Hydrosilylation in the Design and Functionalization of *ansa*-Metallocene Complexes

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The *ansa*-ligand precursors $Me(H)Si(C_5HMe_4)(C_5H_5)$ (**2**) and $Me(H)Si(C_5HMe_4)_2$ (**3**) and their dilithium derivatives $[Me(H)Si(C_5Me_4)(C_5H_4)]Li_2$ (**4**) and $[Me(H)Si(C_5Me_4)_2]Li_2$ (**5**) have been prepared. The group 4 metal complexes $[Me(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$ (M = Ti (**6**), Zr (**7**), Hf (**8**)) and $[Me(H)Si(\eta^5\text{-}C_5Me_4)_2]MCl_2$, (M = Ti (**9**), Zr (**10**), Hf (**11**)) were synthesized from the reaction of the lithium *ansa* derivative and the tetrachloride salts of the transition metal. **6**−**8** reacted with $Si(CH{=}CH_2)_4$ and $Me_2Si(CH{=}CH_2)_2$ to give the hydrosilylation products $[Me\{(CH_2{=}CH)_3SiCH_2CH_2\}Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$, (M = Ti (**12**), Zr (**13**), Hf (**14**)) and $[Me\{(CH_2{=}CH)Me_2SiCH_2CH_2\}Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$ (M = Ti (**15**), Zr (**16**), Hf (**17**)). **12**, **13**, **15**, and **16** reacted with the silane reagent $HSiEt_3$ to give $[Me\{(Et_3SiCH_2CH_2)_3SiCH_2CH_2\}Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$ (M = Ti (**18**), Zr (**19**)) and $[Me\{(Et_3SiCH_2CH_2)Me_2SiCH_2CH_2\}Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$ (M = Ti (**20**), Zr (**21**)). The molecular structure of **10** has been determined by single-crystal X-ray diffraction studies.

Introduction

The discovery by Sinn and Kaminsky[1] of the catalytic activity of group 4 metallocene compounds in the polymerization of olefins has led to a rapid and ongoing development in this area.[2] The principal efforts in this research field are centered on the design of metallocene catalysts capable of originating materials with “user defined” physical properties.

ansa-Cyclopentadienyl systems have, for many years, been at the forefront of metallocene catalysis chemistry.[3] The so-called “*ansa* effect” has been discussed in several articles which confer on the *ansa* system a profound influence on chemical behavior.[4] In addition, high stereoselectivity in asymmetric catalysis can be obtained by incorporating substituted *ansa*-cyclopentadienyl ligands in the metallocene complex.[5] For example, *rac*-$[Me_2Si(\eta^5\text{-}C_5H_3Me)_2]ZrCl_2$ is isospecific in α-olefin polymerization.[6] The majority of *ansa*-metallocene complexes reported contain silicon as the bridging atom, but there are only a few examples with functional groups attached to the bridgehead atom.[7]

The current trend in the field of metallocene catalysis is moving toward supported catalysts that allow homogeneous single-site selectivity in a heterogeneous medium.[8] The introduction of functional groups in the ligand system can be exploited in immobilizing the catalyst on different substrates without greatly altering the general structure of the metallocene complex.[7a,9]

As a continuation of our previous work related to single-site catalysts,[10] we now report the synthesis of

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(1) Andresen, A.; Cordes, H.-G.; Herwig, J.; Kaminsky, W.; Merck, A.; Mottweiler, R.; Pein, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 630.

(2) See for example: (a) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (c) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (d) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *3*, 6, 1143.

(3) (a) *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 4. (b) Rieger, B.; Jany, G.; Fawzi, R.; Steimann, M. *Organometallics* **1994**, *13*, 647.

(4) (a) Conway, S. L. J.; Dijkstra, T.; Doerrer, L. H.; Green, J. C.; Green, M. L. H.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1998**, 2689. (b) Shin, J. H.; Parkin, G. *Chem. Commun.* **1999**, 887. (c) Lee, H.; Bridgewater, B. M.; Parkin, G. *Dalton Trans.* **2000**, 4490. (d) Shapiro, P. J. *Coord. Chem. Rev.* **2002**, *231*, 67.

(5) Huttenloch, M. E.; Dorer, B.; Rief, U.; Prosenc, M.-H.; Schmidt, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1997**, *541*, 219.

(6) (a) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1989**, 1853. (b) Röll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 279. (c) Rieger, B.; Reinmuth, A.; Röll, W.; Brintzinger, H. H. *J. Mol. Catal.* **1993**, *82*, 67. (d) Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 359.

(7) (a) Tian, J.; Soo-Ko, Y.; Metcalf, R.; Feng, Y.; Collins, S. *Macromolecules* **2001**, *34*, 3120. (b) Yamaguchi, Y.; Suzuki, N.; Mise, T.; Wakatsuki, Y. *Organometallics* **1999**, *18*, 996. (c) Zhu, H.; Jin, G.-X.; Hu, N. *J. Organomet. Chem.* **2002**, *655*, 167. (d) Takayama, C.; Yamaguchi, Y.; Mise, T.; Suzuki, N. *Dalton Trans.***2001**, 948. (e) Huhn, T.; Suzuki, N.; Yamaguchi, Y.; Mise, T.; Chihara, T.; Wakatsuki, Y. *Chem. Lett.* **1997**, 1201.

(8) (a) Hlatky, G. C. *Chem. Rev.* **2000**, *100*, 1347. (b) Lee, B. Y.; Oh, J. S. *Macromolecules* **2000**, *33*, 3194. (c) Galan-Fereres, M.; Koch, T.; Hey-Hawkins, E.; Eisen, M. S. *J. Organomet. Chem.* **1999**, *580*, 145. (d) Lee, B. Y.; Oh, J. S. *J. Organomet. Chem.* **1998**, *552*, 313.

(9) See for example: (a) Van Looveren, L. K.; Geysen, D. F.; Vercruysse, K. A.; Wouters, B. H.; Grobet, P. J.; Jacobs, P. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 517. (b) Tudor, J.; O'Hare, D. *Chem. Commun.* **1997**, 603.

(10) (a) Antiñolo, A.; López-Solera, I.; Orive, I.; Otero, A.; Prashar, S.; Rodríguez, A. M.; Villaseñor, E. *Organometallics* **2001**, *20*, 71. (b) Antiñolo, A.; López-Solera, I.; Otero, A.; Prashar, S.; Rodríguez, A. M.; Villaseñor, E. *Organometallics* **2002**, *21*, 2460. (c) Alonso-Moreno, C.; Antiñolo, A.; López-Solera, I.; Otero, A.; Prashar, S.; Rodríguez, A. M.;

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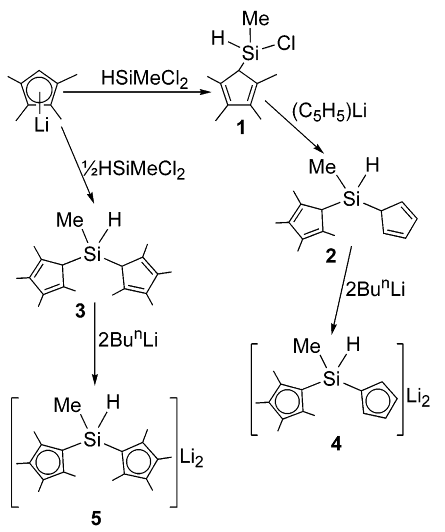
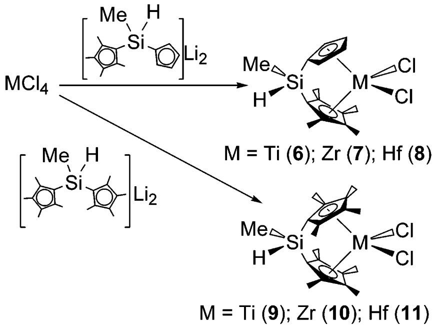
Scheme 1



Scheme 2



new group 4 *ansa*-metallocene complexes and the reactivity of the ansa-bridge Si−H bond in its hydrosilylation of unsaturated silane substrates.

Results and Discussion

The ligand systems Me(H)Si(C_5HMe_4)Cl (**1**), Me(H)-Si(C_5HMe_4)(C_5H_5) (**2**), and Me(H)Si(C_5HMe_4)$_2$ (**3**) were synthesized via conventional methods (Scheme 1) and characterized by ^{1}H NMR spectroscopy and electron impact mass spectroscopy (see Experimental Section). The *ansa* ligands **2** and **3** were lithiated in the normal manner with *n*-butyllithium, giving the dilithium derivatives [Me(H)Si(C_5Me_4)(C_5H_4)]Li$_2$ (**4**) and [Me(H)Si-(C_5Me_4)$_2$]Li$_2$ (**5**) in high yields.

The reaction of the dilithium derivatives **4** and **5** with [TiCl$_4$(THF)$_2$], ZrCl$_4$, or HfCl$_4$ gave the corresponding *ansa*-metallocene dichloride complexes [Me(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]MCl$_2$ (M = Ti (**6**), Zr (**7**), Hf (**8**)) and [Me(H)Si(η^5-C$_5$Me$_4$)$_2$]MCl$_2$ (M = Ti (**9**), Zr (**10**), Hf (**11**)) (Scheme 2).[11]

6−**11** were isolated as crystalline solids and characterized spectroscopically. The compounds are thermically stable and are not highly air-sensitive. The C_s-symmetric complexes **9**−**11** gave in the ^{1}H NMR spectra four singlets, in the region δ 1.6−2.1, corresponding to the permethyl-substituted *ansa* ligand. The mixed cyclopentadienyl chiral complexes **6**−**8** gave eight signals, assigned to the four protons of the unsubstituted cyclopentadienyl moiety and to the four methyl groups of the tetramethylcyclopentadienyl fragment. The ^{13}C{^{1}H} NMR spectra for **6**−**11** showed the expected signals for the different ligand systems present (see Experimental Section). The ^{29}Si NMR spectra revealed the presence of a doublet of quadruplets centered at ca. δ 32 for **6**−**8** and ca. δ 38 for **9**−**11**, corresponding to the silicon atom coupled to its hydride substituent (^1J = ca. 210 Hz) and to the three protons of the methyl substituent of the *ansa* bridge (^2J = ca. 7.6 Hz).

