13 (s, 3H, C(CH_3)$_2$). ^{13}C NMR (δ, $CDCl_3$): 129.1, 128.2 (IndC_q), 127.3, 125.8, 123.7, 123.5, 121.9, 120.8, 120.1, 119.3, 118.1 (Ar*C*H, Cpβ*C*H, IndC_q), 105.8, 102.3 (Cpα*C*H), 94.7 (CpC_q), 41.0 (*C*(CH$_3$)$_2$), 28.7, 28.2 (C(*C*H$_3$)$_2$), 16.6 (Ind-2-*C*H$_3$), 10.7 (Ind-3-*C*H$_3$).

Synthesis of [Isopropylidene(cyclopentadienyl)(3-ethyl-2-methylindenyl)]zirconium Dichloride (17). A solution of *n*-BuLi (7.94 mmol) in hexanes was added dropwise to a solution of **9** (1.00 g, 3.78 mmol) in diethyl ether (30 mL) at 0 °C. After 6 h, a solution of $ZrCl_4$ (881 mg, 3.78 mmol) in THF (ca. 30 mL) was added in portions via cannula to the cold (0 °C) bright orange solution, and a dark orange color was immediately developed. The resulting mixture was stirred overnight at room temperature, the solvent was removed in vacuo, and the product was extracted with CH_2Cl_2. Removal of the solid byproduct by filtration afforded a dark orange solution, which was evaporated to dryness. The solid product was extracted with toluene/CH_2Cl_2 (ca. 3:1), and filtration afforded a yellow solution, which yielded an orange powder upon concentration and storage at −40 °C. Combined yield (two crops): 470 mg (29%). Anal. Calcd for $C_{20}H_{22}Cl_2Zr$: H, 5.22; C, 56.59. Found: H, 5.00; C, 56.71.^{1}H NMR (δ, $CDCl_3$): 7.76 (d, 9.1 Hz, 1H, Ar), 7.52 (d, 8.6 Hz, 1H, Ar), 7.29 (dd, 8.5, 6.8 Hz, 1H, Ar), 6.95 (dd, 9.0, 6.8 Hz, 1H, Ar), 6.25 (m, 1H, Cp), 6.24 (m, 1H, Cp), 5.82 (m, 1H, Cp), 5.66 (m, 1H, Cp), 2.79 (*AB*, J_{AB} = 14.5 Hz, ^3J = 7.5 Hz, 2H, CH_2CH$_3$), 2.27 (s, 3H, C(CH_3)$_2$), 2.19 (s, 3H, Ind-CH_3), 2.13 (s, 3H, C(CH_3)$_2$), 1.10 (t, 7.5 Hz, CH$_2$CH_3). ^{13}C NMR (δ, CD_2Cl_2): 128.9, 127.2 (IndC_q), 126.0, 125.5, 124.2, 123.8, 121.3, 120.7, 120.2, 119.0 (Ar*C*H, Cpβ*C*H, IndC_q), 106.3, 102.7 (Cpα*C*H), 95.6 (CpC_q), 41.4 (*C*(CH$_3$)$_2$), 28.9, 28.3 (C(*C*H$_3$)$_2$), 19.1 (Ind-*C*H$_2$−CH$_3$), 16.4 (Ind-*C*H$_3$), 13.8 (Ind-CH$_2$-CH$_3$).

Synthesis of [Dimethylsilylene(cyclopentadienyl)(2,3-dimethylindenyl)]zirconium Dichloride (18). A solution of *n*-BuLi (8.20 mmol) in hexanes was added dropwise to a cold (0 °C) solution of 10 (1.04 g, 3.90 mmol) in ca. 40 mL of THF. The resulting orange solution was allowed to warm to room temperature and stirred for an additional 16 h. Removal of the solvent in vacuo yielded an off-white pale orange solid, which was mixed with $ZrCl_4$ (910 mg, 3.91 mmol) in a drybox. Addition of toluene at 0 °C to the two solids caused the formation of an orange suspension, which was stirred for 5 days at room temperature. Filtration through Celite afforded a yellow/orange solution, which was concentrated until turbidity appeared. The solution was stored at −40 °C, and a yellow powder precipitated, which was filtered, washed with pentane (3 × 15 mL), and dried under vacuum. Combined yield after a

