Thermally Stable Dialkylzirconocenes with *β*-Hydrogens. Synthesis and Diastereoselectivity

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Alkylation of $Cp^r_2ZrCl_2$ (Cp^r = Cp (η^5-C_5H_5), Cp′ (η^5-C_5H_4Me), Cp* (η^5-C_5Me_5)) and $CpCp^*Zr(CH_3)Cl$ with 1-lithio-2-methylpentane (R^1Li) gives the corresponding dialkylzirconocenes $Cp^r_2ZrR^1_2$ and $CpCp^*Zr(CH_3)R^1$, in high yields. Such alkyls have unprecedented thermal stabilities, especially for the CpCp* ligand framework. The diastereomers of the $Cp^r_2ZrR^1_2$ complexes are formed in a statistical distribution, whereas the diastereomers of $CpCp^*Zr(CH_3)R^1$ form in a 2:3 ratio.

Introduction

Alkylzirconocene cations are currently of interest due to their role as single-site Ziegler−Natta olefin polymerization catalysis.[1] Common precursors to these cationic catalysts include dimethyl- and dibenzylzirconocenes, which are stable species.[1,2] On the other hand, dialkylzirconocenes with *β*-hydrogens are normally thermally unstable species and have mostly been investigated as precursors to "Cp_2Zr^{II}" in the context of organic synthesis: for example, in bicyclization reactions of enynes.[3] The thermal stability of mixed methyl/butyl compounds prepared in situ has been studied, and it was shown that the stability decreases in the order *β*-methine > *β*-methylene > *β*-methyl.[4]

A simple model of the transition state of the stereospecific Ziegler−Natta polymerization of propylene would be $[CpCp^*Zr(2\text{-methylpentyl})L]^+$ or $[CpCp'Zr(2\text{-methylpentyl})L]^+$ (L = neutral two-electron donor), for which there is chirality at the metal and the *β*-carbon. In the interest of finding possible precursors to such cations, we report the synthesis and characterization of some asymmetric dialkylzirconocenes containing a 2-methylpentyl group. The thermal stability of these compounds and the diastereoselectivity of the alkylation reaction are discussed.

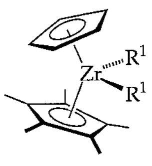
Results and Discussion

Mixed-cyclopentadienyl zirconocene dichlorides have been obtained by the reaction of Cp^*ZrCl_3 (Cp* = η^5-C_5Me_5) with sodium or lithium salts of various cyclopentadienyls.[5,6] By the same principle $CpCp'ZrCl_2$ (**1**; Cp = η^5-C_5H_5, Cp′ = η^5-C_5H_4Me) was obtained in good yield from the reaction of $CpZrCl_3(DME)$ with LiCp′ in toluene.

Reaction of 1 equiv of CH_3Li with $CpCp^*ZrCl_2$ does not afford the desired $CpCp^*Zr(CH_3)Cl$ (**2**). Thus, an alternative procedure was employed: treatment of $CpCp^*Zr(CH_3)_2$ with $PbCl_2$, a reaction that is considerably slower for the more bulky CpCp* as compared with the parent bis(cyclopentadienyl) ligand system.[7] Compound **2** thus obtained is not analytically pure; it is contaminated by a small amount (approximately 5%) of the dichloride, but this does not interfere with the subsequent alkylation, probably since **2** is more reactive than $CpCp^*ZrCl_2$.

$$Cp^r_2ZrCl_2 \xrightarrow{R^1Li/Et_2O} Cp^r_2ZrR^1_2 \qquad (1)$$

$$(R^1 = CH_2CH(CH_3)CH_2CH_2CH_3)$$



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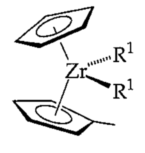

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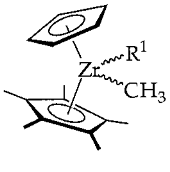

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1-Lithio-2-methylpentane was obtained from lithium metal and racemic 1-bromo-2-methylpentane. Two equivalents of the alkyllithium thus obtained was allowed to react with asymmetric zirconocene dichlorides according to reaction 1. Similarly, the reaction of **2** with 1 equiv of R^1Li gives the mixed-dialkyl compound $CpCp^*Zr(CH_3)R^1$ (**5**). The dialkylzirconocenes were obtained as thick oils or sticky solids that were characterized by multinuclear 1D and 2D NMR. Because of their oily character the complexes could not be recrystallized and subjected to elemental analysis. The