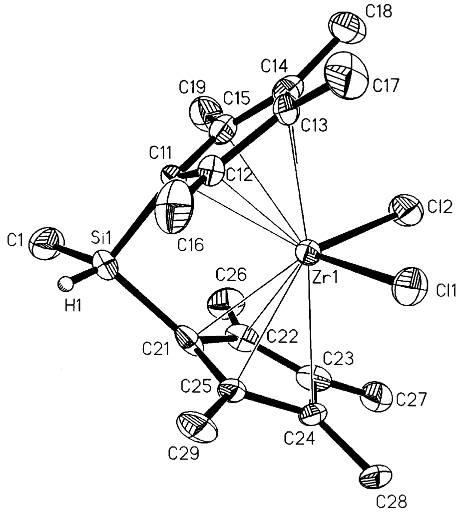


Figure 1. Molecular structure and atom-labeling scheme for [Me(H)Si(η^5-C$_5$Me$_4$)$_2$]ZrCl$_2$ **(10)**, with thermal ellipsoids at 30% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 10

Zr(1)−Cent(1)	2.229	Zr(1)−Cl(1)	2.415(5)
Zr(1)−Cent(2)	2.231	Zr(1)−Cl(2)	2.438(5)
av Zr(1)−C(Cent(1))*	2.534	Si(1)−H(1)	1.597
av Zr(1)−C(Cent(2))*	2.537		
Cent(1)−Zr(1)−Cent(2)	128.5	Cl(2)−Zr(1)−Cent(1)	106.3
Si(1)−C(11)−Cent(1)	162.1	Cl(2)−Zr(1)−Cent(2)	107.5
Si(1)−C(21)−Cent(2)	162.6	Cl(1)−Zr(1)−Cl(2)	98.85(6)
C(11)−Si(1)−C(21)	96.2(2)	H(1)−Si(1)−C(1)	109.0
Cl(1)−Zr(1)−Cent(1)	106.3	H(1)−Si(1)−C(11)	125.3
Cl(1)−Zr(1)−Cent(2)	105.6	H(1)−Si(1)−C(21)	121.7

Cent(1) and Cent(2) are the centroids of C(11)−C(15) and C(21)−C(25), respectively. *Refers to the average bond distance between Zr(1) and the carbon atoms of the C$_5$ ring of the corresponding cyclopentadienyl moiety.

The molecular structure of **10** was established by single-crystal X-ray diffraction studies. The molecular structure and atomic numbering scheme are shown in Figure 1. Selected bond lengths and angles for **10** are given in Table 1.

The structure of **10** is, to our knowledge, the only example of an *ansa*-zirconium complex with a hydrogen-substituted silylene bridge. The usual bent-metallocene conformation is observed, with the geometry around the zirconium atom being pseudo-tetrahedral. The *ansa* ligand chelates the zirconium atom, and both C$_5$ rings

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Villaseñor, E. *J. Organomet. Chem.* **2002**, *656*, 129. (d) Antiñolo, A.; Fernández-Galán, R.; Orive, I.; Otero, A.; Prashar, S. *Eur. J. Inorg. Chem.* **2002**, 2470. (e) Antiñolo, A.; Fernández-Galán, R.; Gallego, B.; Otero, A.; Prashar, S.; Rodríguez, A. M. *Eur. J. Inorg. Chem.* **2003**, 2626. (f) Antiñolo, A.; Fajardo. M.; Gómez-Ruiz, S.; López-Solera, I.; Otero, A.; Prashar, S.; Rodríguez, A. M. *J. Organomet. Chem.* **2003**, *683*, 11.

(11) Constrained-geometry complexes that contain Me(H)Si bridges have recently been reported: (a) Vázquez, A. B.; Royo, P. *J. Organomet. Chem.* **2003**, *671*, 172. (b) Vázquez, A. B.; Royo, P.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *683*, 155.

Table 2. Selected Structural Data of *ansa*-Zirconocene Complexes

complex	Zr−Cp[a] (Å)	Zr−Cl (Å)	Cp−Zr−Cp (deg)	Cl−Zr−Cl (deg)	C_{Cp}−Si−C_{Cp}	ref
$[Me(H)Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$ (**10**)	2.230	2.427	128.5	98.85(6)	96.15(19)	this work
$[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$	2.329	2.4334(7)	128.6	92.28	95.7(1)	12
$[Me(CH_2{=}CH)Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$	2.220	2.418	128.76	99.32(7)	95.8(2)	10f

[a] Cp refers to the C_5Me_4 moiety.

Table 3. Ethylene Polymerization Results for $[Me(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ (7), $[Me(H)Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$ (10), $[Me\{(Et_3SiCH_2CH_2)_3SiCH_2CH_2\}\text{-}Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$ (19), $[Me\{(Et_3SiCH_2CH_2)Me_2SiCH_2CH_2\}\text{-}Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$ (21), $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$, and $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$[a,b]

catalyst	activity[b]	M_w	M_w/M_n
$(\eta^5\text{-}C_5H_5)_2ZrCl_2$	24 600	200 000	5.5
$[Me(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ (**7**)	9 633	162 900	3.3
$[Me(H)Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$ (**10**)	26 407	151 300	3.6
$[Me\{(Et_3SiCH_2CH_2)_3SiCH_2CH_2\}Si\text{-}(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$ (**19**)	3 907	743 300	4.2
$[Me\{(Et_3SiCH_2CH_2)Me_2SiCH_2CH_2\}Si\text{-}(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$ (**21**)	11 100	341 200	5.0
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$	16 073	175 500	3.2
$[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$	11 500	332 800	3.9

[a] Conditions: 20 °C, 2 bar of monomer pressure, 200 mL of toluene, $[Al] = 9 \times 10^{-2}$ mol L^{-1}, $[Zr] = 3 \times 10^{-5}$ mol L^{-1}, t_{Pol} = 15 min. [b] In units of kg of Pol ((mol of Zr) h)$^{-1}$.

are bound to the metal in an η^5 mode. The centroids of the tetramethylcyclopentadienyl rings form an angle with the zirconium atom of 128.5°, which is typical for dichloride *ansa*-zirconocene complexes. Selected structural data of **10** with similar *ansa*-zirconocene complexes can be compared using Table 2.

The polymerization of ethylene using the zirconium derivatives **7** and **10** as catalysts with a MAO to metal catalyst ratio of 3000:1 has been carried out. The polymerization experiments were conducted at 20 °C and at an olefin pressure of 2 bar over 15 min. Polymerization was also carried out with the reference compounds $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$, and $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$ under the same experimental conditions. The catalytic activities and polymer molecular weight and distribution values are given in Table 3. Complex **10** was observed to be more active than $(\eta^5\text{-}C_5H_5)_2ZrCl_2$. **7**, surprisingly, gave one of the lowest activities of the zirconium complexes tested (nearly 3 times less than **10**). Under similar conditions the titanium and hafnium complexes **6**, **8**, **9**, and **11** gave very low catalytic activities.

The polymerization of propylene using the zirconium derivatives **7** and **10** as catalysts with a MAO to metal catalyst ratio of 3000:1 has also been carried out. The polymerization experiments were conducted at 20 °C and at an olefin pressure of 2.5 bar over 30 min. Polymerization was also carried out with the reference compounds $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$, and $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$ under the same experimental conditions. The catalytic activities observed for **7** and **10** are similar to but greater than those recorded for their Me_2Si *ansa*-bridged analogues (see Table 4). However, the activities were less than that recorded for $(\eta^5\text{-}C_5H_5)_2ZrCl_2$. The titanium and hafnium complexes **6**, **8**, **9**, and **11** gave very low catalytic activities.

Table 4. Propylene Polymerization Results for $[Me(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ (7), $[Me(H)Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$ (10), $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$, and $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$[a−c]

catalyst	activity [b]	M_w	M_w/M_n
$(\eta^5\text{-}C_5H_5)_2ZrCl_2$	4920	205 200	13.1
$[Me(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ (**7**)	2167	178 000	10.7
$[Me(H)Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$ (**10**)	1967	186 000	10.8
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$	1567	201 300	13.9
$[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$	1317	183 000	12.2

[a] Conditions: 20 °C, 2.5 bar of monomer pressure, 200 mL of toluene, $[Al] = 9 \times 10^{-2}$ mol L^{-1}, $[Zr] = 3 \times 10^{-5}$ mol L^{-1}, t_{Pol} = 30 min. [b] In units of kg of Pol ((mol of Zr) h)$^{-1}$. [c] ^{13}C NMR spectra showed essentially atactic polymers.

