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Elastomeric Poly(propylene): Influence of Catalyst Structure and Polymerization Conditions on Polymer Structure and Properties[1a]

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ABSTRACT: A number of propylidene- and dimethylsilylene-bridged metallocene complexes of titanium, zirconium, and hafnium were prepared and employed in a study of propylene polymerization in the presence of methylaluminoxane. This work has revealed that catalysts based on hafnium are desirable for the production of elastomeric poly(propylene) in that they polymerize propylene to high molecular weight polymer and are indefinitely stable under typical polymerization conditions. Two of the zirconium complexes prepared have been characterized by X-ray crystallography. [2-Propylidene(η^5-indenyl)(η^5-cyclopentadienyl)]zirconium dichloride **3**: Space group $Pna2_1$; $a = 9.792$ (2), $b = 12.156$ (3), $c = 12.751$ (3) Å; $V = 1517.8$ (5) Å^3; $Z = 4$; $R = 0.0176$, $R_w = 0.0196$ for 2188 reflections with $F > 6.0\sigma(F)$. [Dimethylsilylene(η^5-indenyl)(η^5-cyclopentadienyl)]zirconium dichloride **5**: Space group $Pbca$; $a = 13.174$ (4), $b = 15.873$ (5), $c = 15.353$ (4) Å; $V = 3210.6$ (15) Å^3; $Z = 8$; $R = 0.0351$, $R_w = 0.0349$ for 2538 reflections with $F > 6.0\sigma(F)$. The microstructure of the poly(propylene) produced was sensitive not only to changes in catalyst structure but also to polymerization conditions such as temperature. The stereoregularity of the polymer was surprisingly sensitive to changes in monomer concentration (i.e., pressure). By varying both catalyst structure and polymerization conditions, it is possible to produce elastomeric poly(propylene) that exhibits excellent elastic properties.

Introduction

The study of substituted metallocene catalysts of the group 4 elements for olefin polymerization has led to significant insight concerning the role of steric and/or electronic effects on propagation and chain transfer processes as well as stereoregulation in α-olefin polymerization.[2]

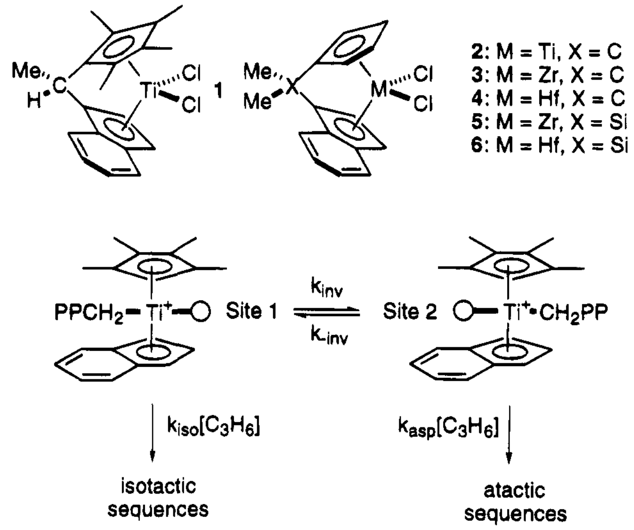
Rational changes in catalyst structure have led to the development of active catalysts for the production of inter alia isotactic and syndiotactic poly(propylene) (iPP and sPP, respectively).[2a,b,e,k] Moreover, fundamental studies and modeling of the catalytic intermediates involved in these processes have shed considerable light on the origins of stereoselectivity observed.[3,4]

Recently, a catalyst system derived from titanocene complex **1** (Scheme 1) and methylaluminoxane (MAO) has been used to polymerize propylene and, depending on polymerization conditions, produces elastomeric PP (elPP).[5]

Elastomeric PP has been previously isolated by solvent fractionation of PP prepared with classical Ziegler–Natta catalysts[6a,b] and has also been prepared using supported catalysts developed at DuPont.[6c–f] Unlike these materials, the elPP produced using catalyst **1** is uniform in composition (e.g., completely soluble in ether) and features a narrow molecular weight distribution, and thus this catalyst system represents a significant advance in this area.

Further development of commercially viable catalysts for the production of elPP requires an understanding of the crucial structural features necessary for the preparation of this material. From the outset, it was not particularly clear what structural features embodied in catalyst **1** were important for imparting elastomeric properties to PP; catalyst **1** only produces elPP over a narrow temperature range and the zirconium analog produces low molecular weight material and is less active.[5d] We thus elected to study propylene polymerization using a series of structurally related catalysts (**2**–**6**; Scheme 1). We were interested in investigating the role of the metal and bridging unit on catalyst stability and activity as well as polymer molecular weight and stereoregularity. In particular, the latter two features were expected to significantly impact on the physical properties of elPP, whereas catalyst activity and stability are important if one wishes to prepare large amounts of this material at reasonable catalyst loadings; catalyst **1** is not particularly stable at conventional polymerization temperatures.[5d]

Scheme 1



The mechanism that has been invoked to account for the presence[7] of crystallizable and amorphous segments in PP prepared using catalyst **1** is patterned after a two-state model for propagation originally described by Coleman and Fox.[8]

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In this model (Scheme 1),[9] the formation of crystalline domains involves consecutive insertions from one of the lateral coordination sites (site 1) of catalyst **1** so as to give rise to isotactic sequences, whereas consecutive insertions at the other site (site 2) should give rise to atactic, amorphous sequences. Interconversion between these two states must occur within the lifetime of a given polymer chain in order to generate a physically cross-linked network and is believed to occur via occasional isomerizations of the polymer chain (i.e., inversion at the metal center). Thus, the microstructure of elPP produced using catalyst **1** is considered to be built up of blocks of atactic and isotactic sequences, with the latter being of sufficient length to cocrystallize with similar sequences on other polymer chains.

It can be appreciated from Scheme 1 that catalysts **2**–**6** also have two, inequivalent sites for monomer coordination and insertion and thus should provide PP with similar properties to that produced using catalyst **1**. This paper describes the preparation and characterization of catalysts **2**–**6**, their use in propylene polymerization, and the properties of the polymers produced.[10]

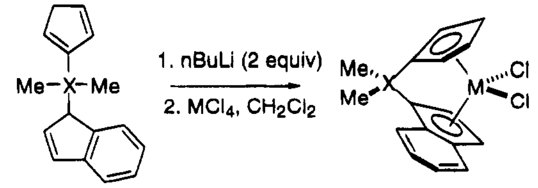
In a subsequent paper, three limiting models for propagation related to that outlined in Scheme 1 are presented and critically discussed.[11]

Results and Discussion

Catalyst Preparation and Characterization. The zirconium complexes **3** and **5** have been previously prepared and briefly evaluated in propylene polymerizations by Spaleck and co-workers.[2h]

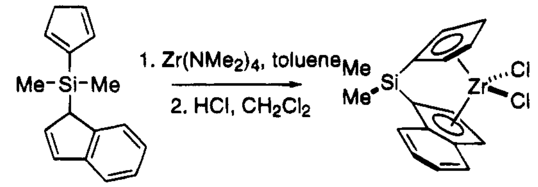
We prepared the titanium and hafnium analogs of **3** and the hafnium analog of **5** by reaction of the dilithio salt of the requisite ligand with the metal tetrachloride in dichloromethane suspension as shown in eq 1. The synthetic yields were far from satisfactory but this procedure, as opposed to that reported, was found to be reproducible in our hands.

