Organometallics **2000,** *19,* 4095−4103

2-Hetaryl-Substituted Bis(indenyl)zirconium Complexes as Catalyst Precursors for Elastomeric Polypropylene Formation

Thorsten Dreier, Gerhard Erker,* Roland Fröhlich,† and Birgit Wibbeling†

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40,
D-48149 Münster, Germany

Received January 14, 2000

2-Indanone was treated with 2-lithio-5-methylfuran and the addition product dehydrated to yield the 2-(5′-methyl-2′-furyl)-substituted indene **2**. Deprotonation with *n*-butyllithium followed by transmetalation to zirconium gave the bis(2-furylindenyl)$ZrCl_2$ complex **4a**. Subsequent reaction with methyllithium yielded the corresponding bis(2-furylindenyl)$ZrMe_2$ system **6a**. The related bis[2-(5′-methyl-2′-furyl)indenyl]hafnium complexes (**5a**, **7a**) and the bis[2-(5′-methyl-2′-thienyl)indenyl]zirconium and -hafnium complexes **4b**−**6b** were synthesized analogously. In the crystal the bis(2-furylindenyl)$ZrCl_2$ (**4a**) and -$HfCl_2$ (**5a**) complexes exhibit *meso*-like metallocene conformations, as shown by X-ray diffraction. In contrast, the bis(2-furylindenyl)$ZrMe_2$ system (**6a**) shows a chiral, close to C_2-symmetric *rac*-like metallocene conformation in the solid state. Hydrolysis of 2-(5′-methyl-2′-furyl)indene (**2a**) followed by Paal−Knorr pyrrole synthesis of the resulting 1,4-diketone **8** with methylamine gave (5′-methyl-2′-*N*-methylpyrrolyl)indene (**9**), which was deprotonated and transmetalated to yield the substituted bis(2-pyrrolylindenyl)$ZrCl_2$ (**11**), -$HfCl_2$ (**12**), and -$ZrMe_2$ (**13**) complexes. Treatment of the [2-(5′-methyl-2′-furyl)indenyl]- and [2-(5′-methyl-2′-thienyl)indenyl]$ZrCl_2$ systems **4a**,**b** with excess methylalumoxane gave active homogeneous Ziegler catalysts for the production of elastomeric polypropylene. The catalyst derived from **11** yielded only propene oligomers.

Introduction

We have shown that the metallocene conformational equilibrium of a series of 2-terpenyl-substituted bis(indenyl)- and bis(tetrahydroindenyl)$ZrCl_2$ complexes is markedly substituent dependent. Moreover, the stereospecificity of the propylene polymerization process at the homogeneous metallocene Ziegler catalysts derived from these systems seemed to depend on the specific metallocene conformational equilibrium. Thus, the bis(2-neoisomenthylindenyl)$ZrCl_2$ complex, for example, which features a >95% population of the C_2-symmetric bis-central:syn metallocene conformer **A** (see Scheme 1), gave polypropylene with a higher isotacticity (76% *mmmm* at −30 °C) than the catalyst system derived from, for example, bis(2-neomenthylindenyl)-$ZrCl_2$ (24% *mmmm* at −30 °C), which exhibits a markedly lower population of the C_2-symmetric metallocene rotamer **A** in the conformational equilibrium.[1−3]

For bis(2-phenylindenyl)$ZrCl_2$-derived catalysts Waymouth has proposed that an active conformational change between chiral (*rac*) and achiral (*meso*) metallocene rotamers is taking place in the course of the propene polymerization process and leads to the formation of an isotactic/atactic block structure of the resulting polymer, hence determining the specific elastomeric properties of the product derived from these catalyst systems (see the bottom section of Scheme 1).[4,5] In view of the pronounced substituent dependence of the metallocene conformational equilibrium shown in our earlier study (see above), it was tempting to investigate the response of Waymouth's system to specific changes in

---

* To whom correspondence should be addressed. Fax: +49 251 83 36503. E-mail: erker@uni-muenster.de.

† X-ray crystal structure analyses.

[1] Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermühle, D.; Krüger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590−4601.

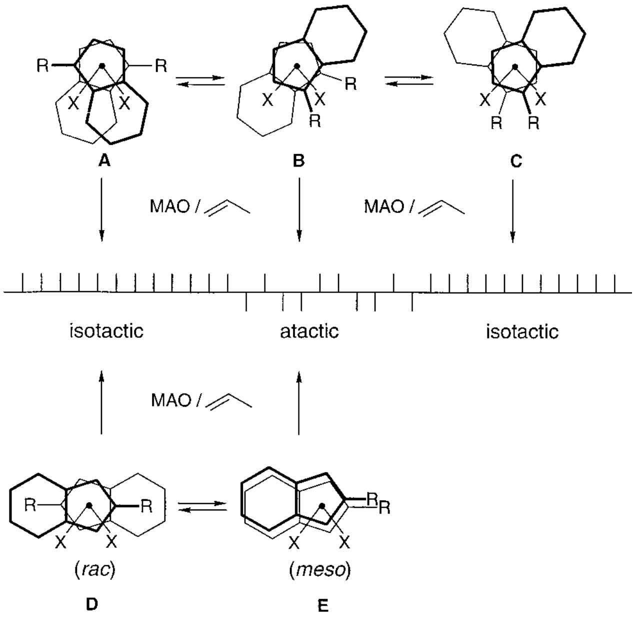
[2] Knickmeier, M.; Erker, G.; Fox, T. *J. Am. Chem. Soc.* **1996**, *118*, 9623−9630. Whether a block structure or a mixture of polymers is formed at these catalyst systems has not yet been unequivocally resolved.

[3] For selected examples, see e.g.: Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422−6433. Dusausoy, Y.; Protas, J.; Renaut, P.; Gautheron, B.; Tainturier, G. *J. Organomet. Chem.* **1978**, *157*, 167−172. Luke, W. D.; Streitwieser, A. *J. Am. Chem. Soc.* **1981**, *103*, 3241−3243 and references therein. Howie, R. A.; McQuillan, G. P.; Thompson, D. W. *J. Organomet. Chem.* **1984**, *268*, 149−154. Howie, R. A.; McQuillan, G. P.; Thompson, D. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213−220. Antinolo, A.; Lappert, M.; F. Singh, A.; Winterborn, D. J. W.; Engelhardt, L. M.; Raston, C.; White, A. H.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1463−1472. Oduka, J. *J. Organomet. Chem.* **1988**, *356*, C43−C46. Broussier, R.; Da Rold, A.; Gautheron, B.; Dromzee, Y.; Jeannin, Y. *Inorg. Chem.* **1990**, *29*, 1817−1822. Mallin, D. T.; Rausch, M. D.; Mintz, E. A.; Rheingold, A. L. *J. Organomet. Chem.* **1990**, *381*, 35−44. Winter, C. H.; Dobbs, D. A.; Zhou, X.-X. *J. Organomet. Chem.* **1991**, *403*, 145−151. See also: Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291−393. Krüger, C.; Nolte, M.; Erker, G.; Thiele, S. *Z. Naturforsch.* **1992**, *47B*, 995−999. Krüger, C.; Lutz, F.; Nolte, M.; Erker, G.; Aulbach, M. *J. Organomet. Chem.* **1993**, *452*, 79−86. Sitzmann, H.; Zhou, P.; Wolmershäuser, G. *Chem. Ber.* **1994**, *127*, 3−9. Okuda, J. *Top. Curr. Chem.* **1991**, *160*, 97−145.

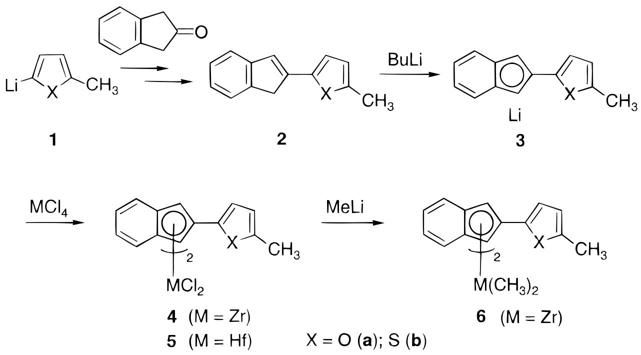
[4] Waymouth, R. M.; Coates, G. W. *Science* **1995**, *267*, 217−219. Hauptmann, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586−11587. See also: Collette, J. W.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.; Su, A. C. L.; Harrell, J. R.; Mülhaupt, R.; Anderson, B. C. *Macromolecules* **1989**, *22*, 3851−3866.

10.1021/om0000313 CCC: $19.00
Publication on Web 09/07/2000

Scheme 1. Conformational Control of Metallocene Reactivity



Scheme 2



the aryl substituents at their 2-indenyl positions. We here report about syntheses to 2-furyl-, thienyl-, and pyrrolyl-substituted analogues and their application in homogeneous metallocene Ziegler catalysis leading to the formation of elastomeric polypropylene.[6]

Results and Discussion

Syntheses and Characterization of the (2-Hetarylindenyl)MX$_2$ Systems. The following scheme was used for the synthesis of the 2-furyl-substituted metallocene system **6a**. 2-Methylfuran was treated with *n*-butyllithium in ether/hexane to yield 5-lithio-2-methylfuran (**1a**). This was then added to 2-indanone. Workup, including elimination of water, gave the furyl-substituted indene **2a** in ca. 60% yield after chromatography (Scheme 2). Subsequent deprotonation then generated the 2-furyl-substituted indenyllithium reagent **3a**, which was transmetalated to zirconium by treatment with zirconium tetrachloride in toluene to give bis[2-(5′-methyl-2′-furyl)indenyl]ZrCl$_2$ (**4a**) in ca. 50% yield as a yellow solid. Treatment of **4a** with 2 molar equiv of methyllithium then furnished the corresponding bis[2-(5′-methyl-2′-furyl)indenyl]Zr(CH$_3$)$_2$ complex **6a**, which was used for an X-ray crystal structure characterization of the system.