For **7** the metallocene catalyst should be syndiospecific in the polymerization of propylene. However, Morokuma and co-workers have predicted, via theoretical studies, that catalytic systems based on the $H_2Si(C_5Me_4)(C_5H_4)$ ligand will be substantially nonenantioselective, due to repulsive interactions between the methyl group of the propylene and the methyl groups of the C_5Me_4 ligand.[13] Our results concur with this affirmation, with the polypropylene obtained using **7** as catalyst being of low stereospecificity (as observed by ^{13}C NMR spectroscopy of the polymer). This is in agreement with previous studies conducted on the metallocene complexes $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ and $[Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$ (M = Ti, Zr), where this phenomenon was explained by the assumption that the polymer chain experiences counterbalanced steric forces exerted by the monomer methyl group on one hand and from the β-methyl cyclopentadienyl ($C_5\mathit{Me}_4$) substituents on the other.[10b,c,14] An alternative proposal based on theoretical and experimental studies carried out by Schaverien and co-workers suggests that the steric constraints imposed by the *ansa*-bridging group directly influence the stereospecificity of the catalyst. The larger "bite angles" of Si-bridged systems should produce polypropylene with lower stereoregularity than for analogous C-bridged catalysts.[15]

The modification of the *ansa*-metallocene systems via hydrosilylation processes opens up the possibility of supporting the single-site catalysts on silane substrates. Suzuki and co-workers have reported the hydrosilylation of *ansa*-zirconocene complexes, with vinyl substituents at the silicon *ansa* bridge to give derivatives which were subsequently supported on silica.[16] However, with our previously synthesized compounds $[Me(CH_2{=}CH)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ and $[Me(CH_2{=}CH)Si(\eta^5\text{-}C_5\text{-}$

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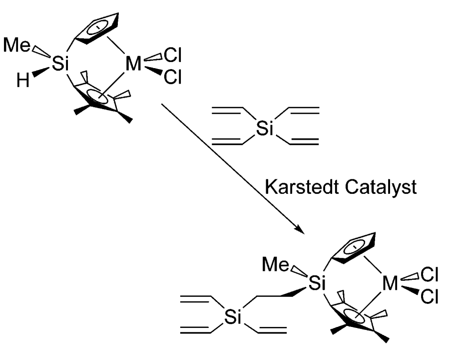
(12) Koch, T.; Blaurock, S.; Somoza, F. B.; Voigt, A.; Kirmse, R.; Hey-Hawkins, E. *Organometallics* **2000**, *19*, 2556.

(13) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, *114*, 8687.

(14) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253.

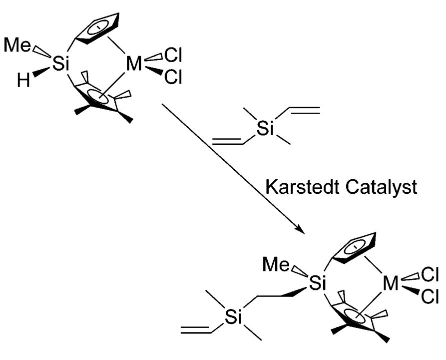
(15) Schaverien, C. J.; Ernst, R.; Terlouw, W.; Schut, P.; Sudmeijer, O.; Budzelaar, P. H. M. *J. Mol. Catal. A: Chem.* **1998**, *128*, 245.

Scheme 3



M = Ti (**12**); Zr (**13**); Hf (**14**)

Scheme 4



M = Ti (**15**); Zr (**16**); Hf (**17**)

$Me_4)_2]ZrCl_2$,[10f] we were unable to repeat this reactivity.[17] Alt and co-workers have also recently published their work relating to the modification by hydrosilylation of *ansa*-cyclopentadienyl ligands and their subsequent incorporation in group 4 metallocene systems.[18] Our strategy differs from that employed by Alt in that our reactivity occurs with group 4 metallocene complexes and not from previous modification of the organic ligand.

Collins and co-workers have reported the anchoring, on modified silica surfaces, of *ansa*-metallocene complexes via hydrosilylation reactions.[7a] Seyferth and co-workers have also carried out work incorporating group 4 metallocene fragments in organosilicon dendrimers.[19] In a similar way it should be possible to support the MeSiH bridge *ansa*-metallocene complexes **6**−**11** via hydrosilylation of vinyl-functionalized silica or dendrimeric systems.

As a first step toward the goal of immobilizing single-site catalysts we have studied the reaction of the *ansa*-metallocene complexes in hydrosilylation molecular processes. We have found for the permethyl-substituted *ansa* complexes **9**−**11** that the Si−H bond is not sufficiently reactive (even at high temperatures) to participate in the hydrosilylation reaction.

The hydrosilylation of $Si(CH{=}CH_2)_4$ by **6**−**8** in the presence of the Karstedt catalyst (platinum(0) divinyltetramethylsiloxane) gave $[Me\{(CH_2{=}CH)_3SiCH_2CH_2\}Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$, (M = Ti (**12**), Zr (**13**), Hf (**14**)), formed by the reaction of only one of the double bonds of the silane substrate (Scheme 3). This occurred even when different and extreme stoichiometries were employed. **12**−**14** were isolated as oils and characterized by NMR spectroscopy. The ^1H NMR spectra showed the expected signals for the cyclopentadienyl moieties: namely, four singlets and four multiplets. The three unreacted vinyl groups of the silane gave an ABX system in the ^1H NMR spectra and signals at ca. δ 133 (C_α) and 136 (C_β) in the $^{13}C\{^1H\}$ NMR spectra. The $-CH_2CH_2-$ fragment resulting from the hydrosilylation of the vinyl group gave a complex set of multiplets with geminal and vicinal couplings. Two signals were observed in the $^{29}Si\{^1H\}$ NMR spectra at ca. δ −18 and −11, corresponding to the vinyl-substituted and *ansa*-bridge silicon atoms, respectively. The hydrosilylation reaction can also give the alternative regioisomer $[Me\{(CH_2{=}CH)_3SiCH(CH_3)\}Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$, via α-addition.[20f] This minor product was detected, in quantities of ca. 5−10%, by ^1H NMR spectroscopy.

The *ansa*-bridge silicon atom is chiral, and thus, the α-protons of the ethylene unit are diastereoscopic. The hydrosilylation of only one of the vinyl groups is supported not only by the integral ratios recorded in the ^1H NMR spectra but also by the fact that only one major product was observed. The reaction of various vinyl groups of the silane substrate would lead to the presence of more than one chiral center and therefore various diastereoisomers. Mass spectrometry data for **12**−**14** confirmed the hydrosilylation of only one of the vinyl groups, giving as the highest mass ion peak that corresponding to the molecular formula proposed (see Experimental Section).

Similar reactions have been carried out between **6**−**8** and the divinylsilane $Si(CH{=}CH_2)_2Me_2$. These gave the products $[Me\{(CH_2{=}CH)Me_2SiCH_2CH_2\}Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]MCl_2$, (M = Ti (**15**), Zr (**16**), Hf (**17**)), formed by the hydrosilylation of only one of the double bonds of the silane substrate (Scheme 4).

The NMR spectra of **15**−**17** are similar in all aspects to those previously discussed for **12**−**14** and showed in addition the presence of the minor regioisomer produced by α-addition (5−10%). Two signals were observed in the $^{29}Si\{^1H\}$ NMR spectra. The *ansa*-bridge silicon atom gave a signal with a chemical displacement similar to that recorded for **12**−**14** (ca. δ −10). However, the monovinyl-substituted silicon gave a signal shifted downfield (ca. δ −3) with respect to the trivinyl-substituted silicon in **12**−**14** (ca. δ −18), indicative of the increase in electron density at the silicon atom in **15**−**17**. Mass spectrometry confirmed the proposal that hydrosilylation takes place at only one of the vinyl groups of the silane substrate (see Experimental Section).

Further hydrosilylation of the vinyl groups of **12**−**17** was not possible when the hydrogen−silicon bond corresponded to the *ansa*-metallocene complexes **6**−**8**. It appears that the reaction of one of the vinyl groups with the *ansa*-metallocene complex deactivates the remaining vinyl groups toward hydrosilylation by the Si−H of the *ansa* bridge. This may be attributed to electronic and/or steric effects. However, with triethyl-

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(16) Suzuki, N.; Yu, J.; Shioda, N.; Asami, H.; Nakamura, T.; Huhn, T.; Fukuoka, A.; Ichikawa, M.; Saburi, M.; Wakatsuki, Y. *Appl. Catal., A* **2002**, *224*, 63.

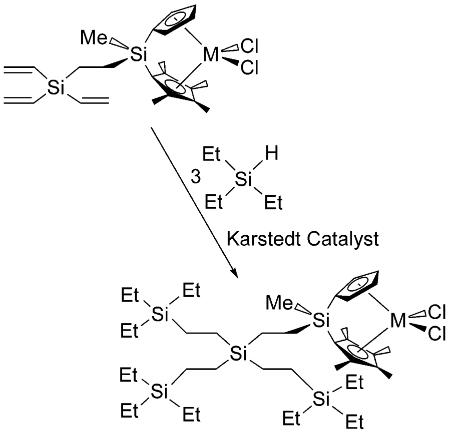
(17) Prashar, S.; Gómez-Ruiz, S. Unpublished results.

(18) Alt, H. G.; Ernst, R.; Böhmer, I. *J. Mol. Catal. A: Chem.* **2003**, *191*, 177.

(19) Seyferth, D.; Wyrwa, R. U.S. Patent 5,969,073, 1999.

(20) See for example: Krska, S. W.; Seyferth, D. *J. Am. Chem. Soc.* **1998**, *120*, 3604.

Scheme 5



M = Ti (**18**); Zr (**19**)

silane, hydrosilylation took place at all the remaining vinyl groups of **12**, **13**, **15**, and **16**, to give [Me{(Et$_3$SiCH$_2$CH$_2$)$_3$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]MCl$_2$ (M = Ti (**18**), Zr (**19**)) and [Me{(Et$_3$SiCH$_2$CH$_2$)Me$_2$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]MCl$_2$ (M = Ti (**20**), Zr (**21**)) (Scheme 5).

18−**21** were isolated as oils and characterized by NMR spectroscopy. The reaction was deemed to have gone to completion by the absence of any signals in ^{1}H and ^{13}C{^{1}H} NMR spectroscopy corresponding to the vinyl groups of the parent complexes. The ^{1}H NMR spectra showed the expected signals for the C$_5$H$_4$ and C$_5$Me$_4$ moieties. In addition, two multiplets, assigned to the ethyl groups of SiEt$_3$, and a complex set of multiplets, corresponding to the two distinct −CH$_2$CH$_2$− fragments, were observed. The presence of the minor α-addition regioisomers was again detected (5−10%). ^{29}Si{^{1}H} NMR spectra revealed three signals, corresponding to the three distinct silicon atoms present. Mass spectrometry data for **18**−**21** gave as highest mass ion peaks those corresponding to the molecular formulas proposed (see Experimental Section).