Recently, Teuben and co-workers have reported an alternative approach to the synthesis of *ansa*-metallocene complexes.[12] We briefly investigated this approach for the synthesis of **5**; treatment of the requisite ligand with tetrakis(dimethylamido)zirconium in toluene solution furnished the intermediate dimethylamido complex in high yield (eq 2). Subsequent treatment of this material with 2.0 equiv of anhydrous HCl in dichloromethane at low temperature provides dichloride **5** in 75% overall yield.



eqn. 1

2-6
(5-50%)



eqn. 2

5
(75 %)

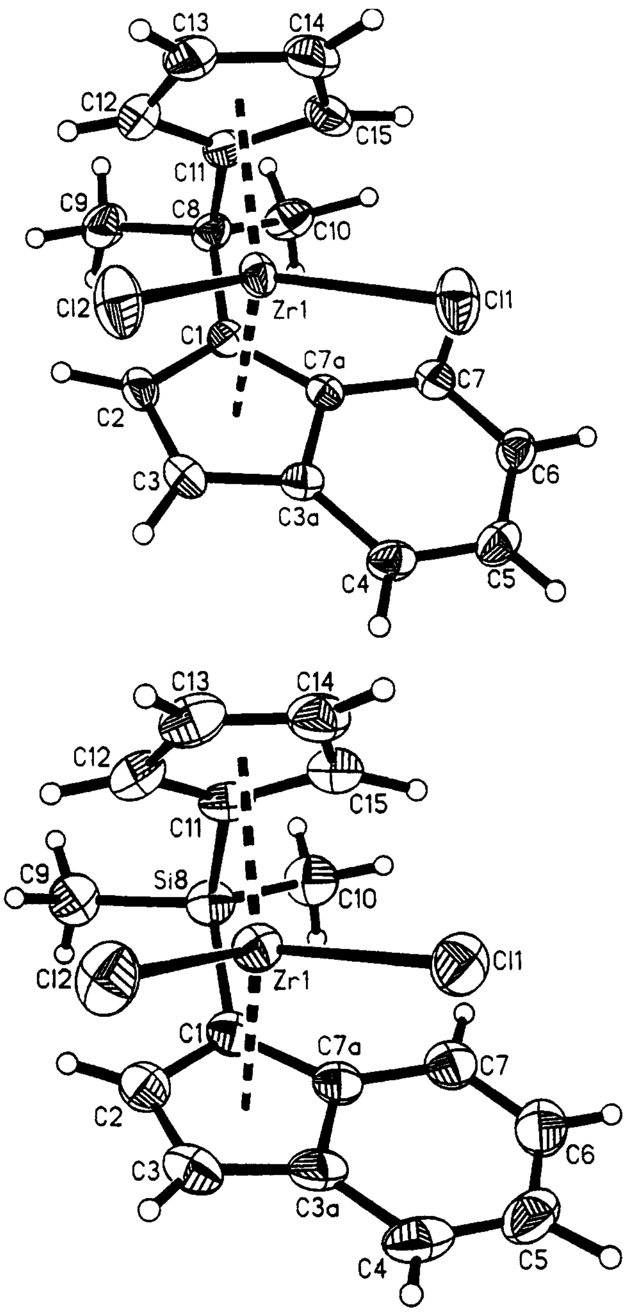


Figure 1. Molecular structures of compounds **3** and **5** with 30% thermal ellipsoids depicted.

Compounds **3** and **5** were characterized by X-ray crystallography. The molecular structures of these two complexes are depicted in Figure 1, and selected crystallographic and structural data appear in Tables 1 and 2, respectively.

Somewhat surprisingly, there is very little difference in the metal–ligand bond distances when the structures are compared (Table 2). The two, significantly different Zr–Cl bond lengths found in each structure are the same to within 3σ when **3** and **5** are compared, and the metal–centroid distances in **5**, while somewhat longer than those in **3**, are not dramatically so. The Zr–C bond lengths to the indenyl ring in the two structures are also rather similar.

The geometry about the metal in the two structures is, however, dramatically different when one compares angles about the metal. In the case of **3**, the Cn(1)–Zr(1)–Cn(2) angle is 117.1 (1)° whereas the corresponding value in **5** is 126.9 (1)°. The latter value is normal

Table 1. Selected Crystallographic and Refinement Data for Metallocenes 3 and 5

	compound **3**	compound **5**
emp formula	$C_{17}H_{16}Cl_2Zr$	$C_{16}H_{16}Cl_2SiZr$
formula wt	382.4	398.5
color; habit	orange prism	yellow plate
crystal dimensions (mm)	0.44 × 0.44 × 0.32	0.46 {100} × 0.20 {010} × 0.11 {001}
space group	$Pna2_1$	*Pbca*
unit cell dimensions		
a (Å)	9.792 (2)	13.174 (4)
b (Å)	12.156 (3)	15.873 (5)
c (Å)	12.751 (3)	15.353 (4)
vol (Å^3)	1517.8 (5)	3210.6 (15)
Z	4	4
ϱ_{calc} (g/cm^3)	1.674	1.649
abs coeff (cm^{-1})	10.62	10.79
2θ range (deg)	4.0–60.0	4.0–56.0
scan type	ω	ω
scan range (ω) (deg)	1.40	1.20
ind reflections	2316	3896
obs reflections [$F > 6.0\sigma(F)$]	2188	2538
R (%)	1.76	3.51
R_w (%)	1.96	3.49
GOF	1.91	1.82

Table 2. Selected Bond Lengths and Angles for Metallocenes 3 and 5[a]

	compound **3**	compound **5**
Bond Lengths (Å)[b]		
Zr(1)–Cl(1)	2.420 (1)	2.421 (1)
Zr(1)–Cl(2)	2.444 (1)	2.438 (1)
Zr(1)–Cn(1)[c]	2.212 (3)	2.227 (5)
Zr(1)–Cn(2)[c]	2.185 (3)	2.198 (5)
Zr(1)–C(1)	2.434 (2)	2.455 (4)
Zr(1)–C(2)	2.462 (3)	2.473 (4)
Zr(1)–C(3)	2.562 (3)	2.573 (5)
Zr(1)–C(3a)	2.631 (2)	2.634 (4)
Zr(1)–C(7a)	2.520 (2)	2.537 (4)
Bond Angles (deg)[b]		
Cl(1)–Zr(1)–Cl(2)	100.1 (1)	97.1 (1)
Cn(1)–Zr(1)–Cn(2)[c]	117.1 (1)	126.9 (1)
C(1)–X(8)–C(11)[d]	99.2 (2)	93.8 (2)
C(9)–X(8)–C(10)[d]	108.6 (2)	114.7 (2)

[a] For numbering scheme, consult Figure 1. [b] Estimated standard deviation in parentheses. [c] Cn(1) and Cn(2) are the centroids of the indenyl and cyclopentadienyl ring, respectively. [d] X is C and Si for compounds **3** and **5**, respectively.