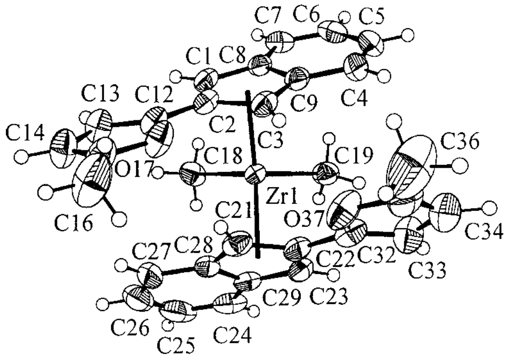


Figure 1. View of the molecular structure of complex **6a**. Selected bond lengths (Å) and angles (deg): Zr1−C18 = 2.267(2), Zr2−C58 = 2.263(2), Zr1−C19 = 2.259(2), Zr2−C59 = 2.258(2), Zr1−C1 = 2.555(2), Zr1−C21 = 2.491(2), Zr2−C41 = 2.547(2), Zr2−C61 = 2.496(2), Zr1−C2 = 2.522(2), Zr1−C22 = 2.523(2), Zr2−C42 = 2.522(2), Zr2−C62 = 2.525(2), Zr1−C3 = 2.495(2), Zr1−C23 = 2.560(2), Zr2−C43 = 2.511(2), Zr2−C63 = 2.565(2), Zr1−C8 = 2.625(2), Zr1−C28 = 2.592(2), Zr2−C48 = 2.620(2), Zr2−C68 = 2.593(2), Zr1−C9 = 2.595(2), Zr1−C29 = 2.620(2), Zr2−C49 = 2.602(2), Zr2−C69 = 2.624(2), C2−C12 = 1.452(3), C22−C32 = 1.463(4), C42−C52 = 1.448(3), C62−C72 = 1.456(3); C18−Zr1−C19 = 97.6(1), C58−Zr2−C59 = 95.1(1).

The X-ray crystal structure analysis of **6a** shows a pseudotetrahedral coordination arrangement around zirconium. The overall geometry is close to C_2 symmetric and thus chiral. The zirconium−methyl σ-bonds amount to 2.267(2) Å (Zr1−C18) and 2.259(2) Å (Zr1−C19), respectively. The indenyl−Cp subunits are η^5-coordinated. The Zr1−C(1−3) bonds are only slightly shorter (2.555(2), 2.522(2), 2.495(2) Å) than the adjacent Zr1−C(8/9) linkages (2.625(2), 2.595(2) Å). The methyl-substituted furyl ring system is attached at the position C2 of the indenyl ring system (C2−C12 = 1.452(3) Å), and it is oriented coplanar with the π-indenyl ring system (θ(C3−C2−C12−O17) = 7.3(3)°; θ(C23−C22−C32−O37) = −179.7(2)°). The furyl substituents have attained one of the two possible coplanar arrangements with the indenyl ligands at the bent metallocene framework where their ring oxygen atoms point toward the narrow backside of the metallocene complex. In the crystal, the 2-furyl-substituted bis(indenyl)ZrMe$_2$ complex **6a** features a metallocene conformation which is very similar to that of the *rac*-bis(2-phenylindenyl)ZrX$_2$ isomer (**7**, see below), which was described by Waymouth et al.[4,5] In this conformation (see Figures 1 and 3) the annelated phenylene rings of the indenyl systems are found oriented almost C_2 symmetric, shielding opposite sectors at the front of the bent metallocene framework above and below the (methyl)C−Zr vectors.

---

(5) Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S. *Macromolecules* **1995**, *28*, 3771−3778. Gauthier, W. J.; Collins, S. *Macromolecules* **1995**, *28*, 3779−3786. Pietsch, M. A.; Rappé, A. K. *J. Am. Chem. Soc.* **1996**, *118*, 10908−10909. Bruce, M. D.; Coates, G. W.; Hauptmann, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174−11182. Maciejewski Petoff, J. L.; Bruce, M. D.; Waymouth, R. M.; Masood, A.; Lal, T. K.; Quan, R. W.; Behrend, S. J. *Organometallics* **1997**, *16*, 5909−5916. Kravchenko, R.; Masood, A.; Waymouth, R. M.; Myers, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 2039−2046. Tagge, C. D.; Kravchenko, R. L.; Lal, T. K.; Waymouth, R. W. *Organometallics* **1999**, *18*, 380−388.

(6) Furan and thiophene annelated Cp−ligand systems (at zirconium) were recently reported: Ewen, J. A.; Jones, R. L.; Elder, M. J.; Rheingold, A. L.; Liable-Sands, L. M. *J. Am. Chem. Soc.* **1998**, *120*, 10786−10787.

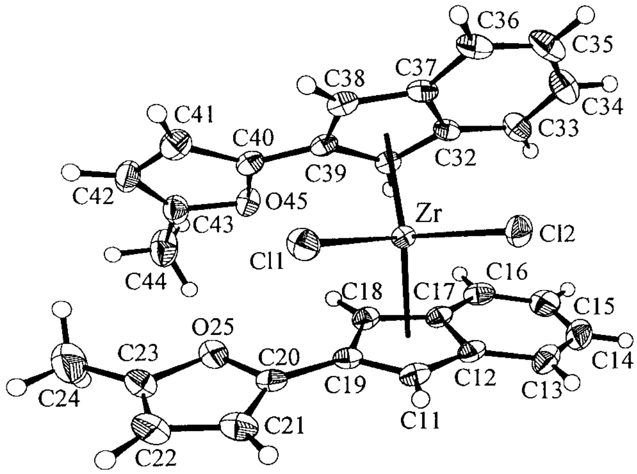


Figure 2. Molecular structure of **4a**. Selected bond lengths (Å) and angles (deg): Zr−Cl1 = 2.4130(6), Zr−Cl2 = 2.4212(7), Zr−C11 = 2.536(2), Zr−C31 = 2.464(2), Zr−C12 = 2.607(2), Zr−C32 = 2.585(2), Zr−C17 = 2.558(2), Zr−C37 = 2.647(2), Zr−C18 = 2.487(2), Zr−C38 = 2.556(2), Zr−C19 = 2.556(2), Zr−C39 = 2.516(2), C19−C20 = 1.443(3), C39−C40 = 1.443(3); Cl1−Zr−Cl2 = 95.76(2).

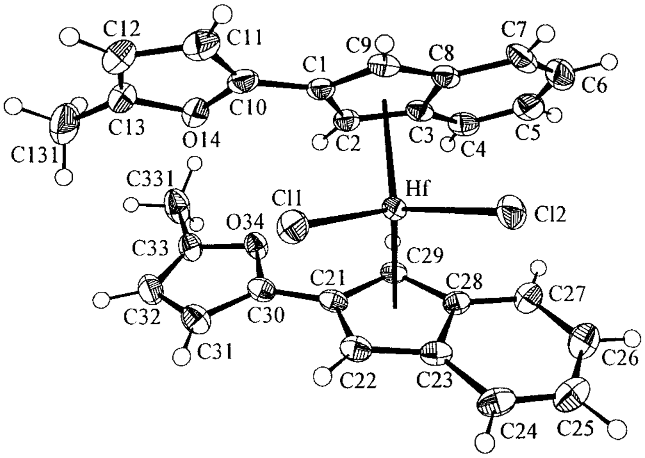


Figure 3. Molecular geometry of complex **5a**. Selected bond lengths (Å) and angles (deg): Hf−Cl1 = 2.3842(7), Zr−Cl2 = 2.3952(8), Hf−C1 = 2.535(3), Hf−C21 = 2.490(3), Hf−C2 = 2.464(3), Hf−C22 = 2.536(3), Hf−C3 = 2.541(3), Hf−C23 = 2.634(3), Hf−C8 = 2.587(3), Hf−C28 = 2.569(3), Hf−C9 = 2.514(3), Hf−C29 = 2.441(3), C1−C10 = 1.435(4), C21−C30 = 1.448(5); Cl1−Hf−Cl2 = 95.36(3).

At the stage of an active metallocene Ziegler catalyst this (2-furylindenyl)Zr conformation would probably favor the formation of isotactic blocks at the polypropylene chain.

In solution, complex **6a** probably undergoes rapid rotation around both the Zr−Cp(ind) vector and the indenyl−furyl σ-bond on the NMR time scale, even at low temperature.[7] Thus, there is a single set of ^{1}H/^{13}C NMR resonances of the indenyl moiety, featuring, for example, single signals of the C1/C3 (δ 95.9), C8/C9 (δ 124.3), C4/C7 (δ 124.5), and C5/C6 (δ 124.6) pairs. The Zr−CH_3 resonance occurs at δ 35.8 (^{13}C)/δ −1.33 (^{1}H NMR), and the furyl methyl group signal is observed at δ 13.9 (^{13}C)/2.45 (^{1}H). Analogous spectroscopic behavior due to dynamic symmetrization on the NMR time scale was observed for the bis(2-furylindenyl)zirconium dichloride complex **4a** and also for its parent (2-furylindenyl)lithium reagent, **3a**[8] (for details see the Experimental Section). The bis[2-(5′-methyl-2′-furyl)-indenyl]$ZrCl_2$ complex **4a** was also characterized by X-ray diffraction. In contrast to **6a** (see above) the zirconium dichloride complex exhibits a *meso*-like conformation in the solid state. Characteristically, both 2-methylfuryl substituents are oriented in the same lateral sector of the bent metallocene moiety above and below the major metallocene σ-ligand plane, although the species is not crystallographically C_s symmetric. The furyl rings are arranged coplanar with the η^5-indenyl planes. The furyl oxygen atoms point toward the narrow backside of the bent metallocene wedge. The annelated phenylene rings of the indenyl ligand systems are oriented analogously above and below the Zr−Cl2 vector (2.4212(7) Å; distance of the phenylene centroids to Cl(2) 3.257 and 3.734 Å).

