Synthesis of Novel Tetrahydrofluorenyl-Containing Group IV Metallocenes for the Ziegler−Natta Type Polymerization of α-Olefins

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Received June 15, 2000

Several new, novel bridged and unbridged bis-tetrahydrofluorenyl zirconocenes were synthesized and evaluated as Ziegler−Natta type catalysts for ethylene and propylene polymerization. The complexes were found to be highly stable compared to some bis-fluorenylzirconocenes. Polypropylene and polyethylene were produced in good yield using the new catalyst precursors with MAO or Trityl/TIBA as cocatalysts. Both the unsubstituted and substituted bridged bis-tetrahydrofluorenyl zirconocenes were isolated as 50:50 mixtures of *rac* and *meso* isomers, which produced mostly atactic polypropylene. Partially crystalline polypropylene was obtained at low temperatures with bis(3-methyltetrahydrofluorenyl)-zirconium dichloride.

Introduction

The study of group 4 metallocenes as Ziegler−Natta type catalysts for the polymerization of α-olefins is a highly active field. One area of great interest is the polymerization of propylene. Different polypropylene (PP) microstructures can be produced (atactic, syndiotactic, isotactic, and elastomeric). Many studies have been carried out investigating the relationship between the structure of the catalyst precursor and its polymerization behavior, particularly the resulting polymer properties.[1] In the mid 1980s, Kaminsky et al. showed that *rac*-ethylene bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride (a C_2 symmetric complex) could produce highly isotactic polypropylene (*i*-PP) in good yield.[2] Following this finding much work has been done to optimize this class of C_2 symmetric catalysts to improve polymerization behavior.[3]

The use of fluorenyl (Flu) as the π-ligand has been less studied than cyclopentadienyl (Cp) or indenyl (Ind) for several reasons. First, bis-fluorenyl complexes are C_{2v} symmetric and therefore generally produce only atactic polypropylene.[4] Second, bis-fluorenyl complexes have often been found to be much less stable than bis-indenyl complexes.[4,5] The unbridged systems such as those reported by Razavi et al.[5] were very unstable in organic solvents and decomposed rapidly in air. Resconi et al. also discussed the instability of dimethylsilylene bis-fluorenyl zirconium dichloride.[4d,e] In our research, we have found that certain mixed ring indenyl−fluorenyl silicon-bridged complexes are unstable in solution.[6] This instability has been attributed to the internal ligand rearrangement which occurs readily, changing the hapticity of the fluorenyl moiety and resulting in the displacement of the ligand in solution by solvent molecules.[5] However, ethylene bis-fluorenyl zirconium dichloride was shown to be a stable and highly active catalyst for both ethylene and propylene, producing very high molecular weight polymers in both cases, and therefore fluorene remains of interest as a ligand.[4]

Recently, studies have been published using the saturated fluorenyl analogue octahydrofluorene.[7] The complex dimethylsilylene octahydrofluorenyl-(−)-menthylcyclopentadienyl zirconium dichloride was shown to have higher activity than its fluorenyl analogue, and the PP obtained was more isotactic. Similar trends were observed when indenyl was replaced by its saturated analogue tetrahydroindenyl.[2,3b] We therefore were very interested to study the effect of using a partially saturated fluorenyl ligand, 5,6,7,8-tetrahydrofluorenyl, in place of fluorenyl itself with the aim of synthesizing bridged and unbridged complexes with varying substitution patterns. It was hoped that the saturation of one of the six-membered rings would lead to more stable zirconocene complexes and also that by introducing substitution on the rings, the symmetry of the com-

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(1) (a) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, J. L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem. Macromol. Symp*. **1991**, *48/49*, 253, (b) Razavi, A.; Napfliotis, L.; Peters, L.; Vereecke, D.; Den Dauw, K.; Atwood, J. L.; Thewald, U. *Macromol. Symp*. **1995**, *89*, 345, (c) Zambelli, A.; Pellecchia, C.; Oliva, L. *Makromol. Chem. Macromol. Symp*. **1991**, *48/49*, 297. (d) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 1143.

(2) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P *Angew. Chem*. **1985**, *97*, 507; *Angew. Chem., Int. Ed. Eng*. **1985**, *24*, 507.

(3) (a) Spaleck, W.; Kuber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. *Organometallics* **1994**, *13*, 954. (b) Schneider, N.; Huttenloch, M. E.; Stehling, U.; Kirsten, R.; Schaper, F.; Brintzinger, H. H. *Organometallics* **1997**, *16*, 3413.

(4) (a) Chen, Y.-X.; Rausch, M. D.; Chien, J. C. W. *Macromolecules* **1995**, *28*, 5399, (b) Alt, H. G.; Milius, W.; Palackal, S. J. *J. Organomet. Chem*. **1994**, *472*, 113. (c) Alt, H. G.; Köppl, A. *Chem. Rev*. **2000**, *100*, 1205. (d) Resconi, L.; Jones, R. L.; Albizzati, E.; Camurati, I.; Piemontesi, F.; Guglielmi, F.; Balbontin, G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 663. (e) Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998.