The polymerization of ethylene using the zirconium derivatives **19** and **21** as catalysts with a MAO to metal catalyst ratio of 3000:1 has been carried out. The polymerization experiments were conducted at 20 °C and at olefin pressure of 2 bar over 15 min (Table 3). The low catalytic activity observed for **19** may be due to steric factors, as proposed previously by De Jesus and co-workers for similar modified metallocene systems.[21] However, **19** produced polyethylene with a much higher molecular weight in comparison with the values obtained for the other tested catalysts.

Conclusions

We have prepared a new family of *ansa*-metallocene group 4 complexes which are catalytically active in the polymerization of olefins. These complexes, via the Si−H bond, act as hydrosilylation reagents toward unsaturated silane compounds, thus opening up not only the possibility of ligand design and modification but also the potential of supporting the catalysts on distinct substrates.

Experimental Section

General Procedures. All reactions were performed using standard Schlenk tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from the appropriate drying agents and degassed before use.

C$_5$H$_2$Me$_4$, (C$_5$H$_5$)Li, TiCl$_4$(THF)$_2$, ZrCl$_4$, HfCl$_4$, HSiMeCl$_2$, Si(CH=CH$_2$)$_4$, SiMe$_2$(CH=CH$_2$)$_2$, and HSiEt$_3$ were purchased from Aldrich and used directly. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrophotometer. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian Mercury FT-400 spectrometer. Microanalyses were carried out with a Perkin-Elmer 2400 or LECO CHNS-932 microanalyzer. Mass spectroscopic analyses were preformed on a Hewlett-Packard 5988A (*m*/*z* 50−1000) instrument.

Me(H)Si(C$_5$HMe$_4$)Cl (1). HSiMeCl$_2$ (2.00 g, 17.39 mmol) in THF (50 mL) was added to a solution of (C$_5$HMe$_4$)Li (2.23 g, 17.39 mmol) in THF (50 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 15 h. Solvent was removed in vacuo, and hexane (150 mL) was added to the resulting orange oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as a yellow oil (3.35 g, 96%). ^{1}H NMR (400 MHz, CDCl$_3$; for the predominant isomer): δ 0.10 (d, 3H, Si*Me*), 1.81 (3H), 1.91 (3H), 1.98 (3H), 2.03 (3H) (s, C$_5$*Me*$_4$), 2.73 (m, 1H, *H*C$_5$), 4.82 (m, 1H, Si*H*). MS electron impact (*m*/*e* (relative intensity)): 225 (55) [M$^+$], 191 (28) [M$^+$ − Cl], 121 (50) [M$^+$ − Me(CH$_2$=CH)SiCl], 105 (100) [M$^+$ − C$_5$HMe$_4$]. Anal. Calcd for C$_{10}$H$_{17}$ClSi: C, 59.82; H, 8.53. Found: C, 59.46; H, 8.41.

Me(H)Si(C$_5$HMe$_4$)(C$_5$H$_5$) (2). Me(H)Si(C$_5$HMe$_4$)Cl (**1**) (2.50 g, 12.45 mmol) in THF (50 mL) was added to a solution of (C$_5$H$_5$)Li (0.90 g, 12.45 mmol) in THF (50 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 15 h. Solvent was removed in vacuo, and hexane (150 mL) was added to the resulting orange oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as a dark orange oil (2.67 g, 93%). ^{1}H NMR (400 MHz, CDCl$_3$; for the predominant isomer): δ −0.12 (d, 3H, Si*Me*), 1.81 (3H), 1.86 (3H), 1.96 (3H), 2.07 (3H) (s, C$_5$*Me*$_4$), 2.98 (1H), 3.50 (1H) (m, *H*C$_5$), 4.47 (m, 1H, Si*H*), 6.60 (1H), 6.62 (1H), 6.68 (1H), 6.75 (1H) (m, C$_5$*H*$_4$). MS electron impact (*m*/*e* (relative intensity)): 230 (51) [M$^+$], 165 (100) [M$^+$ − C$_5$H$_5$], 121 (16) [M$^+$ − Me(H)SiC$_5$H$_5$], 109 (46) [M$^+$ − C$_5$HMe$_4$]. Anal. Calcd for C$_{15}$H$_{22}$Si: C, 78.19; H, 9.62. Found: C, 77.98; H, 9.55.

Me(H)Si(C$_5$HMe$_4$)$_2$ (3). Me(H)SiCl$_2$ (1.80 g, 15.60 mmol) was added to a solution of (C$_5$HMe$_4$)Li (4.00 g, 31.21 mmol) in THF (50 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 15 h. Solvent was removed in vacuo, and hexane (150 mL) was added to the resulting orange oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as a dark orange oil (4.30 g, 96%). ^{1}H NMR (400 MHz, CDCl$_3$; for the predominant isomer): δ −0.19 (d, 3H, Si*Me*), 1.76 (12H), 1.89 (6H), 1.92 (6H) (s, C$_5$*Me*$_4$), 2.75 (m, 2H, *H*C$_5$), 4.00 (m, 1H, Si*H*). MS electron impact (*m*/*e* (relative intensity)): 286 (16) [M$^+$], 225 (82) [M$^+$ − 4 Me], 165 (100) [M$^+$ − C$_5$HMe$_4$], 121 (32) [M$^+$ − Me(H)SiC$_5$HMe$_4$], 105 (43) [M$^+$ − 4 Me − C$_5$HMe$_4$]. Anal. Calcd for C$_{19}$H$_{30}$Si: C, 79.64; H, 10.55. Found: C, 79.55; H, 10.45.

[Me(H)Si(C$_5$Me$_4$)(C$_5$H$_4$)]Li$_2$ (4). ^{n}BuLi (1.6 M in hexane; 14.5 mL, 23.18 mmol) was added dropwise to a solution of **2** (2.67 g, 11.59 mmol) in Et$_2$O (100 mL) at −78 °C. The mixture was warmed to 25 °C and stirred for 15 h. Solvent was removed in vacuo to give a white solid, which was washed with hexane (2 × 50 mL) and dried under vacuum to yield a free-flowing white solid of the title complex (2.36 g, 84%). Anal. Calcd for C$_{15}$H$_{20}$Li$_2$Si: C, 74,36; H, 8,32. Found: C, 74.02; H, 8.29.

[Me(H)Si(C$_5$Me$_4$)$_2$]Li$_2$ (5). The preparation of **5** was carried out in a manner identical with that for **4**, using **3** (4.30 g, 15.01

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(21) Andrés, R.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R. *Eur. J. Inorg. Chem.* **2002**, 2281.

mmol) and ^{n}BuLi (1.6 M in hexane; 18.8 mL, 30.02 mmol). Yield: 3.90 g, 87%. Anal. Calcd for $C_{19}H_{28}Li_2Si$: C, 76.48; H, 9.46. Found: C, 76.13; H, 9.37.

[Me(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]TiCl$_2$ (6). THF (50 mL) was added to a solid mixture of [TiCl$_4$(THF)$_2$] (2.00 g, 5.99 mmol) and [Me(H)Si(C$_5$Me$_4$)(C$_5$H$_4$)]Li$_2$ (**4**) (1.45 g, 5.99 mmol). The resulting solution was stirred for 15 h. Solvent was removed in vacuo and toluene added (75 mL) to the resulting solid. The mixture was filtered and the filtrate concentrated (10 mL) and cooled to −30 °C to yield crystals of the title complex (1.00 g, 48%). IR (Nujol mull): ν_{Si-H} 2185 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.00 (d, 3H, Si*Me*) ($^3J(^1H-^1H) = 3.7$ Hz), 1.87 (3H), 1.90 (3H), 2.15 (3H), 2.16 (3H) (s, C$_5$*Me*$_4$), 5.36 (q, 1H, Si*H*), 5.62 (2H), 7.18 (1H), 7.22 (1H) (m, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −5.4 (Si*Me*), 13.6, 13.7, 15.7, 16.2 (C$_5$*Me*$_4$), 100.0 (C^{ipso}), 115.2, 116.5, 132.6, 134.0 (*C*$_5$H$_4$), 95.2, 130.2, 131.3, 144.0, 144.3 (*C*$_5$Me$_4$). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −30.9 (dq) ($^1J(^{29}Si-^1H) = 213.0$ Hz, $^2J(^{29}Si-^1H) = 7.3$ Hz). MS electron impact (*m/e* (relative intensity)): 346 (24) [M$^+$], 310 (48) [M$^+$ − Cl], 274 (47) [M$^+$ − 2 Cl]. Anal. Calcd for $C_{15}H_{20}Cl_2SiTi$: C, 51.89; H, 5.81. Found: C, 51.67; H, 5.80.

[Me(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]ZrCl$_2$ (7). The synthesis of **7** was carried out in a manner identical with that for **6**, using ZrCl$_4$ (1.40 g, 6.01 mmol) and [Me(H)Si(C$_5$Me$_4$)(C$_5$H$_4$)]Li$_2$ (**4**) (1.46 g, 6.01 mmol). Yield: 0.99 g, 42%. IR (Nujol mull): ν_{Si-H} 2155 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.98 (d, 3H, Si*Me*) ($^3J(^1H-^1H) = 4.0$ Hz), 1.98 (3H), 2.01 (3H), 2.06 (3H), 2.07 (3H) (s, C$_5$*Me*$_4$), 5.36 (q, 1H, Si*H*), 5.75 (1H), 5.76 (1H), 7.00 (1H), 7.04 (1H) (m, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −5.1 (Si*Me*), 12.2, 12.4, 14.4, 14.9 (C$_5$*Me*$_4$), 102.9 (C^{ipso}), 112.0, 113.4, 126.2, 127.5 (*C*$_5$H$_4$), 95.1, 124.9, 126.0, 135.7, 136.0 (*C*$_5$Me$_4$). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −32.1 (dq) ($^1J(^{29}Si-^1H) = 211.6$ Hz, $^2J(^{29}Si-^1H) = 7.6$ Hz). MS electron impact (*m/e* (relative intensity)): 390 (100) [M$^+$], 357 (93) [M$^+$ − Cl], 316 (16) [M$^+$ − 2 Cl]. Anal. Calcd for $C_{15}H_{20}Cl_2SiZr$: C, 46.13; H, 5.16. Found: C, 45.89; H, 5.09.