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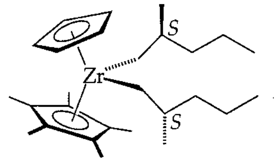
neat compounds seem to be indefinitely stable (>1 year) in the glovebox freezer at approximately −25 °C. In benzene-d_6 solution **4** decomposes with a half-life of about 17 h at room temperature. Complexes **3** and **5** are considerably more stable; **5** has a half-life of approximately 11 days, whereas **3** undergoes 30% decomposition in the same time at room temperature. Compound **3** rapidly ($t_{1/2} \approx 2$ h) decomposes at 85 °C. Such a high stability for dialkylzirconocenes containing β-hydrogens appears to be unprecedented. To our knowledge, there is no report of any such complexes even having been isolated. A number of Cp_2ZrR_2 complexes have been synthesized in situ, and from the thermal stability of these it was shown that the rate of β-H elimination decreases in the order β-methyl > β-methylene > β-methine.[4] However, even the most stable of these species, $Cp_2Zr(CH_2CHMe_2)_2$ and $Cp_2ZrMe(CH_2CHMe_2)$, have half-lives of only 6 h.[4,8] It therefore seems clear that bulkier Cp frameworks afford a much more stable dialkyl species; i.e., the rate of β-hydride elimination (assuming that this is the initial and rate-determining step in these decomposition reactions) from neutral dialkylzirconocenes decreases with increasing steric bulk, similar to what has been found for alkyl hydride zirconocenes, $Cp_2ZrR(H)$.[9] Reaction between **3** and H_2 at 85 °C is complete within 2.5 h and cleanly gives $(CpCp^*ZrH_2)_2$ and 2-methylpentane. The products were identified by comparison with spectra of authentic samples.

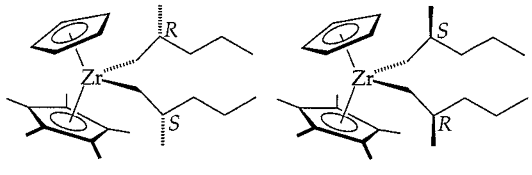
The reactivity difference between **4** and $Cp_2Zr(CH_2CHMe_2)_2$ also indicates that a higher stability is associated with longer alkyl chains. There seems to be a consensus that the first step of these decomposition reactions involves liberation of alkane together with the formation of a zirconium(II)−alkene complex or a Zr(IV) metallacycle.[3,10] At least two pathways for this transformation have been proposed in the literature. In the most comprehensive study Harrod and co-workers suggest that the reaction proceeds via σ-bond metathesis involving the γ-hydrogen to form a zirconacyclobutane.[10] On the other hand Negishi and co-workers favor a pathway that involves σ-bond metathesis with the β-hydrogen to form a zirconacyclopropane: i.e. a zirconium(II)−alkene complex.[3] In this latter case it cannot be excluded that reaction proceeds stepwise via an alkyl hydride zirconium(IV) olefin adduct, which subsequently undergoes reductive elimination of the alkane. Such a five-coordinate intermediate/transition state would better explain the current findings of a decreased reactivity associated with larger steric bulk on the Cp ligands. However, on the basis of the scant data available all mechanistic interpretations are rather speculative.

In all these dialkylzirconocenes the formation of a number of stereoisomers is possible. Compounds **3** and **4** each have three stereogenic centers (the metal and the two β-carbons) and can thus give rise to a maximum of eight different stereoisomers, whereas **5**, having two stereocenters, can give rise to four. For the bis(2-methylpentyl) compounds **3** and **4** symmetry makes some of the eight possible stereoisomers identical, thus reducing the number of possible stereoisomers to four, as shown for **3** in Chart 1. Of these four, two are enantiomers of each other and two are meso forms.