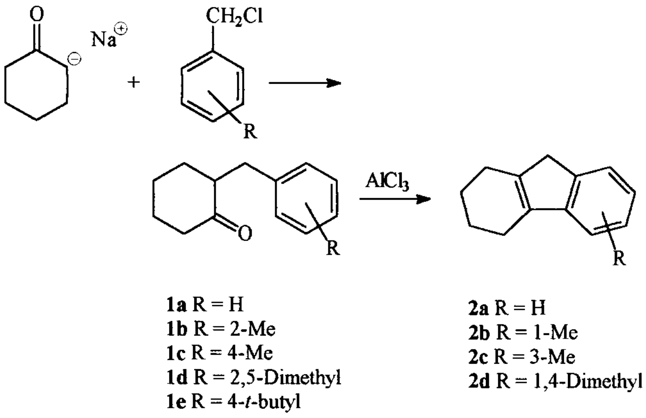
(5) Razavi, A.; Vereecke, D.; Peters, L.; Dauw, K. D.; Nafpliotis, L.; Atwood, J. L. *Ziegler Catalysts*; Fink, G., Mulhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, 1995; p 111.

(6) Thomas, E. J.; Rausch, M. D.; Chien, J. C. W. *Macromolecules* **2000**, *33*, 1546.

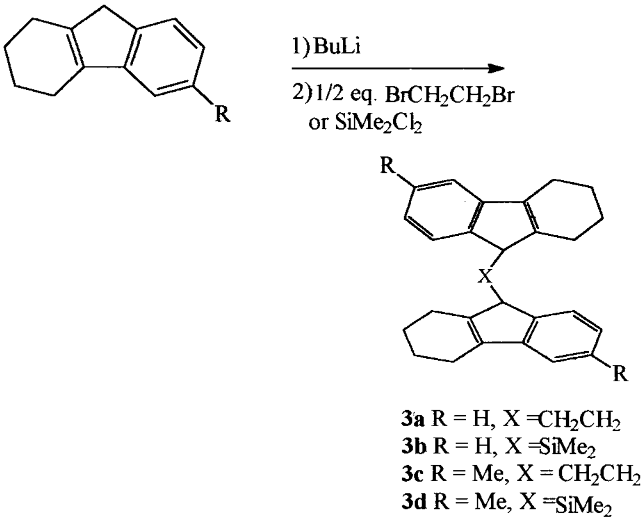
(7) Obora, Y.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 2503.

10.1021/om0005046 CCC: $19.00

Scheme 1



Scheme 2

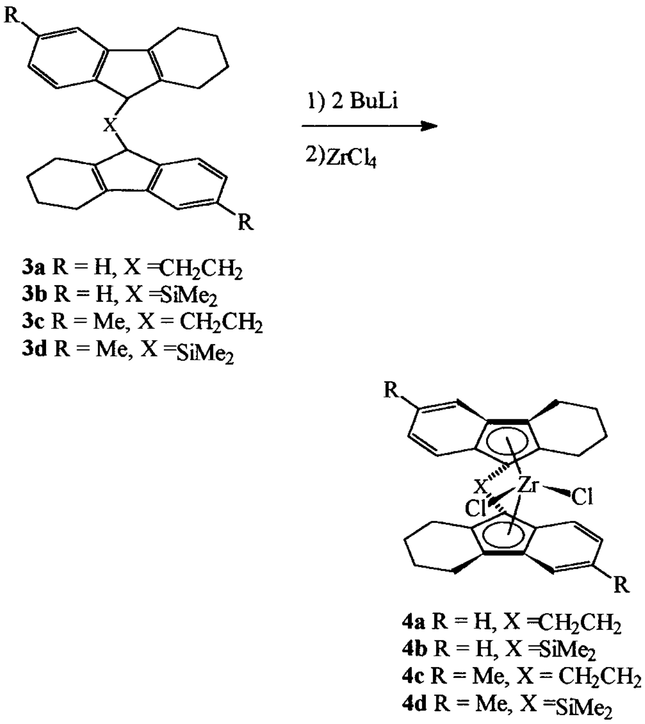


plexes could be altered to give C_2 symmetric catalysts for the production of *i*-PP. The use of tetrahydrofluorenyl as a ligand in group 4 metallocenes has not been reported in the literature to date.[8]

Results and Discussion

Synthesis. In the 1950s, Colonge et al. published a series of papers describing a general synthetic route to substituted tetrahydrofluorenes (Scheme 1) via benzylcyclohexanone intermediates.[9] Using this route, 2-benzylcyclohexanone and several substituted derivatives (**1a**−**e**) were prepared and converted to their corresponding tetrahydrofluorenes (**2a**−**d**). By reaction of these ligands with butyllithium, followed by 0.5 equiv of either 1,2-dibromoethane or dichlorodimethylsilane, the ethylene- and dimethylsilylene-bridged ligands derived from tetrahydrofluorene (**3a**,**b**) and 3-methyltetrahydrofluorene (**3c**,**d**) were prepared (Scheme 2). In the case of 1,4-dimethyltetrahydrofluorene (**2d**), the dimethylsilylene-bridged ligand could not be prepared, although the ethylene-bridged analogue was isolated. The new ligands (**3a**−**d**) were then converted to their corresponding zirconocenes (**4a**−**d**) according to Scheme 3. Attempts to convert ethylene bis(1,4-dimethyl)tetrahydrofluorene to its zirconocene analogue were not successful. Molecular modeling indicates that steric overcrowding prevents formation of this metallocene and also that steric repulsion between the 1-methyl groups and the methyl groups on silicon prevent formation of the silicon-bridged ligand itself.

Scheme 3



The synthesis of one other susbstituted tetrahydrofluorene was attempted. To introduce greater steric bulk to the proposed zirconocene systems, we wanted to prepare 3-*tert*-butyltetrahydrofluorene. The intermediate compound 4-*tert*-butylbenzylcyclohexanone (**1e**) was readily prepared according to Scheme 1. However, reaction of this with aluminum chloride to give the ring-closed product resulted each time in the isolation of pure tetrahydrofluorene **2a**. Upon further investigation of this initially surprising result, we concluded that the reaction proceeds via a cationic dienyl intermediate. Elimination of the highly stable *tert*-butyl radical could then occur, leading to the exclusive formation of the unsubstituted tetrahydrofluorene.