[Me(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]HfCl$_2$ (8). The synthesis of **8** was carried out in a manner identical with that for **6**, using HfCl$_4$ (1.70 g, 5.31 mmol) and [Me(H)Si(C$_5$Me$_4$)(C$_5$H$_4$)]Li$_2$ (**4**) (1.29 g, 5.31 mmol). Yield: 0.97 g, 38%. IR (Nujol mull): ν_{Si-H} 2157 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.96 (d, 3H, Si*Me*) ($^3J(^1H-^1H) = 4.0$ Hz), 2.05 (3H), 2.07 (3H), 2.08 (3H), 2.09 (3H) (s, C$_5$*Me*$_4$), 5.32 (q, 1H, Si*H*), 5.70 (1H), 5.72 (1H), 6.92 (1H), 6.97 (1H) (m, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −5.1 (Si*Me*), 12.1, 12.2, 14.0, 14.6 (C$_5$*Me*$_4$), 105.1 (C^{ipso}), 109.6, 111.0, 125.3, 126.7 (*C*$_5$H$_4$), 97.0, 121.8, 122.9, 133.8, 134.2 (*C*$_5$Me$_4$). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −32.7 (dq) ($^1J(^{29}Si-^1H) = 211.4$ Hz, $^2J(^{29}Si-^1H) = 7.6$ Hz). MS electron impact (*m/e* (relative intensity)): 478 (18) [M$^+$], 442 (31) [M$^+$ − Cl − H], 163 (30) [M$^+$ − (C$_5$H$_4$)HfCl$_2$ − H]. Anal. Calcd for $C_{15}H_{20}Cl_2HfSi$: C, 37.71; H, 4.22. Found: C, 37.50; H, 4.16.

[Me(H)Si(η^5-C$_5$Me$_4$)$_2$]TiCl$_2$ (9). The synthesis of **9** was carried out in a manner identical with that for **6**, using [TiCl$_4$(THF)$_2$] (2.00 g, 5.99 mmol) and [Me(H)Si(C$_5$Me$_4$)$_2$]Li$_2$ (**5**) (1.79 g, 5.99 mmol). Yield: 1.16 g, 48%. IR (Nujol mull): ν_{Si-H} 2165 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.11 (d, 3H, Si*Me*) ($^3J(^1H-^1H) = 4.4$ Hz), 1.83 (6H), 1.85 (6H), 2.11 (6H), 2.12 (6H) (s, C$_5$*Me*$_4$), 5.52 (q, 1H, Si*H*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −3.9 (Si*Me*), 13.7, 13.9, 16.0, 16.5 (C$_5$*Me*$_4$), 89.8, 129.3, 129.8, 143.2, 143.5 (*C*$_5$Me$_4$). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −36.1 (dq) ($^1J(^{29}Si-^1H) = 206.1$ Hz, $^2J(^{29}Si-^1H) = 7.4$ Hz). MS electron impact (*m/e* (relative intensity)): 402 (32) [M$^+$], 366 (82) [M$^+$ − Cl − H], 351 (100) [M$^+$ − Cl − H − Me]. Anal. Calcd for $C_{19}H_{28}Cl_2SiTi$: C, 56.59; H, 7.00. Found: C, 56.35; H, 6.93.

[Me(H)Si(η^5-C$_5$Me$_4$)$_2$]ZrCl$_2$ (10). The synthesis of **10** was carried out in a manner identical with that for **6**, using ZrCl$_4$ (1.40 g, 6.01 mmol) and [Me(H)Si(C$_5$Me$_4$)$_2$]Li$_2$ (**5**) (1.79 g, 6.01 mmol). Yield: 1.13 g, 42%. IR (Nujol mull): ν_{Si-H} 2150 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.07 (d, 3H, Si*Me*) ($^3J(^1H-^1H) = 4.4$ Hz), 1.94 (6H), 1.96 (6H), 2.07 (6H), 2.08 (6H) (s, C$_5$*Me*$_4$), 5.49 (q, 1H, Si*H*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −3.5 (Si*Me*), 12.5, 12.6, 14.8, 15.4 (C$_5$*Me*$_4$), 90.7, 124.8, 125.2, 135.8, 136.1 (*C*$_5$Me$_4$). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −38.0 (dq) ($^1J(^{29}Si-^1H) = 204.7$ Hz, $^2J(^{29}Si-^1H) = 7.6$ Hz). MS electron impact (*m/e* (relative intensity)): 446 (100) [M$^+$], 408 (53) [M$^+$ − Cl], 393 (74) [M$^+$ −Cl − Me]. Anal. Calcd for $C_{19}H_{28}Cl_2SiZr$: C, 51.09; H, 6.32. Found: C, 50.82; H, 6.29.

[Me(H)Si(η^5-C$_5$Me$_4$)$_2$]HfCl$_2$ (11). The synthesis of **11** was carried out in in a manner identical with that for **6**, using HfCl$_4$ (1.60 g, 5.00 mmol) and [Me(H)Si(C$_5$Me$_4$)$_2$]Li$_2$ (**5**) (1.49 g, 5.00 mmol). Yield: 1.17 g, 44%. IR (Nujol mull): ν_{Si-H} 2144 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.05 (d, 3H, Si*Me*) ($^3J(^1H-^1H) = 4.4$ Hz), 2.01 (6H), 2.03 (6H), 2.09 (6H), 2.10 (6H) (s, C$_5$*Me*$_4$), 5.46 (q, 1H, Si*H*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −3.2 (Si*Me*), 12.6, 12.8, 14.9, 15.5 (C$_5$*Me*$_4$), 93.2, 122.1, 122.6, 134.6, 134.9 (*C*$_5$Me$_4$). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −38.5 (dq) ($^1J(^{29}Si-^1H) = 204.3$ Hz, $^2J(^{29}Si-^1H) = 7.3$ Hz). MS electron impact (*m/e* (relative intensity)): 534 (100) [M$^+$], 498 (37) [M$^+$ − Cl], 483 (80) [M$^+$ − Cl − Me]. Anal. Calcd for $C_{19}H_{28}Cl_2HfSi$: C, 42.74; H, 5.29. Found: C, 42.63; H, 5.29.

[Me{(CH$_2$=CH)$_3$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]TiCl$_2$ (12). Two drops of the Karstedt catalyst (platinum(0) divinyltetramethylsiloxane in xylene (3−3.5%)) were added to a solution of tetravinylsilane (0.062 g, 0.45 mmol) in toluene (5 mL), and the mixture was stirred for 5 min at room temperature. To this solution was added dropwise [Me(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]TiCl$_2$ (**6**) (0.150 g, 0.43 mmol) in toluene (10 mL), and the reaction mixture was stirred for 40 h at 100 °C and then cooled to room temperature. Volatiles were removed under reduced pressure to give the title product as a dark yellow oil (0.179 g, 100%). IR (Nujol mull): $\nu_{CH=CH_2}$ 3049, 1591 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$; for the major isomer): δ 0.88 (s, 3H, Si*Me*), 1.00 (2H), 1.23 (1H), 1.28 (1H) (m, C*H*$_2$C*H*$_2$), 1.84 (3H), 1.86 (3H), 2.14 (3H), 2.15 (3H) (s, C$_5$*Me*$_4$), 5.55 (1H), 5.60 (1H), 7.18 (2H) (m, C$_5$*H*$_4$), 5.84 (m, 3H, CH$_2$=C*H*), 6.18 (m, 6H, C*H*$_2$=CH). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$; for the major isomer): δ −3.4 (Si*Me*), 4.5, 7.2 (*C*H$_2$*C*H$_2$), 13.6, 13.7, 16.3, 16.4 (C$_5$*Me*$_4$), 104.2 (C^{ipso}), 115.5, 116.4, 133.5, 133.7 (*C*$_5$H$_4$), 98.5, 130.5, 131.9, 143.8, 144.4 (*C*$_5$Me$_4$), 132.4, 136.0 (CH=CH$_2$). ^{29}Si{^{1}H} NMR (79.49 MHz, CDCl$_3$; for the major isomer): δ −18.1 (*Si*CH=CH$_2$), −9.7 (*Si*C$_5$H$_4$). MS electron impact (*m/e* (relative intensity)): 482 (100) [M$^+$], 446 (96) [M$^+$ − Cl], 410 (20) [M$^+$ − 2 Cl], 121 (33) [M$^+$ − (CH$_2$=CH)$_3$SiCH$_2$CH$_2$Si(Me)(C$_5$H$_4$)TiCl$_2$], 109 (58) [M$^+$ − CH$_2$CH$_2$Si(Me)(C$_5$Me$_4$)(C$_5$H$_4$)TiCl$_2$], 83 (60) [M$^+$ − CH$_2$=CH − CH$_2$CH$_2$Si(Me)(C$_5$Me$_4$)(C$_5$H$_4$)TiCl$_2$]. Anal. Calcd for $C_{23}H_{32}Cl_2Si_2Ti$: C, 57.14; H, 6.67. Found: C, 56.83; H, 6.68.