The analogous methylthienyl-substituted metallocenes were synthesized in a similar way. 2-Indanone was treated with 5-lithio-2-methylthiophene (**1b**) to yield the thienyl-substituted indene system **2b** (40% isolated yield). Deprotonation with *n*-butyllithium followed by treatment with $ZrCl_4$ gave bis[2-(5′-methyl-2′-thienyl)-indenyl]$ZrCl_2$ (**4b**); subsequent treatment with methyllithium furnished the corresponding zirconium dimethyl complex **6b**.

For the thienyl-substituted complex **6b** we have also observed the NMR signals of symmetry-equivalent pairs of indenyl CH 1/3 (δ 97.9 (^{13}C), δ 6.04 (^{1}H)), 4/7 (δ 124.7, 7.09), and 5/6 (δ 124.9, 7.02) NMR resonances, which indicates rapid rotation around the 2′-thienyl/2-indenyl vector as well as rapid metallocene conformational equilibration on the NMR time scale.

The hafnium complex **5a** was prepared by treatment of the (furylindenyl)lithium reagent **3a** with hafnium tetrachloride in toluene at low temperature. The pure complex **5a** was obtained in low yield (ca. 10%) after crystallization from toluene at −20 °C. The X-ray crystal structure analysis of **5a** (see Figure 3) shows this metallocene complex in a different conformational arrangement than **6a** (see above and Figure 1) but analogous to **4a** (see Figure 2). In the crystal, complex **5a** favors a *meso*-like arrangement in which both the annelated phenylene groups point toward the same lateral sector at the bent metallocene wedge, and both the thienyl substituents are oriented on opposite sides of the metallocene framework. The conformation is distorted from the ideal C_s symmetry but chemically can be regarded as an idealized *meso*-metallocene conformation (equivalent to the *meso* conformation **E** in Scheme 1). The furyl substituents are again oriented in plane with the indenyl ligands (dihedral angles θ(C2−C1−C10−C11) = −175.5(3)°, θ(C22−C21−C30−O34) = 176.7(3)°), and the furyl oxygen atoms point toward the backside of the bent metallocene wedge. The hafnium−chloride bond lengths amount to 2.384(1) Å (Hf−Cl1) and 2.395(1) Å (Hf−Cl2), the Cl1−Hf−Cl2 angle is 95.4(1)°. The observed conformation makes the space at the front side of the bent metallocene **5a** rather open and,

---

(7) Krüger, C.; Lutz, F.; Nolte, M.; Erker, G.; Aulbach, M. *J. Organomet. Chem.* **1993**, *452*, 79−86. Fritze, C.; Knickmeier, M.; Erker, G.; Zaegel, F.; Gautheron, B.; Meunier, P.; Paquette, L. A. *Organometallics* **1995**, *14*, 5446−5449.

(8) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776−8789.

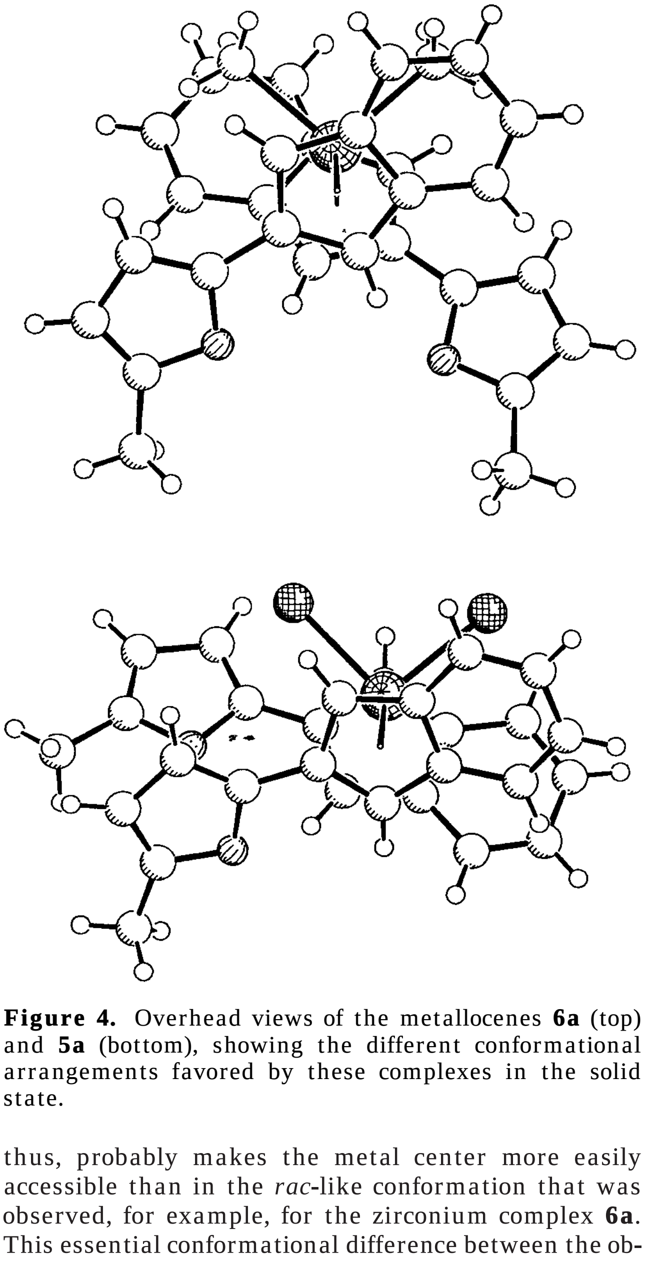


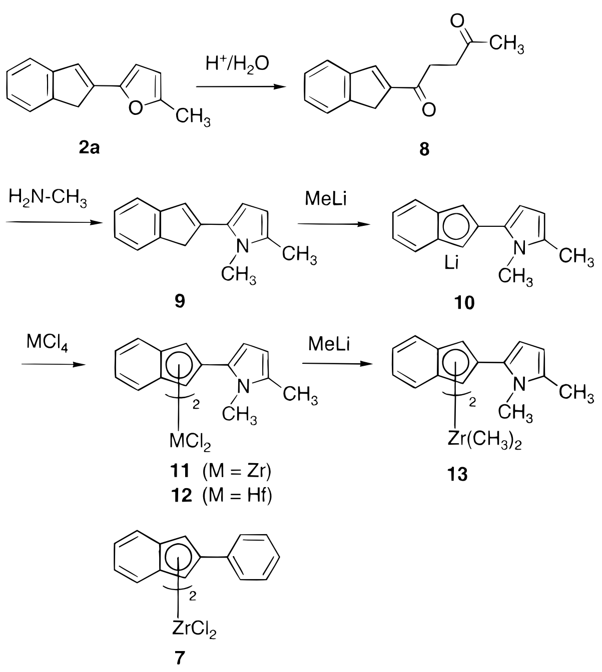
Figure 4. Overhead views of the metallocenes **6a** (top) and **5a** (bottom), showing the different conformational arrangements favored by these complexes in the solid state.

thus, probably makes the metal center more easily accessible than in the *rac*-like conformation that was observed, for example, for the zirconium complex **6a**. This essential conformational difference between the observed structures of the complexes **6a** ($MX_2 = Zr(CH_3)_2$), **4a** ($MX_2 = ZrCl_2$), and **5a** ($MX_2 = HfCl_2$) becomes apparent in the projections depicted in Figure 4.

In solution, again rapid conformational equilibration of complex **5a** was observed by NMR spectroscopy at ambient temperature.

A different synthetic pathway was developed for the preparation of the related pyrrolyl-substituted bis(indenyl)zirconium and -hafnium derivatives. 2-(5′-Methyl-2′-furyl)indene (**2a**) was hydrolyzed at 120 °C in H_2SO_4/acetic acid[9] to yield the corresponding substituted 1,4-diketone **8** (characterized by X-ray diffraction; for details see the Experimental Section). Paal−Knorr pyrrole synthesis was then achieved by treatment of **8** with methylamine in ethanol at reflux temperature to give the (*N*-methylpyrrolyl)indene system **9** (ca. 50% isolated). Deprotonation of **9** was achieved by treatment with methyllithium in diethyl ether. The resulting ((*N*-methylpyrrolyl)indenyl)lithium reagent **10** was then transmetalated by reacting it with zirconium tetrachloride to give the corresponding metallocene dichloride complex **11**. Methylation was achieved by treatment with 2 molar equiv of methyllithium to give **13**. Treatment of hafnium tetrachloride with 2 molar equiv of **10** led to the formation of the related bis[2-(5′-methyl-2′-*N*-methylpyrrolyl)indenyl]hafnium dichloride complex **12**. In a number of cases depicted in the synthetic Schemes 2 and 3 the yields of the final products were only moderate or low because some of these complexes were difficult to obtain pure and required tedious workup.