The novel metallocenes prepared according to Scheme 3 were all isolated in good yield and were found to be highly stable in solution. Furthermore, the complexes did not decompose upon exposure to air for a short periods of time, indicating that tetrahydrofluorenyl as a *hapto* ligand is more stable than fluorenyl and that it behaves more like a substituted indenyl than a fluorenyl. Further evidence of this conclusion can be found in the fact that tetrahydrofluorenyl titanium trichloride (**5**) was readily prepared and found to be a relatively stable product (Scheme 4).

We were also interested in synthesizing unbridged tetrahydrofluorenyl zirconocenes. Generally, it has been shown that a bridge between the two *hapto* ligands of metallocenes is necessary to give the stereorigid C_2

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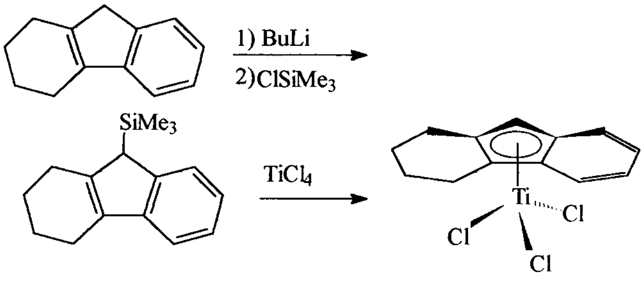
[8] The following patent applications have been filed relating to the use of tetrahydrofluorenyl-containing catalyst precursors: (a) Resconi, L.Bishop, C. E.; Jones, R. L.; Raman, K.; Dang, V.; Yu, L.-C.; Dall'Occo, T.; Galimberti, M. PCT Int. Appl. WO 9527717, 1995, (b) Nickias, P. N.; Newman, T. H.; Klosin, J. U.S Patent Application US 5,670,680, 1997.

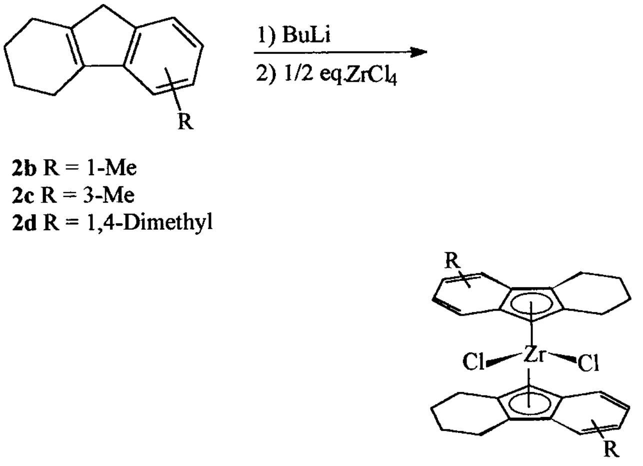
[9] (a) Colonge, J.; Sibeud, J. *Bull. Chim. Soc. Fr.* **1952**, 786. (b) Colonge, J.; Sibeud, J. *Bull. Chim. Soc. Fr.* **1953**, 75.

Scheme 4



(5)

Scheme 5



2b R = 1-Me
2c R = 3-Me
2d R = 1,4-Dimethyl

6b R=1-Me
6c R=3-Me
6d R=1,4-Dimethyl

symmetry required to produce isotactic PP at conventional polymerization temperatures. Unbridged metallocenes have been shown to produce *i*-PP at low temperatures due to restricted rotation of the π-ligands, but at ambient temperatures free rotation of the ligands results in *a*-PP.[10] However, Razavi reported the first unbridged metallocene to produce *i*-PP at high polymerization temperatures.[11] Bis(1-methylfluorenyl)zirconium dichloride was shown to form a stereorigid helical arrangement of the fluorenyl ligands resulting in a C_2 symmetric species capable of *i*-PP production up to 60 °C. We wanted to prepare the (1-methyl)tetrahydrofluorenyl analogue as well as several others to see if a similar effect occurred. The three novel unbridged metallocenes (**6b**–**d**) were prepared according to Scheme 5. Again, the zirconocenes were isolated in good yield and were found to be highly stable species, in contrast to the unbridged bis-fluorenyl complexes discussed by Razavi et al.[5]

We found in the case of the zirconocenes **4a**–**d**, and also for some of the bridged ligands, that a mixture of *rac*-like and *meso*-like isomers were obtained (ca. 50:50 by ^{1}H NMR) which could not be separated by recrystallization. Similarly, for the unbridged complex **6b**, ^{1}H NMR indicated the presence of two isomeric complexes in a 75:25 ratio. Variable-temperature NMR studies from −60 to 60 °C showed no change in the spectra, indicating two separate, noninterchangeable products in all cases. Furthermore, in the case of **3d**, a single isomer was obtained which, upon deprotonation and reaction with $ZrCl_4$, led to a mixture of *rac*-like and *meso*-like zirconocenes.