second crop: 130 mg (8%). Anal. Calcd for $C_{18}H_{20}Cl_2SiZr$: H, 4.73; C, 50.68. Found: H, 4.88; C, 50.44. ^{1}H NMR (δ, $CDCl_3$): 7.57 (d, 8.5 Hz, 1H, Ar), 7.48 (d, 8.6 Hz, 1H, Ar), 7.41 (t, 8.6 Hz, 1H, Ar), 7.02 (t, 8.6 Hz, 1H, Ar), 6.83 (m, 1H, Cp); 6.72 (m, 1H, Cp); 5.83 (m, 1H, Cp); 5.78 (m, 1H, Cp), 2.39 (s, 3H, Ind-3-CH_3); 2.07 (s, 3H, Ind-2-CH_3); 1.07 (s, 3H, Si(CH_3)$_2$); 0.96 (s, 3H, Si(CH_3)$_2$). ^{13}C NMR (δ, $CDCl_3$): 134.9 (IndC_q), 127.5, 126.3, 126.3, 125.4, 124.5, 123.5 (Ar*C*H, Cpβ*C*H, IndC_q), 114.7, 109.7 (Cpα*C*H), 105.0 (CpC_q), 15.6 (Ind-2-*C*H$_3$), 11.0 (Ind-3-*C*H$_3$), −0.4, −0.9 (Si(*C*H$_3$)$_2$).

Synthesis of [Dimethylsilylene(cyclopentadienyl)(3-ethylindenyl)]zirconium Dichloride (19). A solution of *n*-BuLi (7.77 mmol) in hexanes was added dropwise to **11** (1.03 g, 3.87 mmol) in THF (40 mL) at 0 °C. The resulting orange solution was stirred overnight at room temperature, and the solvents were evaporated to yield a yellow solid. $ZrCl_4$ (900 mg, 3.87 mmol) was added to the flask, and the mixture of solids was suspended in dry toluene (ca. 50 mL) at 0 °C. The bright orange suspension was stirred for 1 day at room temperature, prior to the filtration of the solid byproducts which yielded an orange solution, which was concentrated and stored at −40 °C. Complex **19** was obtained as a yellow fine solid, which was washed with pentane and dried under vacuum. A second crop could be obtained after filtration, concentration, and crystallization at −40 °C. Combined yield: 635 mg (39%). Anal. Calcd for $C_{18}H_{20}Cl_2SiZr$: H, 4.73; C, 50.68. Found: H, 4.58; C, 50.59. ^{1}H NMR (δ, $CDCl_3$): 7.61 (d, 8.4 Hz, 1H, Ar), 7.42 (d+dd, 2H, Ar), 7.09 (t, 7.6 Hz, 1H, Ar), 6.80 (m, 1H, Cp), 6.76 (m, 1H, Cp), 5.86 (m, 1H, Cp), 5.85 (s, 1H, IndC*H*), 5.78 (m, 1H, Cp), 2.94 (*AB*$_q$, J_{AB} = 14.5 Hz ^3J = 7.5 Hz, CH_2CH$_3$), 1.27 (t, 7.6 Hz, CH$_2$CH_3), 1.04 (s, 3H, Si(CH_3)$_2$), 0.82 (s, 3H, Si(CH_3)$_2$). ^{13}C NMR (δ, $CDCl_3$): 134.5, 133.8, 126.9, 126.8, 126.4, 125.2, 124.4 (Ar*C*H, Cpβ*C*H, IndC_q), 118.1 (Ind*C*H), 114.3, 111.4 (Cpα*C*H), 105.7 (IndC_q), 98.1 (IndC_q), 86.4 (CpC_q), 21.3 (*C*H$_2$CH$_3$), 14.2 (CH$_2$*C*H$_3$), −2.4, −4.3 (Si-(*C*H$_3$)$_2$).