Table 3. Polymerization of Propylene Using Catalysts 2–6[a]

entry	cat. (mM)	P (psig)	T (°C)	A[b]	10^{-3} M_w[c]	M_w/M_n[c]	% mmmm[d]
1	**2** (25.4)	16	−25	3[e]	nd	nd	71.5
2	**2** (12.4)	16	25	3[e]	nd	nd	35.9
3	**2** (10.5)	bulk	25	24	70.0	2.3	41.6
4	**3** (10.5)	16	25	700	2.2	2.0	15.0
5	**4** (10.5)	16	25	130	30.0	2.1	37.8
6	**4** (10.5)	45	25	330	43.0	2.1	31.5
7	**4** (22.0)	45	0	40	75.0	2.1	29.3
8	**5** (10.5)	16	25	800	9.1	1.8	29.8
9	**6** (10.5)	16	25	170	49.0	1.7	53.6
10	**6** (10.5)	60	25	nd	140.0	1.9	49.6
11	**6** (10.5)	45	0	nd	380.0	1.9	52.2

[a] Polymerizations were conducted in toluene with MAO unless otherwise noted: Al:M = 2000:1. [b] Activity in kg of PP/mol of M × h. [c] M_w and M_w/M_n determined by GPC. [d] Determined from the ^{13}C NMR spectrum. [e] Less than 1.0 g of polymer obtained.

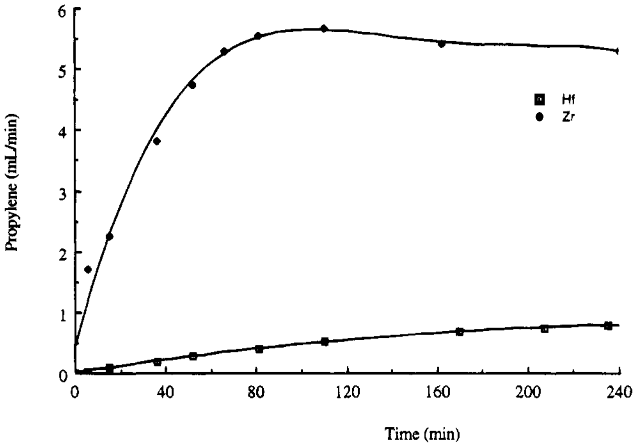


Figure 2. Propylene flow (mL/min) vs time for propylene polymerizations catalyzed by compounds **3** and **4** (conditions: toluene (500 mL); Al:M = 2000:1, 25 °C, 16 psig).

for bent metallocene complexes of Zr(IV) whereas the former is significantly contracted. Less obvious differences are evident in the Cl(1)–Zr(1)–Cl(2) angles; for **3** this angle is somewhat expanded [100.1 (1)°] whereas for **5** a more normal value of 97.1 (1)° is observed.

Thus, the geometrical constraints imposed by the different bridging atoms in the two structures are manifested mainly by angular changes at the metal center. Since there is little change in the metal–centroid distances, the net effect is that the Zr atom in **3** lies somewhat further outside (by about 0.2 Å) the cleft defined by the two π-bound ligands than it does in **5**. This may explain why catalysts that possess the dimethylsilylene-bridged ligand are more stereoselective than their propylidene-bridged analogs (vide infra).

Polymerization of Propylene Using Metallocenes 2–6. Propylene polymerizations using metallocenes **2–6** with MAO as cocatalyst were conducted in toluene solution or in liquid propylene at various pressures and temperatures. Some of the results are summarized in Table 3.

The titanium catalyst **2** failed to provide significant quantities of PP in toluene solution between −50 and −80 °C. The small amount (ca. 100 mg after 1 h) of polymer obtained at low temperatures (<−20 °C) was predominantly isotactic as revealed by ^{13}C NMR spectroscopy (entry 1). In liquid propylene, however, the productivity was substantially higher at conventional temperatures (entry 3).

In contrast, the zirconium and hafnium analogs of **2** (**3** and **4**, respectively) exhibited higher productivities, with the former complex being more active (entry 4 vs 5), in agreement with other literature data.[2]

Changing the bridging group from propylidene to dimethylsilylene had surprisingly little effect on catalyst productivity (Table 3, entries 4 vs 8 and 5 vs 9) but was accompanied by a significant increase in the molecular weight of the polymer produced. Such an effect is consistent with a decrease in the rate of chain transfer processes.

This finding, when coupled with the observation that the principal mode of chain transfer in these systems involves β-hydride elimination (vide infra), suggests that this process may be sterically and electronically impeded in catalysts **5** and **6** when compared with their propylidene-bridged analogs. Similar effects have also been noted with related catalyst systems.[2]

Figure 2 shows a typical C_3H_6 flow profile (mL of propylene/min at constant P) measured using these catalyst systems. It is evident that catalysts such as **3** and **4** are active (and presumably stable) over the entire time period studied. This behavior is in stark contrast to that observed using catalyst **1**, which has negligible

Table 4. Triad Distributions for Poly(propylene) Produced Using Catalysts 4 and 6[a]

		C_3H_6	triad intensity				
entry	cat.	(psig)	mm	mr	rr	2rr/mr	4mm·rr/mr^2
1	**4**[d]	16	0.58	0.28	0.14	1.00	4.14
2	**4**[e]	16	0.57	0.28	0.15	1.11	4.36
3	**4**	16	0.59	0.27	0.14	1.04	4.53
4	**4**	45	0.53	0.30	0.17	1.13	4.00
5	**4**	60	0.52	0.30	0.18	1.20	4.16
6	**4**	bulk	0.46	0.33	0.21	1.27	3.55
7	**6**	16	0.71	0.20	0.09	0.90	6.39
8	**6**	60	0.69	0.22	0.09	0.82	5.13
9	**6**	45[f]	0.72	0.21	0.08	0.76	5.22

[a] Conditions: 25 °C, 10 μM Hf, 20 mM Al in toluene solution except where noted. [b] Test statistic for enantiomorphic-site control. [c] Test statistic for chain-end (Bernoullian) control. [d] 10 μM Hf, 5 mM Al. [e] 10 μM Hf, 50 mM Al. [f] Polymerization performed at 0 °C.

polymerization activity after 30 min under these conditions.[5d] Thus, zirconium- or hafnium-based catalysts may prove more suitable for production of elPP in significant quantities.