Table 1. Propylene Polymerization with Catalyst Precursors 4a–d and 6b–d

complex	cocatalyst	temp, °C	yield, g	activity, $10^{-6\,c}$	T_m, °C[d]	[mmmm] %[e]
4a	MAO[a]	20	1.90	1.1	*a*-PP	*a*-PP
4a	MAO[a]	70	0.45	1.5	*a*-PP	*a*-PP
4b	MAO[a]	20	0.46	0.3	*a*-PP	*a*-PP
4b	MAO[a]	70	0.48	1.6	*a*-PP	*a*-PP
4c	MAO[a]	20	1.64	1.0	*a*-PP	*a*-PP
4c	MAO[a]	70	0.44	1.5	*a*-PP	*a*-PP
4d	MAO[a]	20	0.54	0.3	*a*-PP	*a*-PP
4d	MAO[a]	70	0.48	1.6	*a*-PP	*a*-PP
6b	trityl/TIBA[b]	−10	0.97	0.8	*a*-PP	*a*-PP
6b	MAO[b]	20	0.17	0.2	*a*-PP	*a*-PP
6c	trityl/TIBA[b]	−10	1.08	0.9	70	45
6c	MAO[b]	20	0.10	0.1	*a*-PP	*a*-PP
6d	trityl/TIBA[b]	−10	0.13	0.1	*a*-PP	*a*-PP

[a] Polymerization conditions: [Zr] = 50 μM; cocatalyst MAO; [Al]:[Zr] = 4000:1; monomer pressure = 15 psi; time of polymerization = 1 h. [b] Polymerization conditions: [Zr] = 50 μM; monomer pressure = 15 psi; time of polymerization = 30 min; cocatalyst trityl/TIBA; [Zr]: [trityl]: [Al] = 1:1:20. [c] Activity expressed in g polymer/(mol Zr·[C_3]·h). [d] T_m determined by DSC. *a*-PP samples showed no mp. [e] [mmmm] % determined by ^{13}C NMR.

Table 2. Ethylene Polymerization with Catalyst Precursors 4a–d and 6b–d[a]

catalyst	yield, g	activity, $10^{-7\,b}$	T_m, °C[c]
4a	0.53	4.6	133
4b	0.4	3.5	133
4c	0.67	5.8	132
4d	0.67	5.8	131
6b	0.91	5.9	134
6c	0.28	1.8	134
6d	0.04	0.3	130

[a] Polymerization conditions: [Zr] = 5 μM; monomer pressure = 15 psi; MAO as cocatalysts, Al:Zr = 4000:1; time of polymerization = 10 min. For catalysts 4a–d, polymerization temperature = 50 °C and for 6b–d = 20 °C. [b] Activity expressed in g polymer/(mol Zr·[C_2]·h). [c] T_m determined by DSC.

Polymerization Studies. The precursors (**4a**–**d** and **6b**–**d**) were evaluated as polymerization catalysts with MAO or trityl/TIBA for both ethylene and propylene. The results are summarized in Tables 1 and 2. All of the complexes were shown to be efficient catalysts for both polyethylene and polypropylene production. Activities of 10^7 g polymer/(mol Zr·[C_2]·h) were observed in most cases for ethylene. For propylene, activities of 10^6 were obtained for **4a**–**d** and 10^5 for the unbridged systems **6b**–**d**. As discussed above, we found that for the bridged metallocenes (**4a**–**d**), a 50:50 mixture of *rac*:*meso* isomers was always produced, which could not be separated by crystallization. Similar observations have been reported by Chen et al.,[4a] Alt et al.,[12] and Razavi et al.[5] for bridged bis-fluorenyl complexes. Performing propylene polymerizations with these isomeric mixtures resulted in mostly atactic PP production. Even with methyl substitution on the rings, the racemic isomer in the mixture failed to produce *i*-PP, suggesting that these groups are too far removed from the active site to have

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(10) Foster, P.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1998**, *571*, 171.
(11) Razavi, A.; Atwood, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 7259.
(12) Alt. H. G.; Zenk, R. *J. Organomet. Chem.* **1996**, *512*, 51.

a steric influence on the monomer insertion or the polymer chain and that the presence of a more sterically demanding, saturated ring does not enhance stereoselectivity with respect to a fluorenyl. Some substituted ethylene bis-fluorenyl zirconocenes were also shown to produce poorly stereoregular or atactic PP despite the presence of the racemic isomer in the catalyst mixture.[4c,5,12] From Table 1 it can be seen that in both cases for propylene the ethylene-bridged zircononcenes were slightly more active at 20 °C than the dimethylsilylene-bridged zirconocenes; however, for ethylene polymerization, the activities were comparable.

The unbridged metallocenes **6b**−**d** were found to produce both polyethylene and polypropylene when activated with either MAO or trityl/TIBA, although the activities for propylene were lower than for the bridged metallocenes. At the lower polymerization temperature of −10 °C, bis(3-methyltetrahydrofluorenyl)zirconium dichloride **6c** was found to produce moderately isotactic PP. However, at room temperature, this stereoregularity was lost. For the 1-methyl analogue **6b**, the PP was atactic at both temperatures. For the 1,4-dimethyl analogue **6d**, only trace amounts of atactic polymer were obtained. The activity with this complex was lower than for the monosubstituted complexes probably due to steric overcrowding of the metal center.