Synthesis of [Dimethylsilylene(cyclopentadienyl)(3-(trimethylsilylmethyl)indenyl)]zirconium Dichloride (20). A solution of *n*-BuLi (7.77 mmol) in hexanes was added dropwise to **12** (1.03 g, 3.87 mmol) in THF (40 mL) at 0 °C. The resulting orange solution was stirred for 6 h, and the solvents were evaporated to yield an orange waxy solid, which was washed with pentane (2 × 20 mL) and dried under vacuum. Solid $ZrCl_4$ was added to the orange solid, followed by toluene (40 mL) at 0 °C. The resulting orange suspension was stirred overnight at room temperature, and filtration yielded an orange solution. The solvent was removed, and the resulting orange solid was recrystallized from toluene/pentane (first crop) and toluene (second crop). Combined yield: 511 mg (28%). Anal. Calcd for $C_{20}H_{26}Cl_2Si_2Zr$: H, 5.41; C, 49.56. Found: H, 5.31; C, 49.54. ^{1}H NMR (δ, $CDCl_3$): 7.48 (d, 8.7 Hz, 1H, Ar), 7.43 (d, 8.6 Hz, 1H, Ar), 7.35 (dd, 8.6, 6.6 Hz, 1H, Ar), 7.04 (dd, 8.6, 6.7 Hz, 1H, Ar), 6.77 (m, 1H, Cp), 6.72 (m, 1H, Cp), 5.86 (m, 1H, Cp), 5.73 (m, 1H, Cp), 5.56 (s, 1H, Ind-H), 2.34 (*AB*, J_{AB} =14.2 Hz, CH_2−SiMe$_3$), 1.04 (s, 3H, Si(CH_3)$_2$); 0.79 (s, 3H, Si(CH_3)$_2$); −0.04 (s, 9H, SiMe$_3$). ^{13}C NMR (δ, $CDCl_3$): 133.9, 133.1, 127.1, 127.0, 126.5, 125.0, 124.7 (Ar*C*H, Cpβ*C*H, IndC_q), 117.5 (Ind*C*H), 114.5, 111.5 (Cpα*C*H), 105.9 (IndC_q), 96.1 (IndC_q), 85.7 (CpC_q), 19.1 (*C*H$_2$-SiMe$_3$), −1.4 (SiMe$_3$), −2.3 (Si(*C*H$_3$)$_2$), −4.2 (Si(*C*H$_3$)$_2$).

Synthesis of [Dimethylsilylene(cyclopentadienyl)(2-methyl-3-(trimethylsilylmethyl)indenyl)]zirconium Dichloride (21). A solution of *n*-BuLi (5.28 mmol) in hexanes was added dropwise to **13** (0.81 g, 2.39 mmol) in diethyl ether (40 mL) at 0 °C. The resulting orange solution was stirred overnight, and a suspension of $ZrCl_4$ (557 mg, 2.39 mmol) in diethyl ether (ca. 40 mL) was added in portions via cannula. Stirring for 24 h at room temperature afforded an orange suspension. Removal of the solvents in vacuo yielded an orange solid which was extracted with CH_2Cl_2. Filtration and removal of the solvent afforded crude material as an orange solid. Recrystallization from toluene at −40 °C (4 days) yielded pure **21** as a bright yellow powder. A second crop could be obtained upon cooling the concentrated filtrate. Combined yield: 385 mg (32%). Anal. Calcd for $C_{21}H_{28}Cl_2Si_2Zr$: H, 5.66; C, 50.57. Found: H, 5.63; C, 50.29. ^{1}H NMR (δ, $CDCl_3$): 7.43 (d, 8.6 Hz, 1H, Ar), 7.27 (dd, 8.9, 6.7 Hz, 1H, Ar), 7.23 (d, 9.1 Hz, 1H, Ar), 6.82 (dd, 9.0, 6.7 Hz, 1H, Ar), 6.80 (m, 1H, Cp), 6.61 (m, 1H, Cp), 5.47 (m, 1H, Cp), 5.44 (m, 1H, Cp), 2.43 (*AB*, J_{AB} =14.7 Hz, CH_2−SiMe$_3$), 1.88 (s, 3H, Ind-CH_3), 0.52 (s, 3H, Si-(CH_3)$_2$), 0.41 (s, 3H, Si(CH_3)$_2$), −0.13 (s, 9H, SiMe$_3$). ^{13}C NMR (δ, $CDCl_3$): 133.9, 131.5, 130.86, 127.7, 125.9, 125.7, 125.2, 124.7, 124.4, 123.9 (Ar*C*H, Cpβ*C*H, IndC_q), 115.1, 109.7 (Cpα*C*H), 105.3 (IndC_q), 82.5 (CpC_q), 17.0 (CH$_2$−SiMe$_3$), 16.5 (CH3−Ind), 1.1, −0.2, −0.5, −0.8 (Si(*C*H$_3$)$_3$, Si(*C*H$_3$)$_2$).