Chart 1



rac-**3**
(only one enantiomer shown)



meso-**3A** *meso*-**3B**

The ^1H NMR data for all complexes are given in Table 1. The spectrum for **3** is the cleanest and best resolved and was therefore chosen for a closer analysis. In the cyclopentadienyl region the spectrum of **3** displays three peaks, in a 1:2:1 ratio, indicating a statistical distribution of the three diastereomers *rac*-**3**, *meso*-**3A**, and *meso*-**3B**. This assignment is confirmed by looking at the alkyl region of the spectrum, where there are four triplets of equal intensity from the CH_3CH_2 groups and four doublets from the CH_3CH groups. Upfield from this region there are no less than eight multiplets each corresponding to one proton. They are all doublets of doublets (AMX or ABX spin systems with vicinal and geminal coupling) and can be assigned to the methylene groups adjacent to zirconium. A $^1H\{^1H\}$ COSY NMR spectrum of this region is shown in Figure 1. This, together with NOE difference experiments that link the cyclopentadienyl peaks to the $Zr-CH_2$ resonances originating from the same stereoisomer, shows that each *meso* isomer gives rise to two sets of methylene resonances, whereas the *rac* isomer gives rise to four, what one would anticipate given the mirror plane that is present in the *meso* forms. Essentially the same pattern can be found in the ^{13}C NMR spectrum, the peaks of which were unambiguously assigned using the information in a $^1H\{^{13}C\}$ HMQC spectrum. Thus, there are three C_5H_5 peaks in a 1:2:1 ratio, whereas the upfield part of the spectrum displays sets of four equally intense peaks from all the carbons in the alkyl chains, except for the CH_3CH_2 resonances, where there is some overlap.

The ^1H and ^{13}C NMR spectra of **4** are not as well resolved, but from the Cp region of the proton spectrum and the $ZrCH_2$ resonances in the ^{13}C spectrum it is clear that the isomers also in this case have formed in the statistical 1:2:1 ratio. On the other hand, the two diastereomers of **5** form in an approximate 2:3 ratio. This is evident from the relative intensities of almost all sets of peaks in the ^1H and ^{13}C NMR spectra (cf. Tables 1 and 2).