Tetrahydrofluorenyl titanium trichloride (**5**) was evaluated as a catalyst for styrene polymerization. Syndiotactic polystyrene (*s*-PS) was produced in high yield using **5**/MAO at 50 °C (activity = 1.4×10^7 g PS/(mol Ti·mol styrene·h). The syndiotacticity was found to be 89%, and polymer melting point was 258 °C. These results are comparable to those reported for substituted indenyl titanium trichloride systems.[13]

It is of interest to compare the polymerization properties of the new bridged zirconocenes **4a**−**d** with those of ethylene bis-fluorenyl zirconium dichloride ($EtFlu_2ZrCl_2$)[4a] and dimethylsilylene bis-fluorenyl zirconium dichloride ($Me_2SiFlu_2ZrCl_2$).[4d,e] It has been shown that the latter compounds polymerize propylene to very high molecular weight *a*-PP; in fact the highest M_w *a*-PP to date was obtained with ($Me_2SiFlu_2ZrCl_2$). Resconi et al. studied several bis-Cp and bis-Ind metallocenes, all of which were found to produce low M_w *a*-PP due to high rate of chain transfer.[4d,e] A general trend of increasing M_w with increasing steric bulk around the Cp moiety was found. It was determined that a requirement for lower β-hydride elimination and therefore higher M_w was substitution at the four β-positions of Cp in *ansa*-metallocenes. On the basis of this conclusion the bis-fluorenyl *ansa*-metallocenes were synthesized.[4d,e] Sterically, it can be seen that **4a** and **4b** meet this requirement of substitution around the Cp moiety, although the tetrahydrofluorenyl ligand is less stereorigid than fluorenyl since the saturated ring assumes a half-chair conformation that can undergo inversion as can cyclohexene. Electronically however, one would expect **4a** and **4b** to behave more like a substituted indenyl. This would explain the higher stability of the new zirconocenes due to increased hapticity.

For the polymerization of ethylene, the activities obtained for **4a**−**d** are comparable to that obtained for ($EtFlu_2ZrCl_2$) at 50 °C, 3.5−5.8 × 10^7 and 6.0 × 10 ^{7} g polymer/[(mol Zr)·[C_2]·h), respectively.[4a] For propylene, however, there does appear to be a more significant difference between the polymerization activities. At 20 °C, **4a** was found to produce PP with an activity of 1.1×10^6. This activity increased slightly at 70 °C to 1.5×10^6 g polymer/[(mol Zr)·[C_3]·h). For ($EtFlu_2ZrCl_2$) at 70 °C, an activity of 1.1×10^7 g polymer/[(mol Zr)·[C_3]·h) was obtained; that is, a 10-fold increase in activity is observed in changing the π-ligand from tetrahydrofluorenyl to fluorenyl.[4a]

A further significant difference between these two systems appears to be their chain termination rates for propylene polymerization. For polyethylene, the molecular weights of the polymer sample obtained for **4a** and ($EtFlu_2ZrCl_2$) are comparable, 2.6×10^5 and 2.8×10^5 g/mol, respectively. However, for polypropylene the molecular weights of the polymers from **4a**−**d** appear to be very low. For polymerization runs at 20 °C, the polymers were viscous oils and at 70 °C they were nonviscous liquids. Similar observations were reported for the low M_w polymers obtained with bis-indenyl and bis-cyclopentadienyl zirconocenes.[4d,e] For ($EtFlu_2ZrCl_2$), the M_w was determined to be 2.8×10^5 g/mol,[4a] while for **4a** at 20 °C, a value of 3.3×10^4 g/mol was obtained. The lower molecular weights obtained with the bis(tetrahydrofluorenyl) systems may be attributed to the more indenyl-like character of the systems or to the less rigid geometry of the complexes, allowing for easier β-hydride or β-methyl elimination.[14]

In conclusion, several new, novel bridged and unbridged metallocenes containing tetrahydrofluorenyl as the π-ligand were prepared. These complexes were found to be highly stable and were efficient Ziegler−Natta type catalyst precursors for the polymerization of ethylene and propylene. The stability of the zirconocenes was found to be markedly better than that of similar fluorenyl-containing metallocenes.

Experimental Section

General Procedures. Reactions were carried out under an argon atmosphere using standard Schlenk techniques. Methylaluminoxane (MAO) was purchased as a solution in toluene from Akzo Nobel and used as received. All other reagents were purchased from Aldrich and used without further purification. Diethyl ether, THF, and pentane were distilled from Na/K alloy under argon. Dichloromethane was distilled from CaH_2 under argon. The ligands **2a**−**d** were prepared according to literature procedures.[9,15] ^1H NMR spectra were recorded on a AC-200 spectrometer. ^{13}C NMR spectra obtained for the polypropylene samples (Table 1) were recorded on a DPX 300 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, and mass spectrometry was performed by the Mass Spectrometry Center, University of Massachusetts, Amherst, MA.

Bis(tetrahydrofluorenyl)ethane (3a). Tetrahydrofluorene (**2a**) (3.00 g, 17.6 mmol) was dissolved in 20 mL of dry

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[13] (a) Foster, P.; Rausch, M. D.; Chien, J. C. W. *Organometallics* **1996**, *15*, 4951, (b) Ready, T. E.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1996**, *519*, 21.

[14] (a) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H. *Organometallics* **1992**, *11*, 362. (b) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025.

[15] ^1H NMR data for **2b**,**c**,**d**. **2b** ($CDCl_3$): δ 7.23−6.92 (m, 3 H, arom), 3.14 (s, 2, H C_5), 2.43 (bs, 4 H), 2.33 (s, 3 H, CH_3), 1.82−1.78 (m, 4 H). **2c** ($CDCl_3$): δ 7.29−6.90 (m, 3 H, arom), 3.19 (s, 2 H, C_5), 2.43−2.38 (m, 7 H), 1.81−1.60 (m, 4 H). **2d** ($CDCl_3$): δ 6.93−6.79 (m, 2 H, arom), 3.09 (s, 2 H, C_5), 2.80−2.63 (m, 2 H), 2.50 (s, 3 H, CH_3), 2.49−2.40 (m, 2 H), 2.27 (s, 3 H, CH_3), 1.77−1.75 (m, 4 H). ^1H NMR data for **2a** was published by: Kimmer Smith, W.; Hardin, J. N.; Rabideau, P. W. *J. Org. Chem.* **1990**, *55*, 5301.