We expected that the molecular weight (MW) of the polymer produced would be a significant factor influencing elastomeric properties of these materials, and therefore the effect of different experimental conditions on this property was explored using catalyst **4**.

Increasing monomer concentrations led to significant improvements in both productivity and polymer MW (entries 5 and 6) whereas a decrease in the reaction temperature was accompanied by a dramatic decline in activity coupled with an appreciable increase in MW (entry 6 vs 7). Similar but more dramatic effects were observed using catalyst **6** (entries 9–11).

Thus, for a given catalyst system, as is normally the case, there is considerable latitude for MW modification by controlling both monomer concentration and polymerization temperature. As will become evident, this feature is important in producing elastomeric material with good properties.

In all cases, molecular weight distributions (MWDs) were narrow, consistent with the polymers being produced by a single-site catalyst. We note that the purity of the $HfCl_4$ (>99.99%) used in the preparation of complexes **4** and **6** is crucial; use of $HfCl_4$ of lower purity (e.g., 98%) led to the production of poly(propylene) with bimodal MWDs with the minor, low MW component having a M_n close to that produced by the corresponding zirconium catalyst. This effect, which arises from the presence of small amounts of zirconium in hafnium, has been noted elsewhere.[2d]

Poly(propylene) Microstructure. The microstructure of the PP produced using catalysts **2**–**6** under various conditions was analyzed by ^{13}C NMR spectroscopy, and the measured triad intensities for PP produced using catalyst **4** under various conditions are summarized in Table 4.

In the case of low MW samples (e.g., PP produced using either **3** or **5**), resonances due to vinylidene and *n*-propyl end groups were clearly evident and were present in a 1:1 ratio. This indicates that chain transfer occurs, almost exclusively, by β-hydride elimination. As some of these resonances absorb in the region where the methyl triad resonances are found,[13] the triad distribution in these cases (i.e., using catalysts **3** and **5**) is subject to significant errors.

In all but these cases, the triad intensities obeyed the test statistic 2rr/mr = 1, indicating that the structure of the polymer is consistent with a site model for stereocontrol.[14]

Under identical conditions, catalysts **5** and **6** produce PP which is significantly more stereoregular than that prepared using their propylidene-bridged counterparts (entries 8 and 9 vs 4 and 5, Table 3). This finding may be related to the structural differences between these catalysts discussed earlier.

Somewhat surprisingly, the hafnium catalysts are significantly more stereoregulating than their zirconium counterparts; this may be a reflection of a decrease in propagation rates relative to the rate of interconversion between the two states during polymerization, particularly if the thermodynamically preferred state is that leading to isotactic propagation.

An interesting observation is that increases in monomer concentration led to a measurable decrease in the stereoregularity of PP produced using these catalysts (e.g., Table 4, entries 6–8). This effect has been recently observed using ethylene-bridged complexes, and the mechanistic implications were discussed in terms of an increase in propagation rates relative to isomerization between two conformers of these catalysts.[15]

As was previously mentioned, the polymer produced using catalyst **2** at low temperatures in toluene solution was predominantly isotactic (% mm = 88) whereas at room temperature in liquid propylene or in toluene, material of significantly lower stereoregularity was formed (% mm ~ 61). Interestingly, the opposite behavior is observed using catalyst **1**.[5h] The principal difference between these two catalysts is that the aspecific site in **1** is more sterically hindered than that in **2**. It is possible that at low temperatures, monomer insertion occurs predominantly from one of the lateral sites in these catalysts. The implication of this hypothesis is that the site involved in insertion using catalyst **2** is the isospecific one whereas for **1** it is the aspecific site. This differential behavior may relate to the (thermodynamically) preferred location of the polymer chain at the less hindered site in these catalysts at low temperatures.

As polymer stereoregularity is expected to significantly impact on elastomeric properties as well, these results demonstrate that it can be meaningfully modified by changes in polymerization conditions as well as catalyst structure.

Polymer Crystallinity. Polymer samples produced using various catalysts were analyzed by DSC to determine melting transitions, and the heat of fusion and the results are summarized in Table 5. As previous work had demonstrated that the melting behavior of elPP is dramatically affected by thermal history,[7] all samples were given the same thermal history prior to measurement.

All of the polymers produced using the zirconium catalysts were amorphous as revealed by a lack of a melting endotherm. In contrast, some of the polymers produced using the hafnium (or titanium) catalysts exhibited two distinct melting transitions as had been previously observed using catalyst **1**. The higher melting transition developed more rapidly (hours) on cooling from the melt whereas the lower melting endotherm developed more slowly (days) after annealing at 20 °C.

Table 5. Properties of Elastomeric Poly(propylene) Produced Using Metallocene Catalysts

entry	1	2	3	4	5	6	7	8
cat.	**4**[a]	**4**[b]	**4**[c]	**4**[d]	**6**[c]	**6**[e]	**6**[d]	**1**[f]
$10^{-3}M_w$[g]	46	43	30	75	50	75	380	127
% mmmm[h]	30	32	38	29	54	45	52	40
$T_m(1)$ (°C)[i]	*j*	*j*	47	*j*	54	50	53	
$T_m(2)$ (°C)[i]	*j*	*j*	61	*j*	93	79	84	
ΔH_f(J/g)[i]	0	0	15	0	40	31	35	14
% crystallinity[k]	0	0	7.2	0	19.1	14.8	16.7	6.7
ultimate strength (MPa)			3.0		16.0	16.0	39.0	4.0
apparent strain to break (%)			200		500	750	800	525
elastic recovery (%)								
after 100% strain					92	97	95	93
after 200% strain					90	97	93	91
after break					80	93	84	86

[a] 25 °C, 60 psig. [b] 25 °C, 45 psig. [c] 25 °C, 16 psig. [d] 0 °C, 45 psig. [e] 25 °C, liquid propylene. [f] See refs 5 and 7. [g] Determined by GPC. [h] Determined by ^{13}C NMR. [i] Determined by DSC. [j] Samples were amorphous. [k] % crystallinity = (ΔH_f/209 J g^{-1}) × 100.

As indicated in Table 5, the melting temperatures and the degree of crystallinity (calculated based on the observed heat of fusion) of the polymers are significantly influenced by polymer stereoregularity. Entries 1–3, which differ primarily in their stereoregularity, illustrate that in this MW range (30–50K) the degree of crystallinity can be substantially affected by seemingly minor changes in stereoregularity. Those polymer samples with % mmmm < 35 were amorphous as revealed by the lack of a DSC melting endotherm. Even an increase in M_w to 75K was not sufficient to produce crystallizable material (entry 4).