Scheme 3



Formation of Elastomeric Polypropylene. Propene polymerization reactions were carried out using the furyl-, thienyl- and pyrrolyl-containing bis(2-hetarylindenyl)zirconocene dichloride complexes **4a**,**b** and **11** as catalyst precursors (see Schemes 2 and 3).[10,11] In addition, a homogeneous Ziegler catalyst derived from Waymouth's bis(2-phenylindenyl)zirconocene dichloride system **7** (see Scheme 3) was employed for comparison.[4,5] The metallocene dichlorides were activated by treatment with a large excess of methylalumoxane in toluene (Al:Zr ≈ 1000−2000; see Table 1).[12] Propene polymerization reactions were carried out at three temperatures, 20, 0, and −20 °C, and the polypropylenes isolated from the reaction mixtures were characterized

---

[9] Stetter, H.; Basse, W.; Kuhlmann, H.; Landscheidt, A.; Schlenker, W. *Chem. Ber.* **1977**, *110*, 1007−1019. Weiss, A. Doctoral dissertation, Universität Münster, 1993.

[10] Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem.* **1995**, *107*, 1255−1283; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170.

[11] See the following articles and references cited therein: Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325−387. Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57. Aulbach, M.; Küber, F. *Chem. Unserer Zeit* **1994**, *28*, 197. Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270. See also: Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Fröhlich, R.; Kotila, S. *Angew. Chem.* **1995**, *107*, 1867−1869; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755−1757. Karl, J.; Erker, G.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 11165−11173. Karl, J.; Dahlmann, M.; Erker, G.; Bergander, K. *J. Am. Chem. Soc.* **1998**, *120*, 5643−5652. Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345−354. Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 13−18.

[12] Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99−149.

Table 1. Propene Polymerization with Bis(2-arylindenyl)$ZrCl_2$/MAO and Bis(2-hetarylindenyl)$ZrCl_2$/MAO Catalyst Systems

precursor	Al:Zr	*T* (°C)	activity[a]	polym	% *mmmm*[b]	M_w	M_w/M_n
4a	1907	20	159	PP1	17	*c*	
4b	1681	20	130	PP2	16	*c*	
11	1166	20	17	PP3	2	*c*	
7	1566	20	161	PP4	9	*c*	
4a	1589	0	169	PP5	18	243 000	2.6
4b	1441	0	158	PP6	17	155 000	2.6
11	991	0	51	PP7	3	*c*	
7	1566	0	181	PP8	12	*c*	
4a	1589	−20	392	PP9	19	720 000	2.8
4b	1681	−20	329	PP10	18	585 000	2.4
11	991	−20	59	PP11	4	3 600	2.3
7	2088	−20	423	PP12	13	600 000	2.5

[a] In units of kg of polymer/((mol of Zr) bar h); averaged values from two experiments each. [b] ^{13}C NMR methyl pentad. [c] Not determined.

by ^{13}C NMR spectroscopy (methyl group pentad analysis).[13,14] Molecular weight measurements by GPC were carried out for six representative samples (see Table 1).[15]

From the data compiled in Table 1 a few trends become apparent for the polymerization reactions carried out by this series of catalyst systems. The activities of the **4a**/MAO, **4b**/MAO, and **7**/MAO metallocene Ziegler catalyst systems, bearing furyl, thienyl, and phenyl substituents at the 2-positions of their indenyl ligands, respectively, are very similar. For all three temperatures they are consistently slightly larger for the phenyl-substituted system than for the furyl and thienyl systems, although these differences never become large. It is the 2-pyrrolyl-substituted metallocene catalyst that really falls off in activity. In the complete series of experiments the overall integral catalyst activities grew larger with decreasing temperature. The molecular weights were largest with the furyl-substituted catalyst system, although the differences in the phenyl and thienyl derivatives was not pronounced. Again, it is the 2-pyrrolyl-substituted catalyst system (**11**/MAO) that behaves substantially differently, leading only to the formation of an atactic propene oligomer, even at −20 °C. The isotacticities of the polypropylene produced at the (2-phenylindenyl)Zr catalyst system is in a range between 9 and 13% *mmmm* intensity, increasing slightly with a decreasing polymerization temperature.[16] The ^{13}C NMR methyl pentad *mmmm* intensity value is markedly higher for the polypropylenes formed at the (2-furylindenyl)$_2$Zr- and (2-thienylindenyl)$_2$Zr-derived catalyst systems, ranging from 16 to 19% with a slight tendency to increase with decreasing temperature. Polymer PP9 was separated in pentane-, hexane-, and heptane-soluble fractions with only slightly different isotacticities (15%, 18%, and 20% *mmmm* intensities, respectively).[17]

Table 2. Stress/Strain Data of the Elastomeric Polypropylenes Obtained at the Homogeneous 4a/MAO, 4b/MAO, and 7/MAO Metallocene Ziegler Catalyst Systems

	ϵ_{rest}[b]					
	polym sample, catalyst precursor (polym temp, °C)					
ϵ_{tot}[a]	PP5, **4a** (0)	PP6, **4b** (0)	PP8, **7** (0)	PP9, **4a** (−20)	PP10, **4b** (−20)	PP12, **7** (−20)
100	28	35	46	15	13	21
200	69	86	106	33	32	49
300	120	156	180	59	56	91
400	185	240	270	95	87	147
500	261	341	374	138	123	220
600	360	*c*	488	183	159	299
700	476		609	233	198	401
800	612		731	286	240	494
900	731		854	354	283	624
1000	839		974	425	338	737
1100	*c*		1091	528	412	824
1200			1200	603	484	939
1300			c	697	552	1061
1400				779	606	1172
1500				874	673	1279

[a] In percent; 100% means double elongation relative to the original length of the sample. [b] In percent; 0% means restoration of the original length after the elongation process. [c] Sample torn apart.

The higher isotactic polypropylenes formed at the new **4a**/MAO and **4b**/MAO catalysts showed slightly improved elastomeric properties as compared to the **7**/MAO literature system. This becomes apparent from an inspection of the data presented in Table 2 and a comparison of the stress/strain curves of the first four elongation experiments of the polypropylenes PP9 and PP12, formed at the **4a** (furyl)/MAO and **7** (phenyl)/MAO Ziegler catalyst systems at −20 °C, which are depicted in Figure 5. The latter shows recovery to a ca. 96% elongated state (i.e. ca. 2 times longer than the starting sample length) of PP9 after pulling it to 400% of its original length. In contrast, sample PP12 is relaxed to ca. 150% (i.e. 2.5 times the original lengths) after a 400% elongation. Higher elongations result in even more pronounced differences between the elastomeric polypropylenes derived from the **4a**/MAO, **4b**/MAO, and **7**/MAO series of catalyst systems (see Table 2). From these data it seems that the elastomeric performance of the polypropylene obtained from the furyl-substituted catalyst overall falls in the same range as that obtained from the phenyl-substituted catalyst system. The (2-thienylindenyl)Zr-derived metallocene Ziegler catalyst system forms a slightly improved polypropylene elastomer.

This study shows that hetaryl-containing bis(2-substituted indenyl) group 4 metallocene complexes are readily available by straightforward synthetic routes. Their conformational structures, as far as this can competently be judged from the X-ray crystal structure analyses of the selected examples presented in this account, seem to be equivalent to the previously re-

---

[13] Determined by ^{13}C NMR methyl pentad analysis: Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173−182. Sheldon, R. A.; Fueno, T.; Tsuntsuga, R.; Kurukawa, J. *J. Polym. Sci., Part B* **1965**, *3*, 23−26. Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules* **1975**, *8*, 687−689. Farina, M. *Top. Stereochem.* **1987**, *17*, 1−111.

[14] For the statistical treatment see: Inoue, J.; Itabashi, Y.; Chujo, R.; Doi, Y. *Polymer* **1984**, *25*, 1640−1644. Erker, G.; Nolte, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1989**, *101*, 642−644; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 628−629.

[15] We thank Dr. C. Fritze and Dr. J. Schottek, Axiva GmbH, Frankfurt, Germany, for helping us with these measurements.

[16] A 6% *mmmm* pentad relative intensity would be expected for a completely atactic material. For the influence of 2-indenyl aryl substituents on polypropylene tacticity see e.g.: Witte, P.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 4147−4155.

[17] Hu, Y.; Krejchi, M. T.; Shah, C. D.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 6908−6916. Maciejewski Petoff, J. L.; Agoston, T.; Lal, T. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11316−11322 and references therein.