[Me{(CH$_2$=CH)$_3$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]ZrCl$_2$ (13). The synthesis of **13** was carried out in a manner identical with that for **12**, using [Me(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]ZrCl$_2$ (**7**) (0.160 g, 0.41 mmol) and tetravinylsilane (0.059 g, 0.43 mmol). Yield: 0.216 g, 100%. IR (Nujol mull): $\nu_{CH=CH_2}$ 3049, 1590 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$; for the major isomer): δ 0.87 (s, 3H, Si*Me*), 1.00 (2H), 1.25 (1H), 1.35 (1H) (m, C*H*$_2$C*H*$_2$), 1.94 (3H), 1.95 (3H), 2.06 (6H) (s, C$_5$*Me*$_4$), 5.66 (1H), 5.73 (1H), 7.01 (2H) (m, C$_5$*H*$_4$), 5.85 (m, 3H, CH$_2$=C*H*), 6.18 (m, 6H, C*H*$_2$=CH). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$; for the major isomer): δ −3.1 (Si*Me*), 4.4, 7.3 (*C*H$_2$*C*H$_2$), 12.3, 12.4, 15.0, 15.2 (C$_5$*Me*$_4$), 106.9 (C^{ipso}), 112.1, 113.0, 126.2, 127.2 (*C*$_5$H$_4$), 98.1, 125.1, 126.4, 133.6, 135.2 (*C*$_5$Me$_4$), 132.7, 136.2 (CH=CH$_2$). ^{29}Si{^{1}H} NMR (79.49 MHz, CDCl$_3$) (for the major isomer): δ −18.1 (*Si*CH=CH$_2$), −10.8 (*Si*C$_5$H$_4$). MS electron impact (*m/e* (relative intensity)): 527 (100) [M$^+$], 490 (26) [M$^+$ − Cl], 447 (13) [M$^+$ − 2 Cl], 352 (34) [M$^+$ − Cl − (CH$_2$=CH)$_3$SiCH$_2$CH$_2$], 109 (87) [M$^+$ − CH$_2$CH$_2$Si(Me)(C$_5$Me$_4$)(C$_5$H$_4$)ZrCl$_2$], 83 (38) [M$^+$ − CH$_2$=CH − CH$_2$CH$_2$Si(Me)(C$_5$Me$_4$)(C$_5$H$_4$)ZrCl$_2$]. Anal. Calcd for $C_{23}H_{32}Cl_2Si_2Zr$: C, 52.44; H, 6.12. Found: C, 52.12; H, 6.06.

[Me{(CH$_2$=CH)$_3$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]HfCl$_2$ (14). The synthesis of **14** was carried out in in a manner identical with that for **12**, using [Me(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]-

$\mathrm{HfCl_2}$ (**8**) (0.180 g, 0.38 mmol) and tetravinylsilane (0.054 g, 0.40 mmol). Yield: 0.231 g, 100%. IR (Nujol mull): $\nu_{\mathrm{CH=CH_2}}$ 3049, 1592 cm^{-1}. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ 0.85 (s, 3H, $\mathrm{Si}Me$), 0.96 (2H), 1.24 (1H), 1.34 (1H) (m, $\mathrm{C}H_2\mathrm{C}H_2$), 2.00 (3H), 2.02 (3H), 2.08 (6H) (s, $\mathrm{C_5}Me_4$), 5.62 (1H), 5.68 (1H), 6.93 (2H) (m, $\mathrm{C_5}H_4$), 5.85 (m, 3H, $\mathrm{CH_2{=}C}H$), 6.17 (m, 6H, $\mathrm{C}H_2\mathrm{{=}CH}$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -3.2 ($\mathrm{Si}Me$), 4.4, 7.4 ($C\mathrm{H_2}C\mathrm{H_2}$), 12.1, 12.2, 14.7, 14.9 ($\mathrm{C_5}Me_4$), 108.9 ($\mathrm{C^{ipso}}$), 109.6, 110.6, 125.3, 126.3 ($C_5\mathrm{H_4}$), 100.0, 122.0, 123.3, 133.9, 134.3 ($C_5\mathrm{Me_4}$), 133.6, 135.2 ($\mathrm{CH{=}CH_2}$). ^{29}Si{^{1}H} NMR (79.49 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -18.1 ($Si\mathrm{CH{=}CH_2}$), -11.5 ($Si\mathrm{C_5H_4}$). MS electron impact (*m*/*e* (relative intensity)): 614 (47) [M$^+$], 506 (14) [M$^+$ $-$ $\mathrm{Si(CH_2{=}CH)_3}$], 478 (16) [M$^+$ $-$ $\mathrm{CH_2CH_2Si(CH_2{=}CH)_3}$], 123 (100) [M$^+$ $-$ $\mathrm{CH_2Si(Me)(C_5Me_4)(C_5H_4)HfCl_2}$], 109 (91) [M$^+$ $-$ $\mathrm{CH_2CH_2Si(Me)(C_5Me_4)(C_5H_4)HfCl_2}$], 83 (73) [M$^+$ $-$ $\mathrm{CH_2{=}CH}$ $-$ $\mathrm{CH_2CH_2Si(Me)(C_5Me_4)(C_5H_4)HfCl_2}$]. Anal. Calcd for $\mathrm{C_{23}H_{32}Cl_2HfSi_2}$: C, 44.99; H, 5.25. Found: C, 44.64; H, 5.17.

[Me{(CH$_2$=CH)Me$_2$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]TiCl$_2$ (15). The synthesis of **15** was carried out in in a manner identical with that for **12**, using [Me(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]TiCl$_2$ (**6**) (0.150 g, 0.43 mmol) and dimethyldivinylsilane (0.051 g, 0.45 mmol). Yield: 0.198 g, 100%. IR (Nujol mull): $\nu_{\mathrm{CH=CH_2}}$ 3053, 1601 cm^{-1}. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ 0.18 (s, 6H, $\mathrm{Si}Me_2$), 0.87 (s, 3H, $\mathrm{Si}Me$), 0.82 (2H), 1.22 (1H), 1.35 (1H) (m, $\mathrm{C}H_2\mathrm{C}H_2$), 1.85 (6H), 2.14 (3H), 2.15 (3H) (s, $\mathrm{C_5}Me_4$), 5.55 (1H), 5.60 (1H), 7.18 (1H), 7.20 (1H) (m, $\mathrm{C_5}H_4$), 5.76 (m, 1H, $\mathrm{CH_2{=}C}H$), 6.10 (m, 2H, $\mathrm{C}H_2\mathrm{{=}CH}$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -3.8 ($\mathrm{Si}Me_2$), -3.4 ($\mathrm{Si}Me$), 6.9, 7.3 ($C\mathrm{H_2}C\mathrm{H_2}$), 13.6, 13.7, 16.2, 16.4 ($\mathrm{C_5}Me_4$), 104.4 ($\mathrm{C^{ipso}}$), 115.5, 116.4, 132.5, 133.7 ($C_5\mathrm{H_4}$), 98.6, 130.5, 131.9, 143.8, 144.3 ($C_5\mathrm{Me_4}$), 132.4, 137.7 ($\mathrm{CH{=}CH_2}$). ^{29}Si{^{1}H} NMR (79.49 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -9.8 ($Si\mathrm{C_5H_4}$), -3.4 ($Si\mathrm{CH{=}CH_2}$). MS electron impact (*m*/*e* (relative intensity)): 459 (55) [M$^+$], 424 (100) [M$^+$ $-$ Cl], 387 (16) [M$^+$ $-$ 2 Cl], 121 (19) [M$^+$ $-$ $\mathrm{(CH_2{=}CH)Me_2SiCH_2CH_2Si(Me)(C_5H_4)TiCl_2}$], 85 (69) [M$^+$ $-$ $\mathrm{(CH_2CH_2)Si(Me)(C_5Me_4)(C_5H_4)TiCl_2}$], 59 (81) [M$^+$ $-$ $\mathrm{CH_2{=}CH}$ $-$ $\mathrm{(CH_2CH_2)Si(Me)(C_5Me_4)(C_5H_4)TiCl_2}$]. Anal. Calcd for $\mathrm{C_{21}H_{32}Cl_2Si_2Ti}$: C, 54.90; H, 7.02. Found: C, 54.77; H, 6.96.

[Me{(CH$_2$=CH)Me$_2$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]ZrCl$_2$ (16). The synthesis of **16** was carried out in in a manner identical with that for **12**, using [Me(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]ZrCl$_2$ (**7**) (0.160 g, 0.41 mmol) and dimethyldivinylsilane (0.048 g, 0.43 mmol). Yield: 0.206 g, 100%. IR (Nujol mull): $\nu_{\mathrm{CH=CH_2}}$ 3046, 1586 cm^{-1}. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ 0.17 (s, 6H, $\mathrm{Si}Me_2$), 0.85 (s, 3H, $\mathrm{Si}Me$), 0.79 (2H), 1.18 (1H), 1.34 (1H) (m, $\mathrm{C}H_2\mathrm{C}H_2$), 1.94 (3H), 1.95 (3H), 2.06 (6H) (s, $\mathrm{C_5}Me_4$), 5.66 (1H), 5.72 (1H), 7.02 (2H) (m, $\mathrm{C_5}H_4$), 5.75 (m, 1H, $\mathrm{CH_2{=}C}H$), 6.19 (m, 2H, $\mathrm{C}H_2\mathrm{{=}CH}$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -3.8 ($\mathrm{Si}Me_2$), -3.7 ($\mathrm{Si}Me$), 6.8, 7.4 ($C\mathrm{H_2}C\mathrm{H_2}$), 12.3, 12.4, 14.9, 15.2 ($\mathrm{C_5}Me_4$), 107.1 ($\mathrm{C^{ipso}}$), 112.1, 113.0, 126.2, 127.2 ($C_5\mathrm{H_4}$), 98.2, 125.1, 126.4, 135.8, 136.1 ($C_5\mathrm{Me_4}$), 132.4, 137.8 ($\mathrm{CH{=}CH_2}$). ^{29}Si{^{1}H} NMR (79.49 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -10.9 ($Si\mathrm{C_5H_4}$), -3.4 ($Si\mathrm{CH{=}CH_2}$). MS electron impact (*m*/*e* (relative intensity)): 502 (36) [M$^+$], 464 (21) [M$^+$ $-$ Cl], 449 (12) [M$^+$ $-$ Cl $-$ Me], 415 (21) [M$^+$ $-$ 2 Cl $-$ Me], 352 (34) [M$^+$ $-$ Cl $-$ $\mathrm{(CH_2{=}CH)Me_2SiCH_2CH_2}$], 85 (81) [M$^+$ $-$ $\mathrm{(CH_2CH_2)Si(Me)(C_5Me_4)(C_5H_4)ZrCl_2}$], 59 (100) [M$^+$ $-$ $\mathrm{CH_2{=}CH}$ $-$ $\mathrm{(CH_2CH_2)Si(Me)(C_5Me_4)(C_5H_4)ZrCl_2}$]. Anal. Calcd for $\mathrm{C_{21}H_{32}Cl_2Si_2Zr}$: C, 50.17; H, 6.42. Found: C, 49.99; H, 6.33.