Comparison of our results to that of a sample previously characterized by Chien (entry 3 vs 8)[4,6] reveals that for a given degree of stereoregularity, polymer MW does not significantly affect the degree of crystallinity. However, the tensile properties are noticeably dependent on MW (vide infra).

Elastomeric Properties. The tensile properties of some of these materials were briefly investigated. All samples were compression molded at 120 °C and 300 psig followed by cooling to room temperature over 4 h. Test specimens were further annealed at room temperature for 2 days prior to analysis.

The properties are summarized in Table 5. Excellent elastic recoveries were exhibited by a number of these samples, particularly at low strain, but recovery following break was also generally good. In particular, the polymers produced using catalyst **6** combine excellent elastomeric properties (high ultimate extensions with excellent elastic recoveries) with toughness. The lower molecular weight and less stereoregular polymers produced using catalyst **4** were inferior. The samples were more easily deformed and lacked significant mechanical strength on extension and, as well, showed poor or no recovery at moderate strains. The results of Chien indicate that formation of higher MW polymer results in an improvement in the tensile properties when the degree of crystallinity is similar (Table 5, entry 3 vs 8).[7] It thus appears that the production of high MW polymer is crucial for good elastomeric properties provided measurable crystallinity is present (vide supra).

Conclusions

The results of this study have demonstrated that the minimal requirement of having two inequivalent sites for monomer coordination and insertion in metallocene catalysts is not a sufficient condition for the preparation of elPP. In particular, high MW polymer (M_w > 50K) must be produced to obtain polymer with good elastomeric properties, and on the basis of the results summarized here, control of polymer stereoregularity is paramount in generating measurable crystallinity.

Catalysts such as **6** and to a lesser extent **4** are attractive candidates for further study; they combine reasonable productivity with greatly enhanced catalytic stability—a feature that will lend itself to the production of significant quantities of elPP for more detailed mechanical testing.

We conclude on a cautionary note: The physical properties of elPP as revealed by this study suggest that attempts to increase, e.g., upper use temperature by employing more stereoregulating catalysts of the type studied here may be paradoxically accompanied by a gradual(?) diminution of elastomeric properties; that is, the division between elPP and, e.g., iPP may not be as fundamental as one might think based on the proposed (i.e., block) microstructure of the former polymer.[16]

In the following paper we address whether the microstructure invoked in the literature is in fact reasonable.

Experimental Section

General Synthetic and Characterization Procedures. All chemicals were reagent grade and purified as required. Hafnium tetrachloride (99.99%) was purchased from All Chemie whereas $TiCl_4$ and $ZrCl_4$ were obtained from Aldrich Chemical Co. Methylaluminoxane was purchased as a 10 wt % solution in toluene from Texas Alkyls (Akzo) and the solution evacuated to dryness (10^{-3} mmHg), and the solid MAO was stored in a glovebox and weighed when required. Propylene was chemical grade (99.5%, purchased from Linde Co.) and was deoxygenated and dried by passage through a mixed bed column containing BASF R3-11 catalyst and 4 Å molecular sieves.

Tetrahydrofuran, hexanes, diethyl ether, and toluene were all dried and deoxygenated by distillation from sodium–benzophenone ketyl. Dichloromethane was dried by distillation from calcium hydride. All reactions involving air- or moisture-sensitive reagents or products were conducted under N_2 or Ar, and all glassware was either flame-dried under vacuum or oven-dried prior to use. All air- or moisture-sensitive compounds were stored in either a Vacuum Atmospheres glovebox or a Braun glovebox and used as required.

Solutions of alkyllithium reagents, obtained from Aldrich Chemical Co., were titrated using 1,3-diphenylacetone–*p*-toluenesulfonylhydrazone as described in the literature.[17] Sodium cyclopentadienide was prepared from cyclopentadiene and sodium hydride in THF solution and was obtained as a solid by precipitation from hexanes–THF. 6,6-Dimethylfulvene was prepared by the condensation of cyclopentadiene and acetone according to the procedure reported by Stone and Little and was stored at −20 °C prior to use.[18] Solid indenyllithium was prepared from indene and nBuLi in hexanes and was stored in a glovebox prior to use.

^{1}H and ^{13}C NMR spectra were obtained on Bruker AM-250 or AC-200 spectrometers. Chemical shifts are referenced to residual undeuterated solvent. IR spectra were recorded on a Bomem MB100 FT-IR instrument. Mass spectra were measured on a KRATOS MSX-90 instrument at the University of Guelph, Guelph, ON. Elemental analyses were performed by M.H.W. Laboratories of Phoenix, AZ.

Propylene Polymerizations. Polymerizations were conducted in a 1 L Autoclave Engineer Zipperclave stainless steel reactor equipped with an overhead stirrer and a spiral-wound external cooling jacket. The stirring rate was maintained at 1500 rpm for all polymerizations. A coolant mixture (ethylene glycol/water) was passed through the reactor jacket with the use of a Neslab RTE-110 refrigerating circulator. Temperature control (±0.5 °C) was maintained by using an RTD-220 temperature controller (Neslab) with a remote sensor (Neslab RS2) which monitored the reaction solution temperature and cycled the circulator heater on or off as required. The flow of monomer into the reactor (to maintain a given head pressure) was measured using a mass flow meter and a mass flow controller (Matheson Multiple Dynablender-8219). The progress of polymerizations was monitored (monomer flow rate(s) and internal temperature) using an IBM PC (50286) with a data acquisition card and associated software.

MAO was transferred into the reactor by flushing 500 mL of toluene through a 50 mL sample bomb containing a solution of MAO (typically 0.6 g in 20 mL of toluene). Polymerizations were initiated by injection of a solution of the metallocene in 5.0–10.0 mL of toluene into the reactor that contained MAO and 500 mL of toluene which was presaturated with monomer at the specified temperature and pressure. Polymerizations were terminated by venting the monomer and rapidly draining the polymer slurry into a small volume of methanol. The solvent was partially removed using a rotary evaporator, and the polymer was extracted (entirely) into refluxing toluene using a Soxhlet extractor to remove catalyst and aluminoxane residues. The toluene was then removed using a rotary evaporator. In all cases, the polymer samples were further dried in vacuo at 60 °C and 10^{-2} mmHg overnight.

For polymerizations conducted in liquid propylene, the following procedure was followed: A 150 mL Parr reactor, containing MAO dissolved in 5.0 mL of toluene, was cooled to −50 °C, and propylene was condensed into the reactor for a specified time at a given monomer flow rate. After approximately 50 mL of liquid propylene had been added, the metallocene, dissolved in 5.0 mL of toluene, was injected and the reactor quickly warmed (over 15 min) to the specified polymerization temperature and maintained at this temperature for a specific time. Polymerizations were stopped by cooling the reactor to −50 °C, venting the monomer, and adding methanol. The polymer was isolated and dried in the usual fashion.