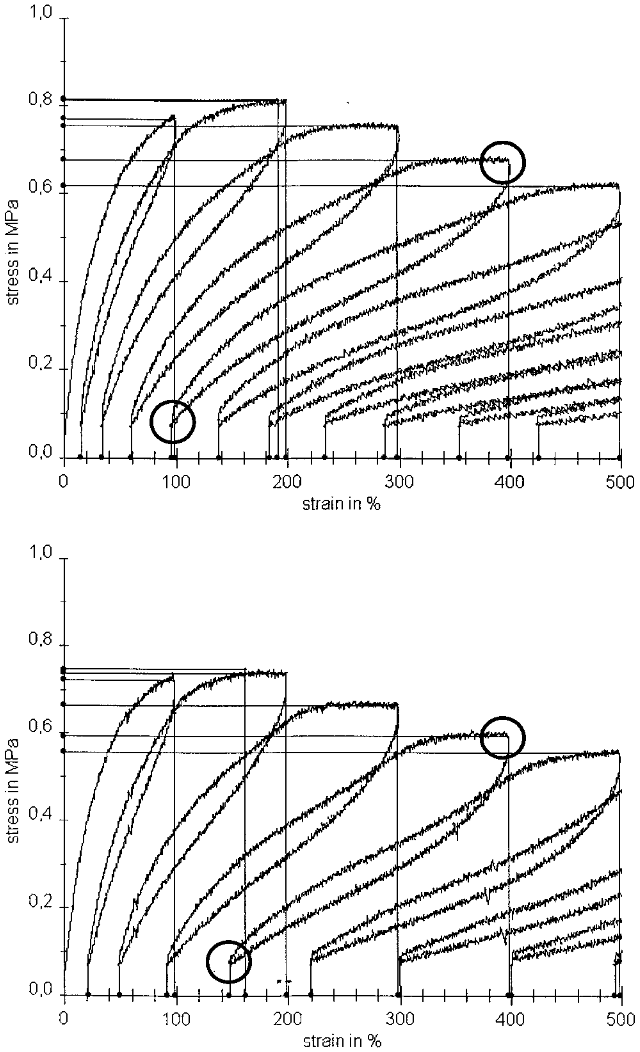


Figure 5. Comparison of a selected segment of the stress/strain curves of the elastomeric polypropylenes PP9 (top) and PP12 (bottom) obtained at −20 °C at the **4a**/MAO and **7**/MAO catalyst systems, respectively.

ported bis(2-arylindenyl)MX_2 systems, namely showing *rac*- and *meso*-type rotamers, here found isolated in the crystalline samples investigated. As expected, elastomeric polypropylenes are formed at the bis(2-furylindenyl)- and bis(2-thienylindenyl)$ZrCl_2$ (**4a**,**b**) derived catalyst systems. Their elastomeric features seem to be slightly improved, which might be due to their increased isotacticity (by ca. a factor of 2) relative to the polypropylene formed at the previously reported (2-phenylindenyl)$ZrCl_2$ derived catalyst. We hope to eventually get a closer insight into the dynamic conformational features of catalysts, which produce elastomeric α-olefin polymers, by using systems bearing a variety of hetaryl substituents at their indenyl ligands. Such investigations are currently being carried out in our laboratory.

Experimental Section

Reactions were carried out under an argon atmosphere using Schlenk-type glassware or in a glovebox. Solvents (including the deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. NMR spectra were recorded on a Bruker AC 200 P NMR spectrometer (^{1}H, 200 MHz; ^{13}C, 50 MHz) at 300 K, a Bruker AMX 400 at 300 K, or a Varian Unity Plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 150 MHz) at 298 K.

5-Lithio-2-methylfuran (1a). *n*-Butyllithium (37.8 mL, 60.4 mmol, 1.6 M in hexane) was added to a stirred solution of 2-methylfuran (4.96 g, 60.4 mmol) in 70 mL of diethyl ether. After the mixture was stirred for 12 h at room temperature, the solvent was removed under reduced pressure and the crude product was used for the reaction with 2-indanone. ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8 10/1): δ 6.72 (s, 1H, 4-H), 6.07 (s, 1H, 3-H), 2.36 (s, 3H, CH_3). ^{13}C NMR (benzene-d_6/tetrahydrofuran-d_8 10/1): δ 154.5 (C, C-5), 125.7 (CH, C-4), 121.2 (C, C-2), 105.1 (CH, C-3), 13.9 (CH_3).

5-Lithio-2-methylthiophene (1b). Analogously as described above, 2.97 g (30.3 mmol) of 2-methylthiophene was reacted with 18.8 mL (30.3 mmol, 1.6 M in hexane) of *n*-butyllithium in 100 mL of diethyl ether at room temperature overnight. After removal of the solvent the crude product was used for the reaction with 2-indanone. ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8 10/1): δ 7.48 (d, 1H, 3-H, ^3J = 2.6 Hz), 7.17 (m, 1H, 4-H), 2.71 (s, 3H, CH_3).

2-(5′-Methyl-2′-furyl)indene (2a). To a stirred solution of **1a** (5.29 g, 60.4 mmol) in 100 mL of diethyl ether was added at −60 °C 2-indanone (8.00 g, 60.4 mmol) in ether (100 mL). The resulting reaction mixture was stirred for 6 h between −60 and −40 °C before warming it to −25 °C and reacting it with 75 mL of 2 M aqueous HCl. After separation of the layers, drying with $MgSO_4$, and column chromatography with isohexane/diethyl ether 4/1 6.90 g (58%) of **2a** was obtained as a white solid. Mp: 61 °C. Anal. Calcd for $C_{14}H_{12}O$ (196.3): C, 85.68; H, 6.18. Found: C, 85.49; H, 5.98. IR (KBr): $\tilde{\nu}$ 3114 (m), 3063 (w), 2921 (w), 1680 (m), 1584 (s), 1459 (s), 1403 (s), 1216 (m), 1023 (s), 921 (m), 859 (m), 796 (vs), 762 (vs), 717 (vs) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 7.17−6.97 (m, 5H, 3-H, 4-H, 5-H, 6-H, 7-H), 6.07 (d, 1H, 3′-H, ^3J = 4.0 Hz), 5.75 (dq, 1H, 4′-H, ^3J = 4.0 Hz, ^4J = 0.9 Hz), 3.29 (s, 2H, 1-H), 1.96 (s, 3H, CH_3). ^{13}C NMR (benzene-d_6): δ 152.2 (C, C-5′), 151.1 (C, C-2′), 145.7, 142.5, 136.8 (C, C-3a, C-7a, C-2), 126.9, 124.8, 124.4, 123.8, 121.2 (CH, C-3, C-4, C-5, C-6, C-7), 108.2 (CH, C-3′), 107.9 (CH, C-4′), 38.2 (CH_2, C-1), 13.5 (5′-CH_3).

2-(5′-Methyl-2′-thienyl)indene (2b). Treatment of **1b** (3.15 g, 30.3 mmol) with 2-indanone (4.00 g, 30.3 mmol) as described above and crystallization at 4 °C from diethyl ether yielded 2.94 g (46%) of the light yellow product. Mp: 154 °C. Anal. Calcd. for $C_{14}H_{12}S$ (212.3): C, 79.20; H, 5.70. Found: C, 79.20; H, 5.81. IR (KBr): $\tilde{\nu}$ 3069 (w), 3041 (m), 2916 (w), 1590 (m), 1533 (m), 1454 (s), 1397 (s), 1216 (m), 1023 (m), 915 (s), 859 (m), 791 (vs), 751 (vs), 717 (vs) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 7.19−7.06 (m, 4H, 4-H, 5-H, 6-H, 7-H), 6.83 (s, 1H, 3-H), 6.72 (d, 1H, 3′−H, ^3J = 3.2 Hz), 6.44 (dq, 1H, 4′-H, ^3J = 3.2 Hz, ^4J = 1.2 Hz), 3.37 (s, 2H, 1-H), 2.13 (s, 3H, CH_3). ^{13}C NMR (benzene-d_6): δ 146.2 (C, C-5′), 143.0 (C, C-2′), 141.5, 139.7, 139.4 (C, C-7a, C-3a, C-2), 126.9, 124.8, 123.7, 121.0 (CH, C-4, C-5, C-6, C-7), 126.2 (CH, C-4′), 125.5 (CH, C-3), 124.3 (CH, C-3′), 39.1 (CH_2, C-1), 15.6 (5′-CH_3).

2-(5′-Methyl-2′-furyl)indenyllithium (3a). Deprotonation of **2a** (2.50 g, 12.7 mmol) with *n*-butyllithium (7.96 mL, 12.7 mmol, 1.6 M in hexane) was carried out in 70 mL of diethyl ether at room temperature. After the mixture was stirred for 2 h, the solvent was removed and the residue was suspended in pentane overnight. A 2.32 g amount (11.5 mmol, 90%) of the beige product was obtained by filtration. ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8 10/1): δ 7.68 (m, 2H, 4-H, 7-H), 6.91 (m, 2H, 5-H, 6-H), 6.63 (s, 2H, 1-H, 3-H), 6.34 (d, 1H, 3′-H, ^3J = 3.0 Hz), 5.95 (dq, 1H, 4′-H, ^3J = 3.0 Hz, ^4J = 1.0 Hz), 2.19 (d, 3H, CH_3, ^4J = 1.0 Hz).^{13}C NMR (benzene-d_6/tetrahydrofuran-d_8 10/1): δ 156.5 (C, C-2′), 147.6 (C, C-5′), 129.8 (C, C-7a, C-3a), 122.4 (C, C-2), 119.9 (CH, C-4, C-7), 115.4 (CH, C-5, C-6), 107.4 (CH, C-4′), 101.2 (CH, C-3′), 89.0 (CH, C-1, C-3), 13.7 (5′-CH_3).

(2-(5′-Methyl-2′-thienyl)indenyl)lithium (3b). Reaction of 2.84 g (13.4 mmol) of **2b** with 8.36 mL (13.4 mmol, 1.6 M in hexane) of *n*-butyllithium as described above and an analogous workup procedure yielded 2.78 g (95%) of a light brown crystalline product. ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8 10/1): δ 7.64 (m, 2H, 4-H, 7-H), 7.04 (d, 1H, 3′-H, $^3J = 3.2$ Hz), 6.91 (m, 2H, 5-H, 6-H), 6.57 (dq, 1H, 4′-H, $^3J = 3.2$ Hz, $^4J = 1.2$ Hz), 6.55 (s, 2H, 1-H, 3-H), 2.28 (d, 3H, 5′-CH_3, $^4J = 1.2$ Hz).