THF and cooled to 0 °C. Butyllithium, 1.6 M in hexane (11.01 mL, 17.62 mmol), was added dropwise to give a red/orange solution, which was stirred at room temperature for 6 h. Upon cooling to 0 °C, 1,2-dibromoethane (1.66 g, 8.81 mmol) was added quickly. The resulting beige suspension was stirred overnight at room temperature. The mixture was hydrolyzed with NH_4Cl(aq) and extracted in THF and diethyl ether. The organics were collected, dried ($MgSO_4$), and filtered, and the solvents were removed to give a yellow solid. Recrystallization from 1:1 toluene/hexane resulted in 1.94 g (60%) of **3a** as a white solid; mp 186−187 °C. ^1H NMR ($CDCl_3$): δ 7.28−7.07 (m, 8 H, arom), 3.14 (bs, 2 H, C_5), 2.41−2.13 (m, 8 H), 1.80−1.77 (m, 8 H), 1.51−1.27 (m, 4 H). Anal. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25. Found: C, 91.47; H, 8.34.

Bis(tetrahydrofluorenyl)dimethylsilane (3b). Following the procedure described for **3a**, tetrahydrofluorene (**2a**) (3.00 g, 17.6 mmol), 1.6 M butyllithium (11.01 mL, 17.62 mmol), and dichlorodimethylsilane (1.07 mL, 8.81 mmol) gave a yellow oil. Recrystallization from hexane gave **3b** (1.33 g, 38%) as a white solid, mp 101−102 °C, which was a mixture of two isomers that could not be separated by repeated crystallizations. ^1H NMR ($CDCl_3$): δ7.49−7.06 (m, 8 H, arom), 3.59−3.52 (bd, 2 H, C_5), 2.51−2.38 (m, 8 H), 1.93−1.51 (m, 8 H), −0.22 - −0.40 (m, 6 H Si−CH_3). Anal. Calcd for $C_{28}H_{32}Si$: C, 84.79; H, 8.13. Found: C, 84.98; H, 8.13.

Bis(3-methyltetrahydrofluorenyl)ethane (3c). Following the procedure described for **3a**, 3-methyltetrahydrofluorene (**2c**) (3.00 g, 16.3 mmol), 1.6 M butyllithium (10.20 mL, 16.30 mmol), and 1,2-dibromoethane (1.53 g, 8.15 mmol) were reacted. After addition of the dibromoethane, the reaction mixture was heated to reflux overnight, resulting in a light brown solid after workup which was recrystallized from 100% ethanol to give **3c** (0.82 g, 26%) as a white solid; mp 162−168 °C. ^1H NMR ($CDCl_3$): δ 7.17−6.91 (m, 6 H, arom), 3.10 (bs, 2 H, C_5), 2.39 (bs, 10 H, CH_3 and bridge), 2.23−2.13, (m, 4 H), 1.79−1.76 (m, 8 H), 1.45−1.43 (m, 4 H). Anal. Calcd for $C_{30}H_{34}$: C, 91.32; H, 8.68. Found: C, 91.32; H, 8.54.

Bis(3-methyltetrahydrofluorenyl)dimethysilane (3d). Following the procedure described for **3a**, 3-methyltetrahydrofluorene (**2c**) (3.00 g, 16.3 mmol), 1.6 M butyllithium (10.20 mL, 16.30 mmol), and dichlorodimethylsilane (0.99 mL, 8.15 mmol) gave **3d** (1.00 g, 29%) as a white solid, which was recrystallized from hexane; mp 179−180 °C. ^1H NMR ($CDCl_3$): δ 7.38−6.90 (m, 6 H, arom), 3.47 (s, 2 H, C_5), 2.50−2.45 (m, 8 H), 2.48 (s, 6 H, CH_3), 1.87−1.58 (m, 8 H), −0.27 (s, 6 H, Si−CH_3). Anal. Calcd for $C_{30}H_{36}Si$: C, 84.84; H, 8.54. Found: C, 84.57; H, 8.70.

Ethylenebis(tetrahydrofluorenyl)zirconium Dichloride (4a). To a suspension of **3a** (1.00 g, 2.73 mmol) in 30 mL of dry diethyl ether at 0 °C was added 2 equiv of 1.6 M butyllithium in hexane (3.41 mL, 5.46 mmol). The resulting yellow suspension was stirred at room temperature for 6 h. The solvent was removed in vacuo, and the solid was washed with 2 × 20 mL of pentane. The solid was suspended in 30 mL of diethyl ether at 0 °C, and $ZrCl_4$ (0.64 g, 2.73 mmol) was added as a solid. The mixture was stirred overnight at room temperature, and the solvent was removed by filtration. The yellow solid was extracted in CH_2Cl_2, concentrated, and stored at −20 °C to give **4a** (0.66 g, 46%), a yellow solid as a mixture of two isomers. ^1H NMR ($CDCl_3$): δ 7.69−6.83 (m, 8 H, arom), 5.30 (s, 0.8 H, CH_2Cl_2), 4.09−3.69 (m, 4 H, bridge), 3.21−2.41 (m, 8 H), 2.20−1.30 (m, 8 H). Anal. Calcd for $C_{28}H_{28}Cl_2Zr\cdot 0.4CH_2Cl_2$: C, 60.84; H, 5.18. Found: C, 61.05; H, 5.23.