Polymer Characterization. ^{13}C NMR spectra of poly(propylene) were obtained in 1,2,4-trichlorobenzene solution (~10 wt %) that contained 0.1 wt % Irganox 1010 and 10% v/v C_6D_6 for field-frequency locking, at 120 °C. A pulse width of 30° was employed with inverse-gated decoupling. A spectral width of 160 ppm was employed for a total repetition time of 3.2 s. Typically, about 10 000 transients were accumulated for each sample. The spectra were integrated to determine the percentage of the main mmmm pentad at 19.7_1 ppm to the total pentad intensity and, when necessary, corrected for the presence of signals due to end groups or regioirregularities.[13]

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using a Waters 150C chromatograph equipped with a differential refractive index detector (concentration) and a Viscotek Model 100 continuous differential viscometer and an LDC/Milton Roy KMX-6 low-angle laser light scattering detector. Jordi mixed-bed and 1000 Å linear columns (1000–25 000 and 25 000–1 000 000) were employed, and samples (0.1% by weight in 1,2,4-TCB containing 0.1% Irganox 1010) were eluted with 1,2,4-TCB at 135 °C at a flow rate of 1.5 mL/min. The columns were calibrated using monodisperse polystyrene standards, and the molecular weight values reported are absolute values.

DSC measurements were conducted using a DuPont Instruments Series 99 thermal analyzer (previously calibrated with indium metal) at a heating rate of 10 °C/min from 15 to 170 °C. Prior to analysis, polymer samples were heated to 120 °C and cooled at 1 °C/min to room temperature and then annealed at room temperature for several days.

Tensile properties were measured on dumbbell-shaped test specimens (0.64 cm × 2.54 cm × 0.16 cm, with a gauge length of 0.80 cm) according to ASTM D412 at a strain rate of 25.5 cm/min using an Instron tensile tester at 25 °C. Test specimens were compression molded at 120 °C and 300 psig, allowed to cool to room temperature and over 4 h, and annealed at room temperature and for at least 2 days prior to analysis. The tensile set was determined by elongating the test specimen to 150% elongation and immediately releasing the test specimen from the applied stress. The tensile set was defined as 100 × $(l_f - l_i)/l_i$, where l_i and l_f were the initial and final lengths, respectively, between bench marks on the sample, and was measured 2 min after the applied stress was released.

Preparation of $Me_2C[Ind][Cp]$ (7). Indenyllithium (3.4 g, 27.9 mmol) was placed in a 1 L round-bottomed flask and cooled to −78 °C. Tetrahydrofuran (250 mL) was slowly added and the solution warmed briefly to dissolve the anion. The flask was cooled to −78 °C and 6,6-dimethylfulvene (3.55 g, 33.4 mmol) was added dropwise over 5 min. The solution was stirred for 30 min and allowed to warm to 0 °C. The reaction was quenched by addition of saturated aqueous ammonium chloride (10 mL). The solution was diluted with 200 mL of pentane, extracted sequentially with H_2O and brine, and then dried over $MgSO_4$. The solution was filtered and the solvent was removed using a rotary evaporator, giving a pale orange oil (6.19 g, 97%). The ligand was purified by flash chromatography (silica gel 60) with hexane as the eluent, giving a clear oil (84%). The product was a mixture of two stereoisomers (1.6:1). IR (NaCl, neat); 3067.6, 3017.9, 2968.2, 2932.9, 2882.12, 1600.5, 1569.2, 1520.5, 1461.5, 1394.6, 1377.9, 1358.7, 1303.7, 1255.6, 1215.1, 1193.6, 1154.6, 1111.9, 1097.3, 1010.3, 977.7, 952.7, 933.3, 897.8, 871.6, 809.9, 766.8, 721.6, 699.28, 681.6, 650.9, 626.6 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 7.67−7.55 (m, 2H), 7.54−7.40 (m, 2H), 7.38−7.25 (m, 4H), 6.65−6.60 (m, 1H), 6.60−6.45 (m, 4H), 6.45−6.35 (m, 3H), 3.52 (pseudo d, 4H), 3.20 (pseudo d, 2H), 2.95 (pseudo q, 2H), 2.95 (pseudo q, 2H), 1.79 (s, 6H), 1.78 (s, 6H). ^{13}C NMR (50.0 MHz, $CDCl_3$): δ (ppm) 156.4, 154.0, 151.9, 151.1, 145.2, 145.1, 144.0 (2C), 133.4, 131.8, 131.2, 126.9, 126.4, 125.6, 125.5, 124.1, 123.9, 123.6, 122.0, 121.8, 41.1, 40.9, 38.2, 37.4, 37.1, 37.0, 28.9, 27.8.

Preparation of $Me_2C[Ind][Cp]Li_2$ (8). The propylidene-bridged ligand (1.55 g, 6.97 mmol) was dissolved in 50 mL of Et_2O, and nBuLi (5.86 mL, 14.64 mmol) was added dropwise over 30 min at −78 °C. The solution was allowed to warm to room temperature and the solvent was removed in vacuo, giving a pale yellow solid. The salt was washed with 2 × 10 mL of hexanes, filtered, and dried in vacuo, giving a white solid (1.55 g, 95%).

Preparation of $Me_2Si[Ind][Cp]$ (9). Indenyllithium (5.50 g, 45 mmol) was dissolved in Et_2O (30 mL) at −78 °C and allowed to warm to room temperature. Dichlorodimethylsilane (10.9 mL, 90 mmol) was dissolved in Et_2O (40 mL) and cooled to 0 °C. The clear, colorless indenyl anion solution was added dropwise to the dichlorodimethylsilane solution over 1.5 h. The solution was stirred briefly, and the solvent and residual Me_2SiCl_2 were removed in vacuo, giving (1-indenyl)dimethylchlorosilane as a colorless oil. Sodium cyclopentadienide (NaCp) (3.97 g, 45 mmol) was dissolved in a mixture of Et_2O (25 mL) and THF (10 mL). The NaCp solution was added slowly over 30 min to the solution of the silyl chloride in Et_2O (50 mL) at 0 °C. The solution was warmed to room temperature briefly, cooled to 0 °C, and quenched by addition of H_2O (50 mL). The organic layer was washed successively with H_2O and brine and then dried over $MgSO_4$. The solution was filtered and the solvent removed in vacuo, giving a pale yellow oil (9.87 g, 92%). IR (NaCl, neat): 3113, 3068, 2960, 2898, 2360, 2337, 1941, 1901, 1830, 1697, 1624, 1536, 1453, 1407, 1382, 1361, 1344, 1251, 1220, 1191, 1144, 1113, 1091, 1063, 1024, 975, 952, 907, 827, 800, 765, 717, 691, 634 cm^{-1}. The product was a mixture of stereoisomers, with the major isomer having the following spectroscopic data. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 7.67−7.61 (m, 2H), 7.55−7.25 (m, 2H), 7.12 (ddd, J = 5.3, 1.9, 0.6 Hz, 1H), 6.84 (dd, J = 5.3, 1.9 Hz, 1H), 6.81−6.53 (m, 3H), 6.53−6.28 (m, 1H), 3.60−3.40 (m, 1H), −0.05 (s, 3H), −0.13 (s, 3H). ^{13}C NMR (50.0 MHz, $CDCl_3$): δ (ppm) 144.7, 144.2, 135.2, 132.7, 130.8, 129.5, 125.1, 123.9, 122.9, 121.2, 49.8, 46.3, −4.8, −6.2. MS (EI): 238 (M^+, $^{35}Cl^{28}Si$).