Liquid Propylene Polymerization Procedure. The experimental conditions described in a previous report were reproduced in order to allow comparison of the results reported herein with those obtained with systems **3**−**5**: Polymerizations were carried out in a 300 mL Parr reactor equipped with a mechanical stirrer, and temperature was controlled using an ethylene glycol/water cooling loop. Catalyst solutions were prepared in a drybox by dissolving the metallocenes in toluene to give stock solutions of $c = (0.9-2.6) \times 10^{-3}$ M. The desired amount of dry MAO was dissolved in toluene followed by addition of an appropriate aliquot of the metallocene solution to give a total volume of 20 mL. The catalyst solutions were stirred for ca. 2 min at room temperature prior to injection. The evacuated reactor was backfilled with N_2, flushed three times with gaseous propylene, filled with 100 mL of liquid propylene, and brought to the desired polymerization temperature. The polymerization was started by injecting the catalyst solution under argon pressure and stirred at 1000 rpm for 20 min. All polymerizations were quenched by injection of 20 mL of MeOH under argon pressure. The polymers were stirred overnight in 5% HCl/MeOH, filtered, washed 3 × 50 mL each with MeOH, saturated $NaHCO_3$ solution, water, and MeOH, and dried in a vacuum oven at 50 °C to constant weight.

Polymer Analysis. ^{13}C NMR spectra of the polypropylene samples were obtained from solutions of 80−100 mg of polymer either in $C_2D_2Cl_4$ or in a 1:3 mixture of $C_2D_2Cl_4$ (lock solvent) and $C_2H_2Cl_4$ at 100 °C using a Varian VXR-300 NMR spectrometer and 5 mm NMR tubes. The [*rrrr*] methyl signal of polypropylene (δ = 20.29 ppm) was used as internal reference. The spectra were recorded using a calibrated 90° pulse, and at least 3000 scans were obtained. Molecular weights and molecular weight distributions were determined by gel permeation chromatography on a Waters 150-C ALC/GPC instrument equipped with two Polymer Laboratories PLGEL 10 μm Mixed-B columns and differential refractive index detector in 1,2,4-trichlorobenzene at 139 °C (sample concentration 0.067% w/v, flow rate 1.0 mL/min). The calibration was made by using polypropylene broad standards. Alternatively, a Polymer Laboratories PL-GPC210 equipped with PLGEL 20 μm Mixed-A columns and PD2040 precision detectors was used for the analysis.

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Supporting Information Available: Tabulated experimental and calculated pentad distributions for PP samples synthesized using systems **15**−**21**/MAO and sample ^{13}C NMR spectra (methyl region) of PP synthesized using **14**/MAO and **16**/MAO. This material is available free of charge via the Internet at http://pubs.acs.org.

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