Dichlorobis[2-(5′-methyl-2′-furyl)indenyl]zirconium (4a). Zirconium tetrachloride (0.29 g, 1.24 mmol) was added to a stirred suspension of 0.5 g **3a** (2.47 mmol) in 80 mL of toluene at −78 °C. The reaction mixture was warmed to room temperature overnight and then filtered. Crystallization from toluene yielded 0.35 g (0.63 mmol, 51%) of **4a** as a yellow solid. Mp: 190 °C. Anal. Calcd for $C_{28}H_{22}Cl_2O_2Zr$ (552.6): C, 60.86; H, 4.01. Found: C, 60.72; H, 4.12. IR (KBr): $\tilde{\nu}$ 3120 (w), 2919 (w), 1616 (m), 1567 (vs), 1439 (s), 1366 (m), 1207 (s), 1029 (vs), 950 (s), 828 (vs), 791 (vs), 742 (vs) cm^{-1}. ^{1}H NMR (dichloromethane-d_2): δ 7.30 (m, 4H, 4-H, 7-H), 7.12 (m, 4H, 5-H, 6-H), 6.55 (s, 4H, 1-H, 3-H), 6.47 (d, 2H, 3′-H, $^3J = 3.6$ Hz), 6.16 (dq, 2H, 4′-H, $^3J = 3.6$ Hz, $^4J = 0.6$ Hz), 2.48 (d, 6H, 5′-CH_3, $^4J = 0.6$ Hz). ^{13}C NMR (dichloromethane-d_2): δ 153.6 (C, C-5′), 147.3 (C, C-2′), 126.7 (C, C-7a, C-3a), 126.6 (CH, C-5, C-6), 125.4 (C, C-2), 124.9 (CH, C-4, C-7), 110.6 (CH, C-3′), 108.6 (CH, C-4′), 100.6 (CH, C-1, C-3), 13.9 (5′-CH_3).

X-ray Crystal Structure Analysis of 4a: formula $C_{28}H_{22}O_2Cl_2Zr$, $M_r = 552.58$, yellow crystal 0.15 × 0.10 × 0.05 mm, $a = 8.850(1)$ Å, $b = 11.145(1)$ Å, $c = 24.065(1)$ Å, $\beta = 99.37(1)°$, $V = 2341.9(4)$ Å^3, $\rho_{calcd} = 1.567$ g cm^{-3}, $\mu = 7.22$ cm^{-1}, empirical absorption correction via SORTAV ($0.899 \leq T \leq 0.965$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 16 710 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.65$ Å^{-1}, 5339 independent ($R_{int} = 0.043$) and 4272 observed reflections ($I \geq 2\,\sigma(I)$), 300 refined parameters, R1 = 0.033, wR2 = 0.061, maximum (minimum) residual electron density 0.37 (−0.64) e Å^{-3}, hydrogens calculated and riding. All data sets were collected with Nonius MACH3 or KappaCCD diffractometers, using a Nonius FR591 rotating anode generator. Programs used: data collection EXPRESS (Nonius BV, 1994) or COLLECT (Nonius BV, 1998); data reduction MolEN (K. Fair, Enraf-Nonius BV, 1990) or Denzo-SMN;[18] absorption correction for CCD data SORTAV;[19] structure solution SHELXS-86 or SHELXS-97;[20] structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, Göttingen, Germany, 1997); graphics (with unsystematical numbering schemes) DIAMOND (K. Brandenburg, Universität Bonn, Bonn, Germany, 1996) and SCHAKAL (E. Keller, Universität Freiburg, Freiburg, Germany, 1997).

Dichlorobis[2-(5′-methyl-2′-thienyl)indenyl]zirconium (4b). Analogously as described above, 2.00 g (9.16 mmol) of **3b** was reacted with 1.07 g of $ZrCl_4$ to yield 0.90 g (1.54 mmol, 34%) of **4b** as a yellow crystalline solid. Mp: 183 °C. Anal. Calcd for $C_{28}H_{22}Cl_2S_2Zr$ (584.7): C, 57.51; H, 3.79. Found: C, 57.08; H, 4.07. IR (KBr): $\tilde{\nu}$ 3056 (w), 2918 (w), 1615 (m), 1510 (s), 1438 (s), 1366 (m), 1338 (m), 1229 (m), 880 (s), 836 (vs), 808 (vs), 753 (vs) cm^{-1}. ^{1}H NMR (dichloromethane-d_2): δ 7.26 (m, 4H, 4-H, 7-H), 7.12 (m, 4H, 5-H, 6-H), 7.00 (d, 2H, 3′-H, $^3J = 3.0$ Hz), 6.78 (dq, 2H, 4′-H, $^3J = 3.0$ Hz, $^4J = 1.2$ Hz), 6.49 (s, 4H, 1-H, 3-H), 2.57 (d, 6H, CH_3, $^4J = 1.2$ Hz). ^{13}C NMR (dichloromethane-d_2): δ 142.1 (C, C-5′), 134.7 (C, C-2′), 129.1 (C, C-2), 126.7 (CH, C-5, C-6), 126.7 (C, C-7a, C-3a), 126.65 (CH, C-4′), 126.61 (CH, C-3′), 124.9 (CH, C-4, C-7), 102.7 (CH, C-1, C-3), 15.6 (5′-CH_3).

Dichlorobis[2-(5′-methyl-2′-furyl)indenyl]hafnium (5a). Analogously as described above, 0.50 g (2.47 mmol) of **3a** was reacted with 0.40 g of $HfCl_4$ in 80 mL of toluene. After workup 0.07 g (9%) of **5a** as a yellow solid was obtained. Mp: 155 °C. Anal. Calcd for $C_{28}H_{22}Cl_2O_2Hf$ (639.9): C, 52.56; H, 3.47. Found: C, 52.40; H, 3.67. IR (KBr): $\tilde{\nu}$ 3108 (w), 3039 (w), 2921 (w), 1617 (m), 1567 (vs), 1437 (s), 1344 (s), 1207 (vs), 1027 (vs), 952 (s), 834 (vs), 809 (vs), 685 (m) cm^{-1}. ^{1}H NMR (dichloromethane-d_2): δ 7.32 (m, 4H, 4-H, 7-H), 7.10 (m, 4H, 5-H, 6-H), 6.44 (d, 2H, 3′-H, $^3J = 3.0$ Hz), 6.37 (s, 4H, 1-H, 3-H), 6.16 (dq, 2H, 4′-H, $^3J = 3.0$ Hz, $^4J = 1.2$ Hz), 2.47 (d, 6H, CH_3, $^4J = 1.2$ Hz). ^{13}C NMR (dichloromethane-d_2): δ 153.5 (C, C-5′), 147.3 (C, C-2′), 126.4 (CH, C-4, C-7), 125.9 (C, C-7a, C-3a), 125.0 (CH, C-5, C-6), 110.4 (CH, C-3′), 108.4 (CH, C-4′), 98.3 (CH, C-1, C-3), 13.9 (5′-CH_3). The resonance of C-2 was not detected.

X-ray Crystal Structure Analysis of 5a: formula $C_{28}H_{22}O_2Cl_2Hf$, $M_r = 639.85$, yellow crystal 0.20 × 0.15 × 0.10 mm, $a = 8.815(1)$ Å, $b = 11.110(1)$ Å, $c = 24.030(1)$ Å, $\beta = 99.48(1)°$, $V = 2321.2(3)$ Å^3, $\rho_{calcd} = 1.831$ g cm^{-3}, $\mu = 47.49$ cm^{-1}, empirical absorption correction via SORTAV ($0.450 \leq T \leq 0.648$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 15 890 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.65$ Å^{-1}, 5307 independent ($R_{int} = 0.051$) and 4814 observed reflections ($I \geq 2\,\sigma(I)$), 300 refined parameters, R1 = 0.024, wR2 = 0.058, maximum (minimum) residual electron density 0.84 (−1.08) e Å^{-3}, hydrogens calculated and riding.

Dichlorobis[2-(5′-methyl-2′-thienyl)indenyl]hafnium (5b). Treatment of **3b** (0.47 g, 2.15 mmol) with $HfCl_4$ (0.35 g, 1.08 mmol) in 40 mL of toluene and subsequent workup procedure analogous to that described above yielded 0.23 g (32%) of **5b** as a yellow solid. Mp: 167 °C. Anal. Calcd for $C_{28}H_{22}Cl_2S_2Hf$ (672.0): C, 50.05; H, 3.30. Found: C, 49.04; H, 3.57. IR (KBr): $\tilde{\nu}$ 3058 (w), 2909 (w), 1617 (m), 1505 (s), 1443 (s), 1369 (m), 1344 (m), 1157 (m), 841 (s), 803 (vs), 747 (vs), 518 (vs) cm^{-1}. ^{1}H NMR (dichloromethane-d_2): δ 7.30 (m, 4H, 4-H, 7-H), 7.10 (m, 4H, 5-H, 6-H), 6.96 (d, 2H, 3′-H, $^3J = 3.6$ Hz), 6.77 (dq, 2H, 4′-H, $^3J = 3.6$ Hz, $^4J = 1.2$ Hz), 6.32 (s, 4H, 1-H, 3-H), 2.57 (d, 6H, CH_3, $^4J = 1.2$ Hz). ^{13}C NMR (dichloromethane-d_2): δ 141.9 (C, C-5′), 134.8 (C, C-2′), 128.6 (C, C-2), 126.54 (CH, C-5, C-6), 126.52 (CH, C-3′), 126.4 (CH, C-4′), 125.8 (C, C-7a, C-3a), 100.4 (CH, C-1, C-3), 15.6 (5′-CH_3).