Preparation of $Me_2Si[Ind][Cp]Li_2$ (10). The silylene-bridged ligand (11.69 g, 49 mmol) was dissolved in hexane (100 mL) and cooled to −78 °C. *n*-Butyllithium (41.2 mL, 2.5 M in hexanes, 10.3 mmol) was added dropwise over 15 min. The solution was allowed to warm to room temperature and stirred for 12 h. The yellow solution was filtered using a Schlenk apparatus, and the precipitate washed with 2 × 20 mL of hexanes, giving the salt as a white solid (11.5 g, 94%).

Preparation of $Me_2X[Ind][Cp]MCl_2$ Metallocenes (2–6). The procedure for preparing compounds **2–6** is similar to that reported by Spaleck with slight modifications.[2h]

Preparation of $Me_2C[Ind][Cp]TiCl_2$ (2). Titanium tetrachloride (0.50 g, 2.14 mmol) was diluted in CH_2Cl_2 (3.75 mL) at 0 °C and quickly added to a suspension of the dilithio salt (**8**) in CH_2Cl_2 at −78 °C. The dark-colored solution was allowed to warm to room temperature and the solvent removed in vacuo. The crude material was extracted into toluene, concentrated, and passed through Biobeads (SX-2) using toluene as the eluent. The green band was collected and the solvent removed in vacuo, giving a green solid (0.03 g, 4%). IR (KBr): 3073, 3001, 1794, 1702, 1607, 1530, 1476, 1441, 1410, 1376, 1354, 1295, 1254, 1213, 1154, 1082, 1047, 987, 929, 887, 873, 848, 825, 812, 744, 719, 591, 573, 545, 495, 468, 440, 419 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.64 (dt, J = 8.5, 1.0 Hz, 1H), 7.59 (dd, J = 8.9, 0.9 Hz, 1H), 7.47 (ddd, J = 8.5, 6.7, 0.7 Hz, 1H), 7.19 (dd, J = 3.5, 0.9 Hz, 1H), 7.02 (ddd, J = 8.9, 6.7, 1.1 Hz, 1H), 6.67–6.77 (m, 2H), 5.77 (d, J = 3.5 Hz, 1H), 5.56 (t, J = 2.5 Hz, 2H), 2.25 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) 136.2, 128.7 (2C), 128.2, 127.6, 126.9, 124.9, 124.3, 119.6, 115.8, 111.4, 111.0, 109.3, 99.1, 38.2, 25.7, 25.0. MS (EI): 338 (M^+, $^{48}Ti^{35}Cl_2$). Elemental analysis calculated for $C_{17}H_{16}Cl_2Ti$: C, 60.21; H, 4.76. Found: C, 60.37; H, 4.88.

Preparation of $Me_2C[Ind][Cp]ZrCl_2$ (3). The dilithio salt **8** (1.55 g, 6.62 mmol) and $ZrCl_4$ (1.54 g, 6.62 mmol) were combined in a 250 mL two-necked round-bottomed flask and the flask was cooled to −78 °C. Methylene chloride (100 mL) was added dropwise and the suspension stirred for 30 min. The white suspension was allowed to warm slowly over 2.5 h to −35 °C and the temperature was maintained at −35 °C for 12 h, giving an orange solution. The solution was allowed to warm to room temperature (no color change). The solvent was removed in vacuo, giving an orange solid. The crude material was extracted with 7 × 2 mL portions of toluene (until most of the orange material was removed). The filtrate was dried in vacuo, giving an orange powder (1.74 g, 69%). Pure material was obtained by recrystallization from benzene. IR (KBr): 3075, 2993, 1823, 1678, 1612, 1527, 1472, 1447, 1407, 1374, 1348, 1325, 1288, 1244, 1208, 1155, 1120, 1076, 1042, 1013, 1004, 985, 928, 886, 862, 846, 808, 752, 743, 725, 704, 634, 555, 532, 495, 464, 438 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) 7.66 (dq, J = 8.8, 1.0 Hz, 1H), 7.62 (dt, J = 8.5, 1.0 Hz, 1H), 7.34 (ddd, J = 8.5, 6.7, 1.0 Hz, 1H), 7.04 (ddd, J = 8.8, 6.7, 1.0 Hz, 1H), 6.84 (dd, J = 3.5, 1.0 Hz, 1H), 6.51 (m, 2H), 6.13 (d, J = 3.5 Hz, 1H), 5.83 (q, J = 2.8 Hz, 1H), 5.7 (q, J = 2.8 Hz, 1H), 2.20 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 130.8, 126.4, 126.2, 126.0, 122.9, 121.4, 120.7, 120.1, 118.1, 113.4, 112.0, 106.0, 104.0, 102.9, 39.0, 26.1, 25.4. MS (EI): 380 (M^+, $^{90}Zr^{35}Cl_2$).

Preparation of $Me_2C[Ind][Cp]HfCl_2$ (4). The dilithio salt **8** (0.50 g, 2.13 mmol) and $HfCl_4$ (99.99%) (0.68 g, 2.14 mmol) were added to a 100 mL round-bottomed flask and cooled to −78 °C. Methylene chloride (50 mL) was added slowly and the suspension stirred at −78 °C for 30 min. The solution was then allowed to warm over 2.5 h to −15 °C and then stirred for 12 h at −15 °C. The yellow suspension was then allowed to warm to room temperature and the solvent removed in vacuo. The crude material was extracted into toluene, giving a bright yellow solid (0.41 g, 41%). Analytically pure metallocene was obtained by recrystallization from benzene. IR (KBr): 3442, 3077, 2976, 2878, 2340, 1678, 1610, 1526, 1475, 1455, 1408, 1378, 1348, 1287, 1248, 1211, 1155, 1140, 1077, 1043, 1008, 982, 929, 865, 813, 768, 751, 727, 494, 460, 441 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) 7.59 (dq, J = 8.9, 1.0 Hz, 1H), 7.48 (dt, J = 8.7, 1.0 Hz, 1H), 7.20 (ddd, J = 8.7, 6.6, 1.0 Hz, 1H), 6.91 (ddd, J = 8.9, 6.6, 1.0 Hz, 1H), 6.63 (dd, J = 3.5, 1.0 Hz, 1H), 6.33 (m, 2H), 5.99 (d, J = 3.5 Hz, 1H), 5.64 (q, J = 2.0 Hz, 1H), 5.55 (q, J = 2.0 Hz, 1H), 2.09 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 140.4, 130.1, 126.3, 125.9, 123.1, 122.3, 120.3, 119.8, 111.7, 109.9, 104.6, 104.2, 103.9, 103.6, 101.7, 39.3, 26.4, 25.8. MS (EI): 470 (M^+, $^{180}Hf^{35}Cl_2$). Elemental analysis calculated for $C_{17}H_{16}Cl_2Hf$: C, 43.47; H, 3.43. Found: C, 43.57; H, 3.55.