What is then the origin of these stereoisomer distributions? It is of course entirely possible, albeit not very likely, that all the isomers of **3** and **4**, respectively, are of the same energy, and thus what we see is a thermo-

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Table 1. ^{1}H NMR Data in Benzene-d_6 for Compounds 1−5

compd	chem shift (multiplicity, coupling constant/Hz, assignt)
1[a]	2.29 (s, $C_5H_4CH_3$), 6.21 (t, J = 2.8, C_5H_4 (2 H)), 6.32 (t, C_5H_4 (2 H)), 6.47 (s, C_5H_5)
2	0.20 (s, $ZrCH_3$), 1.70 (s, $C_5(CH_3)_5$), 5.79 (s, C_5H_5)
rac-**3**	−0.99 (dd, ^2J = 12.1, ^3J = 4.5, ZrC_AHH), 0.66 (dd, ^3J = 8.5, ZrC_AHH), −0.18 (dd ^2J = 12.7, ^3J = 7.5, ZrC_BHH), −0.03 (dd, ^3J = 4.4, ZrC_BHH), 5.82 (s, C_5H_5)
meso-**3A**[b]	−0.62 (dd, ^2J = 12.3, ^3J = 5.2, ZrC*H*H), 0.32 (dd, ^3J = 7.1, ZrCH*H*), 5.80 (s, C_5H_5)
meso-**3B**[b]	−0.48 (dd, ^2J = 12.4, ^3J = 7.0, ZrC*H*H), 0.23 (dd, ^3J = 5.5, ZrCH*H*), 5.84 (s, C_5H_5)
3[c]	0.94, 0.97, 0.98, 1.01 (4 doublets, J = 6.0, CH_3CH), 1.015, 1.016, 1.028, 1.032 (4 triplets, J = 7.0 Hz, CH_3CH_2), 1.20−1.53 (m, $CH_3CH_2CH_2$), 1.69 (s, $C_5(CH_3)_5$), 1.97−2.19 (m, CH_3CH)
4	−0.02−0.10 (m, ZrC*H*H), 0.48−0.62 (m, ZrCH*H*), 0.88 (d, J = 7.0, 12 H, CH_3CH), 0.902, 0.903 (2 doublets, J = 6.5, 12 H each, CH_3CH), 1.00 (t, J = 7.3, CH_3CH_2), 1.15−1.24 (m, $CH_3CH_2CH_2$), 1.32−1.44 (m, $CH_3CH_2CH_2$), 1.916, 1.925 (s, $CH_3C_5H_4$), 1.93−2.02 (m, CH_3CH), 5.54 (b, C_5H_4 (6 H)), 5.56, 5.67, 5.70 (t, J = 2.7, C_5H_4 (2 H)), 5.72 (b, C_5H_4 (4 H)), 5.786, 5.813 (Cp, meso), 5.803 (Cp, rac)
5 (minor)	−0.317 (s, $ZrCH_3$), −0.19 (dd, ^2J = 12.9, ^3J = 5.7, ZrC*H*H), −0.022 (dd, ^3J = 6.6, ZrCH*H*), 0.83 (d, J = 6.5, CH_3CH), 0.99 (t, J = 7.2, CH_3CH_2), 1.68 (s, $C_5(CH_3)_5$), 5.77 (s, C_5H_5)
5 (major)	−0.51 (dd, ^2J = 13.0, ^3J = 3.1, ZrC*H*H), −0.323 (s, $ZrCH_3$), −0.21 (dd, ^3J = 9.1, ZrCH*H*), 1.03 (t, J = 7.5, CH_3CH_2), 1.04 (d, J = 6.5, CH_3CH), 1.67 (s, $C_5(CH_3)_5$), 5.78 (s, C_5H_5)
5[c]	1.24−1.48 (m, $CH_3CH_2CH_2$), 2.02−2.11 (m, CH_3CH)