Dimethylsilylenebis(tetrahydrofluorenyl)zirconium Dichloride (4b). Following the procedure described for **4a**, **3b** (1.00 g, 2.52 mmol), 1.6 M butyllithium (3.15 mL, 5.04 mmol), and $ZrCl_4$ (0.59 g, 2.52 mmol) gave **4b** (0.65 g, 46%), an orange solid as a mixture of two isomers. ^1H NMR ($CDCl_3$): δ 7.66−6.70 (m, 8 H, arom), 3.16−2.42 (m, 8 H), 2.15−1.45 (m, 8 H), 1.42 (s, 1.5 H, Si−CH_3), 1.25 (s, 3 H, Si−CH_3), 1.12 (s, 1.5 H, Si−CH_3). Anal. Calcd for $C_{28}H_{30}Cl_2SiZr$: C, 60.40; H, 5.43. Found: C, 60.22; H, 5.56.

Ethylenebis(3-methyltetrahydrofluorenyl)zirconium Dichloride (4c). Following the procedure described for **4a**, **3c** (0.60 g, 1.52 mmol), 1.6 M butyllithium (1.90 mL, 3.04 mmol), and $ZrCl_4$ (0.35 g, 1.52 mmol) gave **4c** (0.34 g, 40%), a yellow solid as a mixture of two isomers. ^1H NMR ($CDCl_3$): δ 7.59−6.91 (m, 6 H, arom), 3.91−3.63 (m, 4 H, bridge), 3.05−2.53 (m, 8 H), 2.47−2.46 (d, 6 H, CH_3), 1.93−1.45 (m, 8 H). Anal. Calcd for $C_{30}H_{32}Cl_2Zr$: C, 64.96; H, 5.81. Found: C, 63.27, H, 5.80. HRMS (EI) *m*/*z* calcd for $C_{30}H_{32}Cl_2Zr$: 552.0928. Found: 552.0928.

Dimethylsilylenebis(3-methyltetrahydrofluorenyl)zirconium Dichloride (4d). Following the procedure described for **4a**, **3d** (0.65 g, 1.53 mmol), 1.6 M butyllithium (1.91 mL, 3.06 mmol), and $ZrCl_4$ (0.36 g, 1.53 mmol) gave **4d** (0.35 g, 39%), an orange solid as a mixture of two isomers. ^1H NMR ($CDCl_3$): δ 7.51−6.56 (m, 6 H, arom), 3.10−2.50 (m, 8 H), 2.45 (minor), 2.36 (major), 2.32 (minor) (s, 6 H, CH_3), 2.09−1.44 (m, 8 H), 1.37 (s, 1.5 H, Si−CH_3), 1.22 (s, 3 H, Si−CH_3), 1.08 (s, 1.5 H, Si−CH_3). Anal. Calcd for $C_{30}H_{34}Cl_2SiZr$: C, 61.61; H, 5.86. Found: C, 60.63: H, 5.83. HRMS (EI) *m*/*z* calcd for $C_{30}H_{34}Cl_2SiZr$: 582.0854. Found: 582.0850.

(Tetrahydrofluorenyl)titanium Trichloride (5). A solution of **2a** (2.00 g, 11.7 mmol) in 25 mL of dry THF was cooled to 0 °C, and 1.6 M butyllithium in hexane (7.31 mL, 11.7 mmol) was added dropwise. The solution was stirred 5 h at room temperature, and then chlorotrimethylsilane (1.49 mL, 11.7 mmol) was added at 0 °C. The resulting yellow suspension was stirred overnight at room temperature. The solvent was removed under vacuum, and the residue was extracted in 2 × 20 mL of pentane. Removal of the pentane in vacuo yielded 2.34 g (82%) of 9-trimethylsilyltetrahydrofluorene as a yellow oil. ^1H NMR ($CDCl_3$): δ 7.36−7.04 (m, 5 H, arom), 3.21 (s, 1 H, C5), 2.51−2.36 (m, 4 H), 1.95−1.69 (m, 4 H), −0.02 (s, 9 H). 9-Trimethylsilyltetrahydrofluorene (2.34 g, 9.65 mmol) in 20 mL of dry methylene chloride was cooled to 0 °C, and 1.10 mL (10.0 mmol) $TiCl_4$ was added. The dark red solution was stirred overnight at room temperature. The methylene chloride was removed under vacuum, and the residue was extracted in toluene, concentrated, and stored at −20 °C to give **5** (1.24 g, 40%) as a dark red solid. ^1H NMR ($CDCl_3$): δ 7.81−7.45 (m, 4 H, arom), 6.94 (s, 1 H, C_5), 3.65−3.31 (m, 2 H), 3.07−2.74 (m, 2 H), 2.27−2.08 (m, 2 H), 1.90−1.72 (m, 2 H). Anal. Calcd for $C_{13}H_{13}Cl_3Ti$: C, 48.27; H, 4.05. Found: C, 49.05; H, 4.42.

Bis(1-methyltetrahydrofluorenyl)zirconium Dichloride (6b). 1-Methyltetrahydrofluorene (**2b**) (0.80 g, 4.34 mmol) was dissolved in 20 mL of dry diethyl ether and cooled to 0 °C. Butyllithium (1.6 M in hexane, 2.71 mL, 4.34 mmol) was added dropwise, and the resulting pale yellow suspension was stirred for 6 h at room temperature. The solvent was removed in vacuo, and the residue was washed with 2 × 20 mL of pentane. The solid was resuspended in diethyl ether, and cooled to 0 °C, and 0.5 equiv of $ZrCl_4$ (0.51 g, 2.17 mmol) was added as a solid. The bright yellow suspension was stirred overnight at room temperature. The solvent was removed by filtration, and the residue was extracted in methylene chloride, concentrated, and stored at −20 °C to give **6b** (0.31 g, 27%) as a yellow solid. ^1H NMR ($CDCl_3$): δ 7.40−6.90 (m, 6 H, arom), 5.52 (minor), 5.38 (major) (s, 2 H, C_5) 3.34−2.66 (m, 8 H), 2.32 (minor), 2.23 (major) (s, 6 H, CH_3), 1.95−1.55 (m, 8 H). Anal. Calcd for $C_{28}H_{30}Cl_2Zr$: C, 63.61; H, 5.72. Found: C, 63.74; H, 5.76.