Dimethylbis[2-(5′-methyl-2′-furyl)indenyl]zirconium (6a). A 0.50 g (0.90 mmol) amount of **4a** was placed in a 100 mL Schlenk flask, and diethyl ether (20 mL) was added. At 0 °C methyllithium (1.13 mL, 1.80 mmol, 1.6 M in diethyl ether) was added and the reaction mixture was kept for 1 h at this temperature. After the mixture was warmed to room temperature and stirred for an additional 2 h, the solvent was removed in vacuo and 30 mL of pentane was added. After filtration the product was crystallized at −30 °C to yield 0.18 g (0.35 mmol, 38%) of **6a**. Mp: 116 °C. Anal. Calcd for $C_{30}H_{28}O_2Zr$ (511.8): C, 70.41; H, 5.51. Found: C, 69.84; H, 5.38. IR (KBr): $\tilde{\nu}$ 2911 (w), 1564 (m), 1509 (s), 1465 (m), 1439 (m), 1319 (m), 1275 (m), 1184 (m), 1020 (m), 851 (m), 828 (vs), 752 (vs), 740 (vs) cm^{-1}. ^{1}H NMR (dichloromethane-d_2): δ 7.09 (m, 4H, 4-H, 7-H), 7.01 (m, 4H, 5-H, 6-H), 6.35 (d, 2H, 3′-H, $^3J = 3.0$ Hz), 6.18 (s, 4H, 1-H, 3-H), 6.13 (dq, 2H, 4′-H, $^3J = 3.0$ Hz, $^4J = 1.2$ Hz), 2.45 (s, 6H, 5′-CH_3), −1.33 (s, 6H, Zr−CH_3). ^{13}C NMR (dichloromethane-d_2): δ 152.5 (C, C-5′), 148.2 (C, C-2′), 124.6 (CH, C-5, C-6), 124.5 (CH, C-4, C-7), 124.3 (C, C-7a, C-3a), 120.9 (C, C-2), 108.1 (CH, C-4′), 108.0 (CH, C-3′), 95.9 (CH, C-1, C-3), 35.8 (CH_3, Zr−CH_3), 13.9 (5′-CH_3).

X-ray Crystal Structure Analysis of 6a: formula $C_{30}H_{28}O_2Zr$, $M_r = 511.74$, yellow crystal 0.60 × 0.50 × 0.40 mm, $a = 9.497(1)$ Å, $b = 15.382(3)$ Å, $c = 18.276(5)$ Å, $\alpha = 109.83(2)°$, $\beta = 98.49(2)°$, $\gamma = 91.51(1)°$, $V = 2475.6(9)$ Å^3, $\rho_{calcd} = 1.373$ g cm^{-3}, $\mu = 4.68$ cm^{-1}, empirical absorption correction via ψ scan data ($0.767 \leq T \leq 0.835$), $Z = 4$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.710\,73$ Å, $T = 223$ K, $\omega/2\theta$ scans, 10 360 reflections collected ($\pm h$, $\pm k$, $+l$), $(\sin\theta)/\lambda = 0.62$ Å^{-1}, 10 033 independent ($R_{int} = 0.034$) and 8615 observed reflections ($I \geq 2\,\sigma(I)$), 603 refined parameters, R1 = 0.029, wR2 = 0.077, maximum (minimum) residual electron density 0.85 (−0.55) e Å^{-3},

---

[18] Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326.

[19] Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37. Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426.

[20] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

asymmetric unit contains two nearly identical independent molecules, hydrogens calculated and riding.

Dimethylbis[2-(5′-methyl-2′-thienyl)indenyl]zirconium (6b). Treatment of **4b** (0.5 g, 0.86 mmol) with methyllithium (1.06 mL, 1.71 mmol, 1.6 M in diethyl ether) analogously as described above and the use of toluene instead of pentane for the workup procedure yielded 0.12 g (0.22 mmol, 26%) of **6b** as a white solid. Mp: 188 °C. HRMS: found, *m*/*z* 527.040 97; calcd for $C_{29}H_{25}S_2Zr$ (=$M^+ - CH_3$), 527.041 08. IR (KBr): $\tilde{\nu}$ 3114 (w), 3054 (w), 2922 (w), 2868 (w), 1606 (w), 1502 (m), 1453 (s), 1365 (s), 1217 (m), 1145 (m), 877 (s), 827 (vs), 789 (vs), 740 (vs) cm^{-1}. ^1H NMR (dichloromethane-d_2): δ 7.09 (m, 4H, 4-H, 7-H), 7.02 (m, 4H, 5-H, 6-H), 6.91 (d, 2H, 3′-H, $^3J = 3.0$ Hz), 6.78 (dq, 2H, 4′-H, $^3J = 3.0$ Hz, $^4J = 1.2$ Hz), 6.04 (s, 4H, 1-H, 3-H), 2.56 (d, 6H, 5′-CH_3, $^4J = 1.2$ Hz), −1.29 (s, 6H, Zr−CH_3). ^{13}C NMR (dichloromethane-d_2): δ 140.3 (C, C-5′), 136.2 (C, C-2′), 126.4 (CH, C-4′), 124.9 (CH, C-5, C-6), 124.7 (CH, C-4, C-7), 124.3 (CH, C-3′), 97.9 (CH, C-1, C-3), 35.7 (CH_3, Zr−CH_3), 15.6 (5′-CH_3), the resonances of C-2, C-7a and C-3a were not detected.

2-(4′-Oxopentanoyl)indene (8). A 4.00 g (20.4 mmol) amount of **2a** was dissolved in 40 mL of glacial acetic acid, and after addition of 20 mL of water and 1.6 mL of 20% H_2SO_4 the reaction mixture was heated for 5 h at 120 °C under reflux. The cold solution was poured into ice water, and the precipitate was collected by filtration. The crude product was dissolved in diethyl ether/ethyl acetate (30 mL/10 mL) and dried over magnesium sulfate. The beige product **8** (2.80 g, 64%) was obtained after crystallization at −20 °C. Mp: 85 °C. Anal. Calcd for $C_{14}H_{14}O_2$ (214.3): C, 78.48; H, 6.59. Found: C, 78.41; H, 6.81. IR (KBr): $\tilde{\nu}$ 3072 (w), 2918 (w), 1937 (w), 1723 (vs), 1651 (vs), 1558 (m), 1470 (m), 1427 (m), 1388 (m), 1361 (m), 1163 (s), 933 (m), 878 (m), 763 (s), 719 (s) cm^{-1}. ^1H NMR (benzene-d_6): δ 7.26−7.06 (m, 5H, 3-H, 4-H, 5-H, 6-H, 7-H), 3.39 (s, 2H, 1-H), 2.76 (t, 2H, 2′-H, $^3J = 6.6$ Hz), 2.41 (t, 2H, 3′-H, $^3J = 6.6$ Hz), 1.78 (s, 3H, 5′-H). ^{13}C NMR (benzene-d_6): δ 205.9 (C, C-1′), 195.4 (C, C-4′), 146.4, 145.5, 143.7 (C, C-7a, C-3a, C-2), 140.2 (CH, C-3), 128.3, 127.4, 125.1, 124.3 (CH, C-4, C-5, C-6, C-7), 38.2 (CH_2, C-1), 37.3 (CH_2, C-3′), 33.2 (CH_2, C-2′), 29.9 (CH_3, C-5′).

X-ray Crystal Structure Analysis of 8: formula $C_{14}H_{14}O_2$, $M_r = 214.25$, colorless crystal 0.35 × 0.20 × 0.05 mm, $a = 5.490(1)$ Å, $b = 27.089(1)$ Å, $c = 7.571(1)$ Å, $\beta = 100.57(1)°$, $V = 1106.8(3)$ Å^3, $\rho_{calcd} = 1.286$ g cm^{-3}, $\mu = 0.85$ cm^{-1}, empirical absorption correction via SORTAV ($0.971 \le T \le 0.996$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710$ 73 Å, $T = 198$ K, ω and φ scans, 8461 reflections collected ($\pm h, \pm k, \pm l$), $(\sin\theta)/\lambda = 0.71$ Å^{-1}, 3249 independent ($R_{int} = 0.042$) and 2541 observed reflections ($I \ge 2\sigma(I)$), 146 refined parameters, R1 = 0.054, wR2 = 0.135, maximum (minimum) residual electron density 0.32 (−0.26) e Å^{-3}, hydrogens calculated and riding.