[a] In $CDCl_3$. [b] The assigment of peaks to *meso*-**A** and *meso*-**B** is arbitrary. [c] These peaks could not be assigned to any specific isomer.

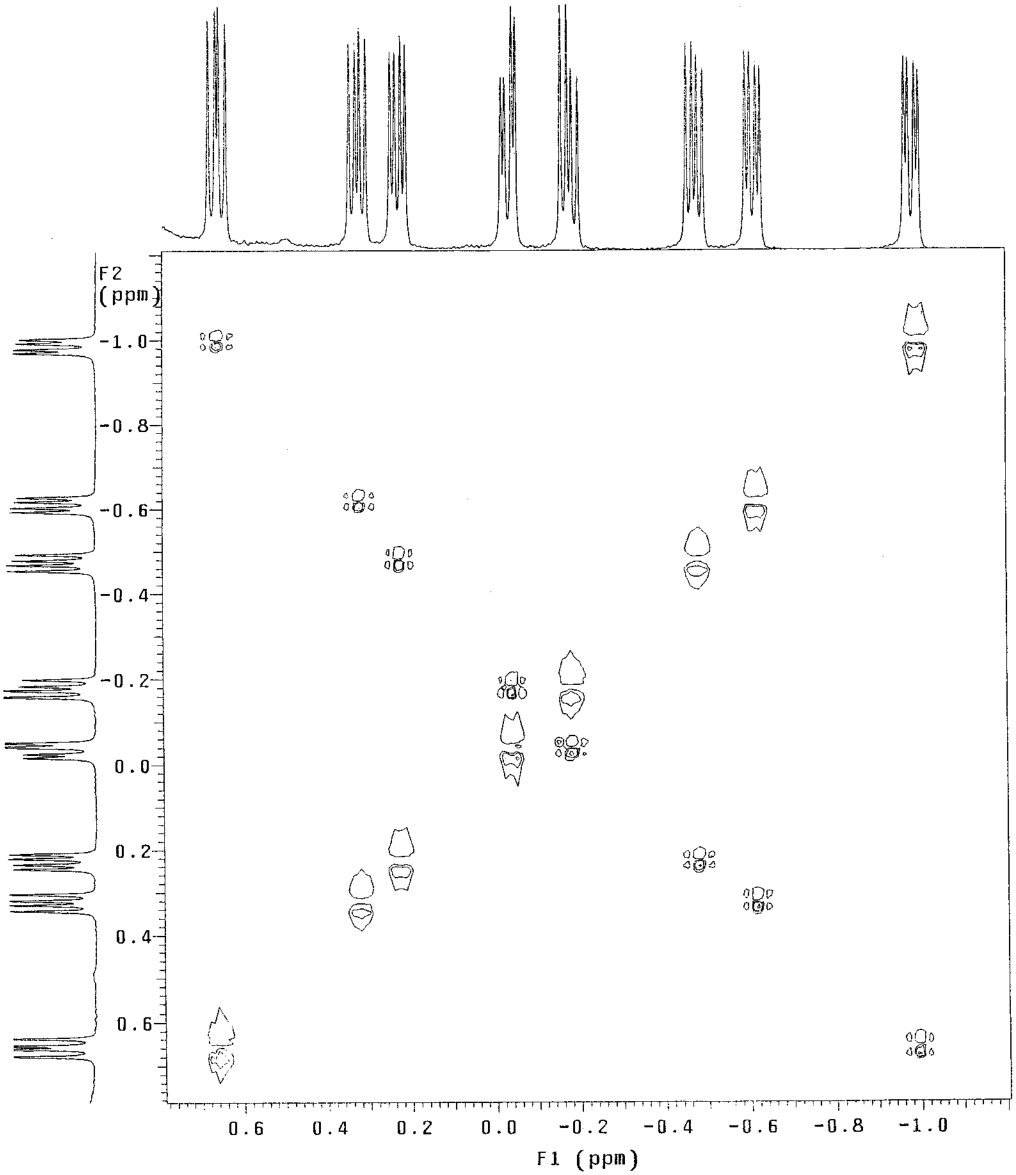


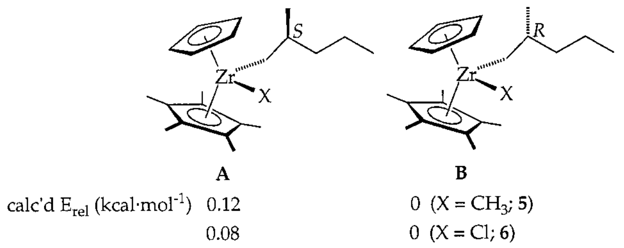
Figure 1. $^1H\{^1H\}$ COSY NMR spectrum of the $ZrCH_2$ region of **3**.

dynamic distribution. To probe this issue, the conformational energies of all the isomers of **3**, **5**, and CpCp*ZrCl(R^1) (**6**) were calculated on the MM2 level using CAChe.[11] Arbitrarily setting the energy of *meso*-**3A** to 0, the *rac*- and *meso*-**3B** isomers have conformational energies of 3.4 and 3.8 kcal mol^{-1}, respectively.

Table 2. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR Data in Benzene-d_6 for Compounds 3−5