Preparation of $Me_2Si[Ind][Cp]ZrCl_2$ (5). Method A. The dilithio salt **10** (1.67 g, 6.65 mmol) and zirconium tetrachloride (1.55 g, 6.65 mmol) were combined and cooled to −78 °C. Dry CH_2Cl_2 (50 mL) was added slowly and the solution allowed to warm to −35 °C over 2 h. The temperature was maintained at −35 °C for 10 h then allowed to warm to room temperature over 2 h. The solvent was removed in vacuo, giving a yellow solid. The crude metallocene was extracted into toluene (ca. 20% yield) and recrystallized from benzene, giving yellow crystals of compound **12** (0.066 g, 2.5%). IR (KBr): 2900.0, 1943.1, 1833.0, 1793.1, 1701.6, 1641.2, 1607.4, 1578.4, 1525.9, 1495.8, 1474.0, 1447.1, 1402.6, 1367.2, 1341.2, 1318.1, 1299.9, 1253.2, 1212.0, 1197.6, 1176.3, 1163.8, 1147.5, 1124.3, 1112.6, 1076.4, 1043.5, 1023.0, 977.6, 962.4, 936.0, 919.8, 903.5, 876.3 cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2): δ (ppm) 7.70 (br d, J = 8.6 Hz, 1H), 7.51 (dd, J = 8.6, 0.6 Hz, 1H), 7.42 (ddd, J = 8.6, 6.7, 0.6 Hz, 1H), 7.11 (ddd, J = 8.6, 6.7, 0.6 Hz, 1H), 7.05 (dd, J = 3.3, 0.6 Hz, 1H), 6.75 (pseudo q, J = 2.6, 1H), 6.71 (pseudo q, J = 2.6, 1H), 6.24 (d, J = 3.3 Hz, 1H), 5.96 (pseudo q, J = 2.4 Hz, 1H), 5.88 (pseudo q, J = 2.4 Hz, 1H), 1.04 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ (ppm) 135.9, 128.3, 127.9, 127.0, 126.6, 126.4, 125.7, 124.8, 115.9, 112.4, 107.8, 91.8, −2.2, −4.2. MS (EI): 396 (M^+, $^{28}Si^{35}Cl_2{}^{90}Zr$).

Method B. A solution of $Zr(NMe_2)_4$ (1.34 g, 5.0 mmol) in toluene (10.0 mL) was added to a solution of ligand **9** (1.19 g, 5.0 mmol) in toluene (5.0 mL) at −40 °C over 5–10 min. The pale yellow solution was warmed to room temperature (2 h) and stirred at room temperature for 3 h. The solvent was removed in vacuo and the oily residue was further dried in vacuo at ca. 50 °C and 0.01 mmHg to provide the crude, bis(dimethylamido) derivative of compound **5** (>90% purity by ^1H NMR, >90% yield).

The bis(dimethylamido) complex was dissolved in CH_2Cl_2 (10.0 mL) and cooled to −78 °C. A solution of anhydrous HCl in CH_2Cl_2 (1.2 M, 8.4 mL, 10.0 mmol) was added dropwise via syringe. The solution was slowly warmed to 0 °C (3 h) and stirred at 0 °C for 3 h. The solvent was removed in vacuo to provide crude product, which was dissolved in a minimal volume of warm toluene. The mixture was filtered, washing with toluene to remove traces of $Me_2NH_2{\cdot}Cl$ and cooled to −20 °C to provide pure material (1.48 g, 75% overall yield from **9**).

Preparation of $Me_2Si[Ind][Cp]HfCl_2$ (6). The dilithio salt **10** (1.60 g, 6.4 mmol) and hafnium tetrachloride (99.99%) (2.05 g, 6.4 mmol) were combined and cooled to −78 °C. Methylene chloride (50 mL) was added slowly and the solution warmed to 0 °C over 4 h. The temperature was maintained at 0 °C for 10 h and then allowed to warm to room temperature over 2 h. The solvent was removed in vacuo, giving a yellow solid. The crude metallocene was extracted into toluene (ca. 10% yield) and recrystallized from benzene, giving bright yellow crystals (0.033 g, 1%). IR (KBr): 3057, 2961, 1790, 1700, 1655, 1524, 1474, 1446, 1398, 1367, 1342, 1320, 1301, 1252, 1211, 1166, 1158, 1148, 1078, 1053, 1039, 963, 907, 875, 828, 796, 752, 712, 683, 673, 629 cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2): δ 7.67 (d, J = 8.6 Hz, 1H), 7.51 (dd, J = 8.6, 0.5 Hz, 1H), 7.39 (dd, J = 8.6, 6.6 Hz, 1H), 7.09 (dd, J = 8.6, 6.6 Hz, 1H), 6.95 (dd, J = 3.1, 0.5 Hz, 1H), 6.68 (pseudo q, J = 2.6 Hz, 1H), 6.63 (pseudo q, J = 2.6 Hz, 1H), 6.20 (d, J = 3.1 Hz, 1H), 5.90 (pseudo q, J = 2.6 Hz, 1H), 5.81 (pseudo q, J = 2.6 Hz, 1H), 1.04 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ 135.1, 127.7, 127.2, 126.7, 126.3, 125.1, 124.8, 119.1, 117.3, 113.6, 109.9, 109.5, 92.1, −2.2, −4.2. MS (EI): 486 (M^+, $^{28}Si^{35}Cl_2{}^{180}Hf$). Elemental analysis calculated for $C_{16}H_{16}SiCl_2Hf$: C, 39.56; H, 3.32. Found: C, 39.40; H, 3.10.

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Supplementary Material Available: Tables of X-ray crystallographic and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters and H atom coordinates, and isotropic thermal parameters for compounds **3** and **5** (20 pages). Ordering information is given on any current masthead page.

References and Notes

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