Bis(3-methyltetrahydrofluorenyl)zirconium Dichloride (6c). Following the procedure described for **6b**, **2c** (1.00 g, 5.43 mmol), butyllithium (3.40 mL, 5.43 mmol), and $ZrCl_4$ (0.63 g, 2.72 mmol) gave **6c** (0.26 g, 18%) as a yellow solid. ^1H NMR ($CDCl_3$): δ 7.76−7.11 (m, 6 H, arom), 4.72 (s, 2 H, C_5), 3.19−2.20 (m, 8 H), 2.47 (s, 6 H, CH_3), 2.00−1.45 (m, 8 H).

Anal. Calcd for $C_{28}H_{30}Cl_2Zr$: C, 63.61; H, 5.72. Found: C, 63.34; H, 5.66.

Bis(1,4-dimethyltetrahydrofluorenyl)zirconium Dichloride (6d). Following the procedure described for **6b**, **2d** (1.00 g, 5.04 mmol), butyllithium (3.15 mL, 5.04 mmol), and $ZrCl_4$ (0.59 g, 2.52 mmol) gave **6d** (0.37 g, 27%) as a yellow solid. ^1H NMR ($CDCl_3$): δ 6.80−6.73 (m, 4 H, arom), 5.42 (s, 2 H, C_5), 3.63−3.50 (m, 2 H), 3.06−2.90 (m, 4 H), 2.75−2.66 (m, 2 H), 2.51 (s, 6 H, CH_3), 2.19 (s, 6 H, CH_3), 2.00−1.50 (m, 8 H). Anal. Calcd for $C_{30}H_{34}Cl_2Zr$: C, 64.72; H, 6.16. Found: C, 63.95; H, 6.05.

4-*tert*-Butylbenzylcyclohexanone (2e). To a solution of cyclohexanone (4.71 g, 0.048 mol) in 50 mL of dry diethyl ether was added portionwise $NaNH_2$ (1.87 g, 0.048 mol). After 3 h at reflux, 4-*tert*-butylbenzyl bromide (10.00 g, 0.044 mol) was added quickly. The mixture was heated at reflux for 5 h. Following an acid/base workup as described for **2a**−**d**, a yellow oil was isolated, which was distilled at 140−141 °C at 1.5 mmHg to give **2e** (3.93 g, 37%) as a colorless oil. ^1H NMR ($CDCl_3$): δ 7.31−7.06 (m, 4 H, arom), 3.25−3.16 (dd, 1 H), 2.60−1.50 (m, 10 H), 1.30 (s, 9 H, *t*-Bu). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.51; H, 9.81.

Polymerizations with MAO Cocatalyst. A 250 mL crown capped glass pressure reactor containing 50 mL of toluene was equilibrated with the appropriate monomer and pressure at the desired temperature. The desired amount of methylaluminoxane (MAO) was added as a solution in toluene via syringe, and the solution was stirred for 5 min. One milliliter of the appropriate catalyst solution in toluene was added, and the mixture was stirred until the desired reaction time was reached. The mixture was quenched with 2% HCl in methanol, filtered, or in the case of atactic PP, extracted in hexane, and dried in a vacuum oven at 60 °C.

Polymerizations with Trityl Cocatalyst. A 250 mL crown capped glass pressure reactor containing 50 mL of toluene was equilibrated with the appropriate monomer and pressure at the desired temperature. The desired amount of TIBA was added as a solution in toluene via syringe, and the solution was stirred for 5 min. One milliliter of the appropriate catalyst solution in toluene was added, and the solution was stirred for 5 min. The desired amount of triphenylcarbenium tetrakis(pentafluorophenyl)borate in toluene was added, and the mixture was stirred for 30 min. The mixture was quenched with 2% HCl in methanol, filtered, and dried in a vacuum oven at 60 °C.

Styrene Polymerizations. To a 250 mL crown capped glass pressure reactor containing 50 mL of toluene was added 5.0 mL of styrene (previously dried over CaH_2). After heating to 50 °C, MAO (2.9 mL of a 3.49 M solution in toluene) was added via syringe, and the solution was stirred for 5 min. One milliliter of the catalyst solution (50 μM in toluene) was added, and the mixture was stirred for 30 min. The mixture was quenched with 2% HCl in methanol, filtered, and dried in a vacuum oven at 60 °C. The percentage of *s*-PS was determined by Soxhlet extraction in 2-butanone. % *s*-PS = [(g of insoluble polymer)/(g of bulk polymer)] × 100.

Polymer Analyses. Melting points were determined by DSC with a Perkin-Elmer DSC-4 system. ^{13}C NMR spectra were determined on a DPX300 spectrometer in $CDCl_3$ at room temperature. Molecular weights were determined by viscometry in decalin at 135 °C.

Acknowledgment. We would like to thank Adlan Ramli for synthetic assistance, Dr. G. Dabkowski for microanalyses, Dr. L. C Dickinson for help with ^{13}C NMR, and Dr. I. Kaltashov for mass spectral data. We would also like to thank SOLVAY Polyolefins Europe−Belgium for their financial support of this research program.

OM0005046