compd	chem shift (assignt)
3	11.9, 12.0 ($\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$); 15.1, 15.1, 15.2 ($\mathit{C}\mathrm{H_3CH_2}$); 21.5, 21.6, 21.7 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$); 24.2, 24.8, 25.3, 25.7 ($\mathit{C}\mathrm{H_3CH}$); 37.5, 37.9, 38.7, 38.9 ($\mathrm{CH_3}\mathit{C}\mathrm{H}$); 44.9, 45.6, 46.2, 46.6 ($\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2}$); 65.5 (rac, $\mathrm{C_B}$), 70.0 (meso-B), 70.2 (meso-A), 74.5 (rac, $\mathrm{C_A}$) ($\mathrm{Zr}\mathit{C}\mathrm{H_2}$); 110.8 (meso), 110.9 (rac), 111.0 (meso) ($\mathrm{C_5H_5}$); 117.0 ($\mathit{C}_5(\mathrm{C}\mathit{H}_3)_5$)
4	14.84, 14.89 ($\mathit{C}\mathrm{H_3CH_2}$, $\mathrm{C_5H_4}\mathit{C}\mathrm{H_3}$); 21.2, 21.3 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$); 24.87, 24.92, 25.3 (double intensity) ($\mathit{C}\mathrm{H_3CH}$); 38.2, 38.3 ($\mathrm{CH_3}\mathit{C}\mathrm{H}$); 45.4, 46.0 ($\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2}$); 64.5, 64.9, 65.0, 65.3 ($\mathrm{Zr}\mathit{C}\mathrm{H_2}$); 110.2 ($\mathit{C}_5\mathrm{H_5}$); 107.8, 112.4 (rac), 107.9, 108.0, 112.18, 112.24 (meso) (C−H ring Cp), 121.4, 121.5 (triple intensity) ($\mathrm{CH_3}\mathit{C}$ ring Cp)
5 (minor)	11.9 ($\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$); 15.0 ($\mathit{C}\mathrm{H_3CH_2}$); 21.4 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$); 26.2 ($\mathit{C}\mathrm{H_3CH}$); 33.1 (Zr-$\mathit{C}\mathrm{H_3}$); 37.0 ($\mathrm{CH_3}\mathit{C}\mathrm{H}$); 44.2 ($\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2}$); 68.5 ($\mathrm{Zr}\mathit{C}\mathrm{H_2}$); 111.4 ($\mathit{C}_5\mathrm{H_5}$); 117.4 ($\mathit{C}_5(\mathrm{CH_3})_5$)
5 (major)	11.8 ($\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$); 15.2 ($\mathit{C}\mathrm{H_3CH_2}$); 21.5 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$); 24.1 ($\mathit{C}\mathrm{H_3CH}$); 34.7 (Zr-$\mathit{C}\mathrm{H_3}$); 36.5 ($\mathrm{CH_3}\mathit{C}\mathrm{H}$); 47.3 ($\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2}$); 66.1 ($\mathrm{Zr}\mathit{C}\mathrm{H_2}$); 111.5 ($\mathit{C}_5\mathrm{H_5}$); 117.4 ($\mathit{C}_5(\mathrm{CH_3})_5$)

Chart 2



The energies of the two diastereomers of **5** are different by only 0.08 kcal mol^{-1}, and for **6** the two diastereomers differ by only 0.12 kcal mol^{-1} (Chart 2). The ratio observed in the product mixture of **5** corresponds to an energy difference of 0.24 kcal mol^{-1} at 298 K, in fairly good agreement with the calculated values. Still, on the basis of the large differences in stability between the isomers of **3**, it is likely that all the observed diastereoselectivities (or rather the absence thereof) are kinetic in origin and arise from the rate of alkylation, a process we conclude therefore is not very selective. It still remains to explain the difference in isomer ratio between mono- and bis-alkylated species. It appears that one diastereomer is slightly favored in the first alkylation (assuming that **2** and $\mathrm{CpCp^{*}ZrCl_2}$ behave similarly) and that this uneven distribution is canceled out in the second alkylation step due to a higher reactivity of the less stable isomer of **6**.

Experimental Section

General Considerations. All air- and/or moisture-sensitive compounds were manipulated using standard high-vacuum-line, Schlenk, or cannula techniques, or in a glovebox under a nitrogen atmosphere as described previously.[12] Argon and hydrogen gases were purified and dried by passage through columns of MnO on vermiculite and activated 4 Å molecular sieves. Solvents were stored under vacuum over titanocene[13] or sodium benzophenone ketyl. $(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{ZrCl_2}$, $(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{ZrMe_2}$,[6] $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{ZrCl_3(DME)}$,[14] $\mathrm{(C_5H_4Me)Li}$,[15] and 1-bromo-2-methylpentane ($\mathrm{R^1Br}$)[16] were prepared as previously reported. 1-Lithio-2-methylpentane ($\mathrm{R^1Li}$) was prepared from the bromide and lithium metal using standard procedures.[17] Concentrations of lithium reagents were determined by titration with 2,6-di-*tert*-butyl-4-methylphenol using fluorene as indicator. All other reagents were purchased (Aldrich) and used as received.

NMR spectra were recorded on General Electric QE300 (300 MHz for ^{1}H) and Varian UNITY Inova (500.13 MHz for ^{1}H) spectrometers. Chemical shifts are given in ppm downfield from TMS using residual proton ($\mathrm{C_6D_5H}$, δ 7.15; $\mathrm{CHCl_3}$, δ 7.26) or carbon ($\mathrm{C_6D_6}$, δ 128.0) signals of the deuterated solvents. The COSY and HMQC spectra were referenced using the corresponding 1D spectra. Elemental analyses were carried out at the Caltech Elemental Analysis Facility by Fenton Harvey.