2-(5′-Methyl-2′-*N*-methylpyrrolyl)indene (9). Compound **8** (2.20 g, 10.3 mmol) was dissolved in 40 mL of ethanol, and 1.77 mL of methylamine (20.6 mmol, 40% in water) was added. The reaction mixture was heated under reflux for 14 h, and after this mixture was cooled to room temperature, the precipitated solids were redissolved by the addition of diethyl ether. After drying over magnesium sulfate the product was crystallized from diethyl ether, yielding 1.00 g (47%) of **9**. Mp: 120 °C. Anal. Calcd for $C_{15}H_{15}N$ (209.3): C, 86.08; H, 7.22; N, 6.69. Found: C, 85.52; H, 7.37; N, 6.20. IR (KBr): $\tilde{\nu}$ 3041 (w), 2980 (w), 2931 (m), 1916 (w), 1677 (w), 1586 (s), 1537 (s), 1445 (s), 1408 (vs), 1213 (m), 1048 (s), 917 (m), 828 (s), 760 (vs), 717 (vs) cm^{-1}. ^1H NMR (benzene-d_6): δ 7.31−7.07 (m, 4H, 4-H, 5-H, 6-H, 7-H), 6.55 (s, 1H, 3-H), 6.35 (d, 1H, 3′-H, $^3J = 3.6$ Hz), 6.02 (d, 1H, 4′-H, $^3J = 3.6$ Hz), 3.58 (s, 2-H, 1-H), 2.99 (s, 3H, N−CH_3), 1.88 (s, 3H, 5′-CH_3). ^{13}C NMR (benzene-d_6): δ 146.8, 141.1 (C, C-7a, C-3a), 139.4 (C, C-2), 131.8 (C, C-5′), 130.0 (C, C-2′), 126.8, 124.2, 123.6, 121.7 (CH, C-4, C-5, C-6, C-7), 120.4 (CH, C-3), 109.8 (CH, C-3′), 107.6 (CH, C-4′), 41.4 (CH_2, C-1), 32.0 (CH_3, N−CH_3), 12.6 (5′-CH_3).

[2-(5′-Methyl-2′-*N*-methylpyrrolyl)indenyl]lithium (10). A sample of 0.50 g (2.89 mmol) of **9** was treated with 1.19 mL of methyllithium (2.29 mmol, 2 M in diethyl ether) in 20 mL of diethyl ether. After 4 h the solvent was removed and the off-white crude product was used for the reaction with $ZrCl_4$. **10**: ^1H NMR (benzene-d_6/tetrahydrofuran-d_8 10/1) δ 7.61 (m, 2H, 4-H, 7-H), 6.84 (m, 2H, 5-H, 6-H), 6.32 (s, 2H, 1-H, 3-H), 6.22 (d, 1H, 3′-H, $^3J = 3.4$ Hz), 5.98 (d, 1H, 4′-H, $^3J = 3.4$ Hz), 3.50 (s, 3H, N−CH_3), 2.10 (s, 3H, 5′-CH_3).

Dichlorobis[2-(5′-methyl-2′-*N*-methylpyrrolyl)indenyl]zirconium (11). Analogously as described above, 0.50 g (0.90 mmol) of **10** was reacted with 0.26 g of $ZrCl_4$ in 40 mL of toluene at −78 °C. Workup as described above yielded 0.10 g (16%) of the yellow crystalline product **11**. Mp: 229 °C. Anal. Calcd for $C_{30}H_{28}Cl_2N_2Zr$ (578.7): C, 62.27; H, 4.88; N, 4.84. Found: C, 61.89; H, 5.31; N, 4.57. IR (KBr): $\tilde{\nu}$ 2911 (w), 1564 (m), 1509 (s), 1465 (m), 1439 (m), 1319 (m), 1275 (m), 1184 (m), 1020 (m), 851 (m), 828 (vs), 752 (vs), 740 (vs) cm^{-1}. ^1H NMR (dichloromethane-d_2): δ 7.28 (m, 4H, 4-H, 7-H), 7.13 (m, 4H, 5-H, 6-H), 6.35 (d, 2H, 3′-H, $^3J = 3.6$ Hz), 6.33 (s, 4H, 1-H, 3-H), 6.02 (d, 2H, 4′-H, $^3J = 3.6$ Hz), 3.60 (s, 6H, N−CH_3), 2.33 (s, 6H, 5′-CH_3). ^{13}C NMR (dichloromethane-d_2): δ 133.6 (C, C-5′), 129.6 (C, C-2′), 126.9 (C, C-2), 126.6 (C, C-3a, C-7a), 126.4 (CH, C-5, C-6), 124.9 (CH, C-4, C-7), 110.9 (CH, C-3′), 107.8 (CH, C-4′), 101.8 (CH, C-1, C-3), 33.1 (CH_3, N−CH_3), 13.1 (5′-CH_3).

Dichlorobis[2-(5′-methyl-2′-*N*-methylpyrrolyl)indenyl]hafnium (12). The preparation was carried out by reacting **10** (0.44 g, 2.04 mmol) with $HfCl_4$ (0.33 g, 1.02 mmol) in 40 mL of toluene followed by workup analogous to that described above to yield 0.13 g (19%) of **12** as a yellow crystalline solid. Mp: 211 °C. Anal. Calcd for $C_{30}H_{28}Cl_2N_2Hf$ (666.0): C, 54.11; H, 4.24; N, 4.21. Found: C, 53.34; H, 4.48; N, 3.93. IR (KBr): $\tilde{\nu}$ 2919 (w), 2853 (w), 1567 (m), 1514 (vs), 1443 (m), 1324 (m), 1277 (m), 1188 (m), 1034 (m), 838 (vs), 743 (vs), 678 (m) cm^{-1}. ^1H NMR (dichloromethane-d_2): δ 7.33 (m, 4H, 4-H, 7-H), 7.13 (m, 4H, 5-H, 6-H), 6.29 (d, 2H, 3′-H, $^3J = 4.2$ Hz), 6.11 (s, 4H, 1-H, 3-H), 6.00 (d, 2H, 4′-H, $^3J = 4.2$ Hz, $^4J = 0.6$ Hz), 3.57 (s, 6H, N−CH_3), 2.33 (d, 6H, 5′-CH_3, $^4J = 0.6$ Hz). ^{13}C NMR (dichloromethane-d_2): δ 133.3 (C, C-5′), 129.6 (C, C-2), 126.8 (C, C-2′), 126.2 (CH, C-5, C-6), 125.7 (C, C-7a, C-3a), 125.1 (CH, C-4, C-7), 110.9 (CH, C-3′), 107.6 (CH, C-4′), 99.3 (CH, C-1, C-3), 33.0 (CH_3, N−CH_3), 13.0 (5′-CH_3).

Dimethylbis[2-(5′-methyl-2′-*N*-methylpyrrolyl)indenyl]zirconium (13). A sample of 0.20 g (0.24 mmol) of **11** was suspended in 20 mL of diethyl ether. Addition of 0.45 mL of methyllithium solution (0.72 mmol, 1.6 M in diethyl ether) led to **13** as a white solid, yield 0.07 g (38%) after a workup procedure analogous to that described above. Mp: 128 °C. HRMS: found, *m*/*z* 521.155 58; calcd for $C_{31}H_{31}N_2Zr$ (=$M^+ - CH_3$), 521.153 44. IR (KBr): $\tilde{\nu}$ 3097 (w), 2938 (s), 2916 (m), 2865 (m), 2774 (w), 1573 (m), 1527 (s), 1442 (vs), 1403 (s), 1352 (s), 1187 (m), 825 (vs), 774 (vs), 757 (vs) cm^{-1}. ^1H NMR (dichloromethane-d_2): δ 7.19 (m, 4H, 4-H, 7-H), 7.06 (m, 4H, 5-H, 6-H), 6.08 (d, 2H, 3′-H, $^3J = 3.0$ Hz), 6.00 (dq, 2H, 4′-H, $^3J = 3.0$ Hz, $^4J = 0.6$ Hz), 5.78 (s, 4H, 1-H, 3-H), 3.52 (s, 3H, N−CH_3), 2.34 (d, 6H, 5′-CH_3, $^4J = 0.6$ Hz), −1.36 (s, 6H, Zr−CH_3). ^{13}C NMR (dichloromethane-d_2): δ 132.0 (C, C-5′), 128.5 (C, C-2′), 128.2 (C, C-2), 124.7 (CH, C-4, C-7), 124.5 (CH, C-5, C-6), 124.4 (C, C-7a, C-3a), 108.8 (CH, C-3′), 107.3 (CH, C-4′), 97.5 (CH, C-1, C-3), 34.3 (CH_3, N−CH_3), 32.7 (CH_3, Zr−CH_3), 13.0 (5′-CH_3).

Polymerization Reactions. All polymerizations were carried out in an 1 L glass autoclave charged with 150 mL of toluene and 20 mL of methylalumoxane (10.5 wt % solution in toluene). At the respective temperature the stirred (600 rpm) mixture was saturated for 30 min with propene at a pressure of 2 bar. The catalyst precursors were injected, and the polymerization reactions were carried out for 2 h under a constant pressure of propene (2 bar). The reaction mixture was cautiously hydrolyzed with a 1:1 mixture of methanol and 2

N HCl and treated additionally with HCl (6 N, 100 mL). The organic layer was separated, the toluene solvent evaporated, and the residue dried under vacuum overnight. Test samples for the elastomeric measurements were prepared according to DIN 53502 and DIN 53504. The measurement rates were limited to 15 iterations. The polymer sample PP9 (see Table 1) was fractionated by successive extraction with pentane, hexane, and heptane under an argon blanket. A 250 mL round-bottom flask was equipped with a Soxhlet extractor and charged with 200 mL of the respective solvent. The polymer sample (6.03 g) was packed into a thimble, and this thimble was layered with a plug of glass wool and capped with filter paper. The sample was extracted for 15 h, and the corresponding fractions were dried under vacuum overnight. The polymer fractions were each characterized by ^{13}C NMR methyl pentad analysis. The following fractions were obtained: 1.45 g, pentane soluble (15% *mmmm*); 2.50 g, hexane soluble (18% *mmmm*); 1.70 g, heptane soluble (20% *mmmm*); a small heptane-insoluble residue.

Acknowledgment. Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Supporting Information Available: Figures giving additional polymer data and tables giving detailed information about the X-ray crystal structure analyses of compounds **4a**−**6a** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0000313