[Me{(CH$_2$=CH)Me$_2$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]HfCl$_2$ (17). The synthesis of **17** was carried out in a manner identical with that for **12**, using [Me(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]HfCl$_2$ (**8**) (0.180 g, 0.38 mmol) and dimethyldivinylsilane (0.044 g, 0.40 mmol). Yield: 0.222 g, 100%. IR (Nujol mull): $\nu_{\mathrm{CH=CH_2}}$ 3048, 1594 cm^{-1}. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ 0.18 (s, 6H, $\mathrm{Si}Me_2$), 0.85 (s, 3H, $\mathrm{Si}Me$), 0.82 (2H), 1.19 (1H), 1.34 (1H) (m, $\mathrm{C}H_2\mathrm{C}H_2$), 2.02 (3H), 2.03 (3H), 2.08 (6H) (s, $\mathrm{C_5}Me_4$), 5.63 (1H), 5.69 (1H), 6.94 (2H) (m, $\mathrm{C_5}H_4$), 5.75 (m, 1H, $\mathrm{CH_2{=}C}H$), 6.16 (m, 2H, $\mathrm{C}H_2\mathrm{{=}CH}$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -3.8 ($\mathrm{Si}Me_2$), -3.7 ($\mathrm{Si}Me$), 6.8, 7.5 ($C\mathrm{H_2}C\mathrm{H_2}$), 12.1, 12.2, 14.6, 14.9 ($\mathrm{C_5}Me_4$), 109.1 ($\mathrm{C^{ipso}}$), 109.6, 110.6, 125.3, 126.3 ($C_5\mathrm{H_4}$), 99.9, 122.0, 123.3, 133.9, 134.2 ($C_5\mathrm{Me_4}$), 132.4, 137.9 ($\mathrm{CH{=}CH_2}$). ^{29}Si{^{1}H} NMR (79.49 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -10.9 ($Si\mathrm{C_5H_4}$), -4.5 ($Si\mathrm{CH{=}CH_2}$). MS electron impact (*m*/*e* (relative intensity)): 590 (15) [M$^+$], 505 (16) [M$^+$ $-$ $\mathrm{(CH_2{=}CH)Me_2Si}$], 477 (16) [M$^+$ $-$ $\mathrm{(CH_2{=}CH)Me_2SiCH_2CH_2}$], 441 (29) [M$^+$ $-$ $\mathrm{(CH_2{=}CH)Me_2SiCH_2CH_2}$ $-$ Cl], [M$^+$ $-$ $\mathrm{Me\{(CH_2{=}CH)Me_2SiCH_2CH_2\}Si(C_5H_4)HfCl_2}$], 123 (100) [M$^+$ $-$ $\mathrm{(C_5Me_4)HfCl_2}$ $-$ $\mathrm{(CH_2{=}CH)Me_2SiCH_2}$], 85 (68) [M$^+$ $-$ $\mathrm{(CH_2CH_2)SiMe(C_5Me_4)(C_5H_4)HfCl_2}$], 59 (50) [M$^+$ $-$ $\mathrm{CH_2{=}CH}$ $-$ $\mathrm{(CH_2CH_2)SiMe(C_5Me_4)(C_5H_4)HfCl_2}$]. Anal. Calcd for $\mathrm{C_{21}H_{32}Cl_2HfSi_2}$: C, 42.75; H, 5.47. Found: C, 42.60; H, 5.45.

[Me{(Et$_3$SiCH$_2$CH$_2$)$_3$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]TiCl$_2$ (18). The synthesis of **18** was carried out in a manner identical with that for **12**, using triethylsilane (0.121 g, 1.04 mmol) and [Me{(CH$_2$=CH)$_3$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]TiCl$_2$ (**12**) (0.160 g, 0.33 mmol). Yield: 0.275 g, 100%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ 0.87 (s, 3H, $\mathrm{Si}Me$), 0.55 (q, 18H, $\mathrm{Si}CH_2\mathrm{CH_3}$), 0.96 (t, 27H, $\mathrm{SiCH_2}CH_3$), 0.4$-$1.4 (16H) (m, $\mathrm{Si}CH_2CH_2\mathrm{Si}$), 1.86 (3H), 1.88 (3H), 2.15 (3H), 2.16 (3H) (s, $\mathrm{C_5}Me_4$), 5.54 (1H), 5.61 (1H), 7.18 (1H), 7.21 (1H) (m, $\mathrm{C_5}H_4$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -3.5 ($\mathrm{Si}Me$), 3.0, 7.7 ($\mathrm{Si}Et$), 2.8, 3.3, 3.4, 7.9 ($C\mathrm{H_2}C\mathrm{H_2}$), 13.6, 13.7, 16.2, 16.4 ($\mathrm{C_5}Me_4$), 104.4 ($\mathrm{C^{ipso}}$), 115.2, 116.6, 132.1, 134.0 ($C_5\mathrm{H_4}$), 98.7, 130.1, 132.1, 143.5, 144.5 ($C_5\mathrm{Me_4}$). ^{29}Si{^{1}H} NMR (79.49 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -10.2 ($Si\mathrm{C_5H_4}$), 8.2 ($Si\mathrm{Et_3}$), 9.7 ($Si\mathrm{CH_2CH_2}$). MS chemical ionization with $\mathrm{CH_4}$ (*m*/*e* (relative intensity)): 832 (1) [M$^+$], 796 (27) [M$^+$ $-$ Cl], 767 (17) [M$^+$ $-$ Cl $-$ Et], 761 (18) [M$^+$ $-$ 2 Cl], 681 (29) [M$^+$ $-$ Cl $-$ $\mathrm{Et_3Si}$], 652 (24) [M$^+$ $-$ Cl $-$ $\mathrm{Et_3SiCH_2CH_2}$], 646 (17) [M$^+$ $-$ 2 Cl, $-$ $\mathrm{Et_3Si}$], 239 (100) [M$^+$ $\mathrm{(Et_3SiCH_2CH_2)_3SiCH_2CH_2Si(Me)(C_5H_4)}$], 115 (49) [M$^+$ $-$ $\mathrm{SiCH_2CH_2Si(Me)(C_5Me_4)(C_5H_4)TiCl_2}$ $-$ 2 $\mathrm{Et_3SiCH_2CH_2}$ $-$ $\mathrm{CH_2CH_2}$]. Anal. Calcd for $\mathrm{C_{41}H_{80}Cl_2Si_5Ti}$: C, 59.17; H, 9.69. Found: C, 58.89; H, 9.65.

[Me{(Et$_3$SiCH$_2$CH$_2$)$_3$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]ZrCl$_2$ (19). The synthesis of **19** was carried out in a manner identical with that for **12**, using triethylsilane (0.138 g, 1.18 mmol) and [Me{(CH$_2$=CH)$_3$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]ZrCl$_2$ (**13**) (0.198 g, 0.38 mmol). Yield: 0.329 g, 100%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ 0.86 (s, 3H, $\mathrm{Si}Me$), 0.56 (q, 18H, $\mathrm{Si}CH_2\mathrm{CH_3}$), 0.96 (t, 27H, $\mathrm{SiCH_2}CH_3$), 0.4$-$1.4 (16H) (m, $\mathrm{Si}CH_2CH_2\mathrm{Si}$), 1.96 (3H), 1.97 (3H), 2.06 (6H) (s, $\mathrm{C_5}Me_4$), 5.65 (1H), 5.74 (1H), 7.02 (2H) (m, $\mathrm{C_5}H_4$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -3.2 ($\mathrm{Si}Me$), 3.0, 7.7 ($\mathrm{Si}Et$), 2.8, 3.3, 3.4, 7.8 ($C\mathrm{H_2}C\mathrm{H_2}$), 12.3, 12.4, 14.9, 15.2 ($\mathrm{C_5}Me_4$), 107.2 ($\mathrm{C^{ipso}}$), 112.0, 113.1, 126.1, 127.4 ($C_5\mathrm{H_4}$), 98.5, 124.9, 126.6, 135.7, 136.2 ($C_5\mathrm{Me_4}$). ^{29}Si{^{1}H} NMR (79.49 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -11.2 ($Si\mathrm{C_5H_4}$), 8.2 ($Si\mathrm{Et_3}$), 9.8 ($Si\mathrm{CH_2CH_2}$). MS chemical ionization with $\mathrm{CH_4}$ (*m*/*e* (relative intensity)): 876 (2) [M$^+$], 840 (11) [M$^+$ $-$ Cl], 724 (13) [M$^+$ $-$ Cl $-$ $\mathrm{Et_3Si}$], 381 (8) [M$^+$ $-$ $\mathrm{(Et_3SiCH_2CH_2)_3Si}$], 313 (15) [M$^+$ $-$ $\mathrm{CH_2CH_2Si(Me)(C_5Me_4)(C_5H_4)ZrCl_2}$ $-$ $\mathrm{Et_3SiCH_2CH_2}$], 115 (100) [M$^+$ $-$ $\mathrm{SiCH_2CH_2Si(Me)(C_5Me_4)(C_5H_4)ZrCl_2}$ $-$ 2 $\mathrm{Et_3SiCH_2CH_2}$, $-$ $\mathrm{CH_2CH_2}$], 87 (22) [M$^+$ $-$ $\mathrm{SiCH_2CH_2Si(Me)(C_5Me_4)(C_5H_4)ZrCl_2}$ $-$ 2 $\mathrm{Et_3SiCH_2CH_2}$ $-$ $\mathrm{CH_2CH_2}$ $-$ Et]. Anal. Calcd for $\mathrm{C_{41}H_{80}Cl_2Si_5Zr}$: C, 56.24; H, 9.21. Found: C, 56.03; H, 9.11.