$\mathbf{CpCp'ZrCl_2}$ (1). A round-bottom flask was charged with $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{ZrCl_3(DME)}$ (3.651 g, 10.35 mmol) and $\mathrm{(C_5H_4Me)Li}$ (0.884 g, 10.27 mmol) and evacuated. Toluene (150 mL) was vacuum-transferred onto the solids, and the resulting mixture was stirred at room temperature for 40 h. In air, the toluene was replaced by methylene chloride and 20 mL of 4 M HCl. The $\mathrm{CH_2Cl_2}$ solution was separated, and the aqueous layer was extracted twice with $\mathrm{CH_2Cl_2}$. The combined organic phases were dried over $\mathrm{MgSO_4}$. After filtration the solvent was evaporated, giving a white solid which was dried in vacuo. Yield: 2.285 g (73%). Anal. Calcd for $\mathrm{C_{11}H_{12}Cl_2Zr}$: C, 43.13; H, 3.95. Found: C, 43.14; H, 3.99.

$\mathbf{CpCp^{*}Zr(CH_3)Cl}$ (2). A round-bottom flask was charged with $(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Zr(CH_3)_2}$ (0.411 g, 1.28 mmol) and $\mathrm{PbCl_2}$ (0.180 g, 0.647 mmol) and fitted with a condenser. On the vacuum line toluene was vacuum-transferred onto the solids; the reaction mixture was heated at 90 °C for 50 h and then cooled overnight. The solvent was removed in vacuo and, in the drybox, the flask was fitted onto a swivel frit assembly. This was evacuated, and toluene (75 mL) was vacuum-transferred onto the solid. After filtration the precipitate was washed once and the solvent was removed from the filtrate to give an off-white solid (0.384 g, 88%).

$\mathbf{CpCp^{*}ZrR^1_2}$ (3). A medium swivelfrit assembly was charged with $(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{ZrCl_2}$ (1.039 g, 2.867 mmol) and evacuated. Diethyl ether (100 mL) was vacuum-transferred onto the solid at −78 °C. At this temperature, against an argon counterflow, 7.5 mL of a light petroleum solution (0.80 M) of $\mathrm{LiR^1}$ was added. The reaction mixture was warmed to room temperature and was stirred for 16 h. The solvent was removed in vacuo, and light petroleum (75 mL) was added by vacuum transfer. The resulting suspension was filtered and the white precipitate washed three times with light petroleum. Removal

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[11] Personal CAChe for Macintosh, CAChe Scientific, Inc. Structures were minimized using augmented MM2 parameters with the CAChe program. Initially the dihedral angles $\mathrm{Zr{-}C_\alpha{-}C_\beta{-}C_\gamma}$ were changed in steps of 15−20° and locked while optimizing all other parameters. With the minima thus obtained as starting points, all parameters were then optimized, giving the overall lowest energy conformation.

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of all the volatiles from the filtrate yielded a tan oil which crystallized to a sticky off-white solid upon standing in the freezer (1.27 g, 96%).

CpCp′ZrR$^1_2$ (4). Starting from **1** (0.294 g, 0.960 mmol) and using the same procedure as for **3** afforded **4** as a dark green oil (0.370 g, 95%).

CpCp*ZrMeR^1 (5). Starting from **2** (0.204 g, 0.596 mmol) and using the same procedure as for **3** afforded **5** as a tan oil, which crystallized to a sticky off-white solid upon standing in the freezer (0.218 g, 93%).

Thermal Stability of Complexes 3−5. A J. Young NMR tube was loaded with a small amount of ferrocene, and around 5 mg of the zirconocene and C_6D_6 was added. The decomposition was monitored by ^{1}H NMR spectroscopy at regular intervals using the ferrocene peak as an internal standard.

Reaction of 3 with Dihydrogen. A J. Young NMR tube was loaded with **3** and C_6D_6. The tube was evacuated and then filled with H_2 at −196 °C. It was warmed and put in an oil bath at 82 °C for 2 h 15 min.

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Supporting Information Available: ^{1}H NMR spectra (500 MHz, benzene-d_6, 25 °C) for compounds **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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