[Me{(Et$_3$SiCH$_2$CH$_2$)Me$_2$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]TiCl$_2$ (20). The synthesis of **20** was carried out in a manner identical with that for **12**, using triethylsilane (0.047 g, 0.41 mmol) and [Me{(CH$_2$=CH)Me$_2$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]TiCl$_2$ (**15**) (0.178 g, 0.39 mmol). Yield: 0.223 g, 100%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ 0.07 (s, 6H, $\mathrm{Si}Me_2$), 0.87 (s, 3H, $\mathrm{Si}Me$), 0.55 (q, 6H, $\mathrm{Si}CH_2\mathrm{CH_3}$), 0.95 (t, 9H, $\mathrm{SiCH_2}CH_3$), 0.4$-$1.4 (8H) (m, $\mathrm{Si}CH_2CH_2\mathrm{Si}$), 1.86 (3H), 1.87 (3H), 2.14 (3H), 2.15 (3H) (s, $\mathrm{C_5}Me_4$), 5.56 (1H), 5.60 (1H), 7.18 (1H), 7.20 (1H) (m, $\mathrm{C_5}H_4$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$; for the major isomer): δ -4.3 ($\mathrm{Si}Me_2$), -4.2 ($\mathrm{Si}Me$), 3.0, 7.7 ($\mathrm{Si}Et$), 3.2, 6.1, 6.8, 7.5 ($C\mathrm{H_2}C\mathrm{H_2}$), 13.6, 13.7, 16.2, 16.5 ($\mathrm{C_5}Me_4$), 104.5 (C^{ipso}), 115.4, 116.5, 132.3, 133.8 (C_5H$_4$), 98.7, 130.4, 132.0, 143.7, 144.4 (C_5Me$_4$). ^{29}Si{^{1}H} NMR (79.49 MHz, CDCl$_3$; for the major isomer): δ −9.9 (SiC$_5$H$_4$), 8.2 (SiEt$_3$), 6.3 (SiCH$_2$CH$_2$). MS electron impact (*m*/*e* (relative intensity)): 574 (12) [M$^+$], 538 (25) [M$^+$ − Cl], 424 (20) [M$^+$ − Cl − Et$_3$Si], 115 (41) [M$^+$ − Me$_2$SiCH$_2$CH$_2$Si(Me)(C$_5$Me$_4$)(C$_5$H$_4$)TiCl$_2$ − CH$_2$CH$_2$], 87 (100) [M$^+$ − Me$_2$SiCH$_2$CH$_2$Si(Me)(C$_5$Me$_4$)(C$_5$H$_4$)TiCl$_2$ − CH$_2$CH$_2$ − Et], 59 (88) [M$^+$ − CH$_2$CH$_2$Si(Me)(C$_5$Me$_4$)(C$_5$H$_4$)TiCl$_2$ − Et$_3$SiCH$_2$CH$_2$]. Anal. Calcd for $C_{27}H_{48}Cl_2Si_3Ti$: C, 56.33; H, 8.40. Found: C, 56.00; H, 8.32.

[Me{(Et$_3$SiCH$_2$CH$_2$)Me$_2$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]ZrCl$_2$ (21). The synthesis of **21** was carried out in a manner identical with that for **12**, using triethylsilane (0.047 g, 0.41 mmol) and [Me{(CH$_2$═CH)Me$_2$SiCH$_2$CH$_2$}Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]ZrCl$_2$ (**16**) (0.193 g, 0.38 mmol). Yield: 0.238 g, 100%. ^{1}H NMR (400 MHz, CDCl$_3$; for the major isomer): δ 0.07 (s, 6H, SiMe_2), 0.85 (s, 3H, SiMe), 0.54 (q, 6H, SiCH_2CH$_3$), 0.95 (t, 9H, SiCH$_2$CH_3), 0.4−1.4 (8H) (m, SiCH_2CH_2Si), 1.95 (6H), 2.01 (6H) (s, C$_5$$Me_4$), 5.66 (1H), 5.73 (1H), 7.02 (2H) (m, C$_5$$H_4$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$; for the major isomer): δ −4.3 (SiMe_2), −3.1 (SiMe), 3.0, 7.7 (SiEt), 3.2, 6.0, 6.8, 7.5 (CH$_2$$CH_2$), 12.3, 12.4, 14.9, 15.2 (C$_5$$Me_4$), 107.2 (C^{ipso}), 112.1, 113.0, 126.2, 127.3 (C_5H$_4$), 98.4, 125.1, 126.5, 134.8, 136.1 (C_5Me$_4$). ^{29}Si{^{1}H} NMR (79.49 MHz, CDCl$_3$; for the major isomer): δ −11.0 (SiC$_5$H$_4$), 8.2 (SiEt$_3$), 6.3 (SiCH$_2$CH$_2$). MS electron impact (*m*/*e* (relative intensity)): 618 (5) [M$^+$], 589 (9) [M$^+$ − 2 Me], 475 (64) [M$^+$ − Et$_3$SiCH$_2$CH$_2$], 87 (100) [M$^+$ − CH$_2$CH$_2$Si(Me)(C$_5$Me$_4$)(C$_5$H$_4$)ZrCl$_2$ − Me$_2$SiCH$_2$CH$_2$ − Et], 59 (91) [M$^+$ − CH$_2$CH$_2$Si(Me)(C$_5$Me$_4$)(C$_5$H$_4$)ZrCl$_2$ − Et$_3$SiCH$_2$CH$_2$]. Anal. Calcd for $C_{27}H_{48}Cl_2Si_3Zr$: C, 52.38; H, 7.82. Found: C, 52.24; H, 7.77.

Polymerization of Ethylene. The zirconocene catalyst (6 μmol), MAO (10% in toluene; 1800 μmol), and toluene (200 mL) were mixed together for 15 min in a 1 L glass autoclave. The N$_2$ pressure inside the autoclave was reduced by applying vacuum. Ethylene pressure of 2 bar was then applied and maintained to the autoclave, and stirring of the mixture commenced (1000 rpm). After exactly 15 min, stirring was halted and the ethylene pressure released. Excess MAO was then destroyed by adding cautiously a mixture of methanol and HCl (90:10). The polymer was isolated by filtration, washed with ethanol, and dried under vacuum at 90 °C for 16 h.

Polymerization of Propylene. The zirconocene catalyst (6 μmol), MAO (10% in toluene; 1800 μmol), and toluene (200 mL) were mixed together for 15 min in a 1 L glass autoclave. The N$_2$ pressure inside the autoclave was reduced by applying vacuum. Propylene pressure of 2.5 bar was then applied and maintained to the autoclave, and stirring of the mixture commenced (1000 rpm). After exactly 30 min, stirring was halted and the propylene pressure released. Solvent was then removed under reduced pressure and methanol (200 mL) added. The mixture was stirred for 16 h and then filtered to isolate the polymer, which was washed with ethanol and dried under vacuum at 50 °C for 16 h.

X-ray Structure Determination for [Me(H)Si(η^5-C$_5$Me$_4$)$_2$]ZrCl$_2$ (10). Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) using a $\omega/2\theta$ scan technique. The final unit cell parameters were determined from 25 well-centered reflections and refined by the least-squares method. Data were corrected for Lorentz and polarization effects but not for absorption. The space group was determined from the systematic absences, and this was vindicated by the success of the subsequent solutions and refinements. The structure was solved by direct methods using the SHELXS computer program[22] and refined on F^2 by full-matrix least squares (SHELXL-97).[23] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions (except H(1), which was located in a difference map) and were refined with an overall isotropic temperature factor using a riding model. Weights were optimized in the final cycles. Crystallographic data are given in Table 5.

Table 5. Crystal Data and Structure Refinement Details for 10

formula	$C_{19}H_{28}Cl_2SiZr$
fw	446.62
T (K)	293(2)
cryst syst	monoclinic
space group	*Cc*
a (Å)	15.347(1)
b (Å)	12.078(1)
c (Å)	11.071(1)
β (deg)	104.87(1)
V (Å^3)	1983.4(3)
Z	4
D_c (g cm^{-3})	1.496
μ (mm^{-1})	0.882
F(000)	920
cryst dimens (mm)	0.3 × 0.3 × 0.2
θ range (deg)	2.17−27.97
hkl ranges	$-19 \le h \le 20$, $-15 \le k \le 15$, $-14 \le l \le 14$
no. of data/params	6049/3149
goodness of fit on F^2	1.052
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0450 wR2 = 0.1077
largest diff peak (e Å^{-3})	1.253/−1.258

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

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Supporting Information Available: Tables giving details of the data collection and refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complex **10**; these data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049791U

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(22) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(23) Sheldrick, G. M. Program for the Refinement of Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Germany, 1997.