

Uncovering Alternative Reaction Pathways Taken by Group 4 Metallocene Cations: Facile Intramolecular CH Activation of Cp–(Dimethylamino)alkyl Substituents by a Methylzirconocene Cation

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Alkyl- and aryllithium reagents add cleanly to the electrophilic carbon center C6 of 6-(*N,N*-dimethylamino)fulvenes to yield the corresponding substituted cyclopentadienyllithium systems $\text{Li}[\text{C}_5\text{H}_4\text{--CR}^1\text{R}^2\text{NMe}_2]$. Subsequent treatment with $\text{ZrCl}_4\cdot 2\text{THF}$ gives the corresponding Cp-functionalized zirconocene dichlorides. These were reacted with methylolithium to give the $(\text{C}_5\text{H}_4\text{CR}^1\text{R}^2\text{NMe}_2)_2\text{Zr}(\text{CH}_3)_2$ complexes **11a** ($\text{R}^1 = \text{R}^2 = \text{CH}_3$) and **11b** ($\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{Ph}$), respectively. Treatment of **11** with tris(pentafluorophenyl)borane was carried out to generate the corresponding alkylmetallocene cations (**12**), which turned out to be unstable under the reaction conditions applied (-20°C) with regard to liberation of 1 equiv of methane by CH activation at a methyl group adjacent to nitrogen and formation of the spiro-metallocene complex systems **13**. CH activation may be a major reaction pathway open to alkylzirconocene cation systems under suitable reaction conditions.

Introduction

Alkylzirconocene cations play a prominent role as the active species in the homogeneous Ziegler polymerization of alkenes.¹ Their chemistry, as it is known so far, has been dominated by the enormous ease with which these systems undergo insertion reactions into the metal to carbon bond (and the metal to hydrogen bond, respectively).² Much less is known about other reaction patterns of alkyl- or hydrido-zirconocene cation systems that might become favored when suitable measures are

taken to suppress the prevailing tendency for insertion reactions.³ Side chains that contain potentially coordinating groups have been attached to the Cp rings of group 4 metallocenes previously,⁴ and it was hoped to alter the metallocene cation chemistry by the ensuing internal coordination. However, the methods of group 4 metallocene cation formation used in those studies were apparently not compatible with the pendent functional groups.⁵ We have now prepared a related series of titanocene and zirconocene complexes having substituted (dimethylamino)methyl substituents at their Cp rings and activated them by treatment with the strong organometallic Lewis acid tris(pentafluorophenyl)borane.⁶ When the Cp-functionalized group 4 metallocene cations are generated in this way, an important alternative reaction pathway becomes apparent, which to our knowledge has remained dormant in previous studies due to other, more favorable alternatives.

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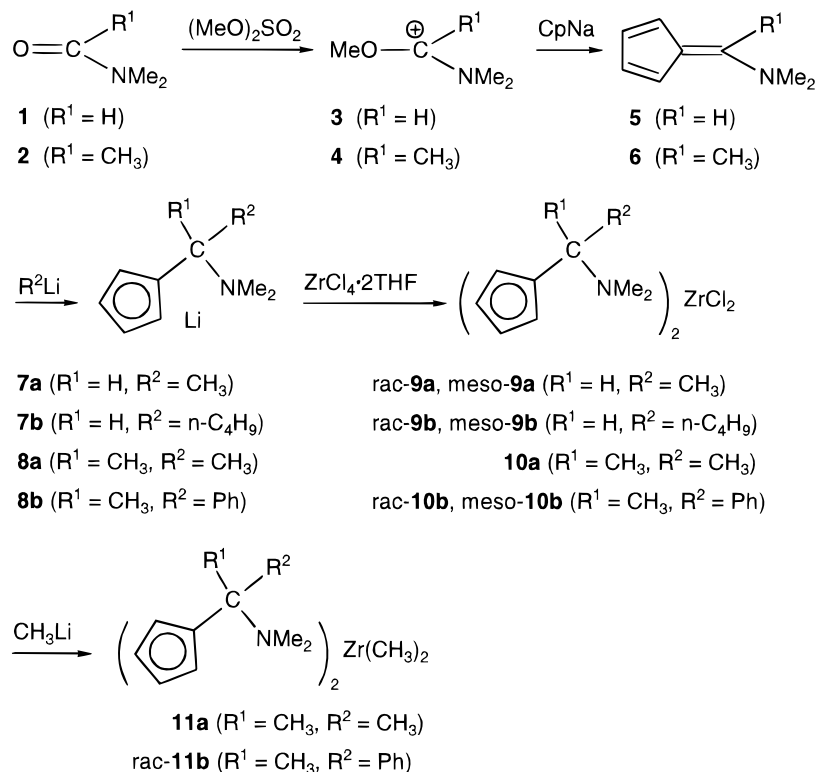
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Scheme 1



Results and Discussion

Preparation of the Cp-(Dimethylamino)alkyl-Substituted Metallocene Complexes. The metal-

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locenes used for this study bear differently substituted (dimethylamino)methyl substituents at their Cp-ligand systems. The specific systems differ with regard to the substituents that they have attached at the single carbon center that connects the Cp ring and the NMe₂ functional group. For the preparation of these Cp-functionalized group 4 metallocene complexes we devised a new synthesis based on the general fulvene route⁷ to Cp-ligand systems.

As a typical example bis[[1-(*N,N*-dimethylamino)-ethyl]cyclopentadienyl]zirconium dichloride (**9a**) was prepared in the following way starting from 6-(dimethylamino)fulvene (**5**) (Scheme 1). The amino-substituted fulvene system **5** is readily available according to Hafner et al.⁸ by treatment of the (*N,N*-dimethylamino)methoxymethyl cation (**3**); which in turn was prepared from *N,N*-dimethylformamide by alkylation with dimethyl sulfate) with sodium cyclopentadienide. Addition of methyllithium to the fulvene **5** produced the substituted cyclopentadienyl ligand system **7a** in excellent yield. The anionic ligand system **7a** was then reacted with ZrCl₄·2THF in a 2:1 molar ratio in diethyl ether.

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Extraction with dichloromethane gave the corresponding 1,1'-bis[1-(*N,N*-dimethylamino)ethyl]-substituted zirconocene dichloride (**9a**) as a 1:1 mixture of the *meso*- and *rac*-diastereomers in a combined yield of 44%.

In a similar way the 1-(*N,N*-dimethylamino)pentyl-substituted metallocene system **9b** was prepared starting from the fulvene **5**, to which *n*-butyllithium was added. Again, the corresponding zirconocene dichloride (**9b**) was obtained as a 1:1 mixture of *meso*-**9b** and *rac*-**9b**. In this case, however, it was possible to separate the *rac*-**9b** isomer from the mixture and obtain it pure, albeit in a low yield of 8%. By applying a solvent diffusion method, single crystals of the chiral metallocene complex **9b** could even be obtained that were suited for an X-ray crystal structure determination (see below).

An analogous synthetic route was then started from *N,N*-dimethylacetamide. O-Methylation followed by condensation with NaCp gave the fulvene **6**. To this was added methylolithium to yield the $\text{Li}[\text{C}_5\text{H}_4\text{CMe}_2\text{NMe}_2]$ reagent (**8a**). Subsequent treatment with $\text{ZrCl}_4 \cdot 2\text{THF}$ then gave the zirconium complex **10a** in good yield (~70% isolated).

Addition of phenyllithium to 6-(*N,N*-dimethylamino)-6-methylfulvene (**6**) furnished **8b**. Subsequent treatment with $\text{ZrCl}_4 \cdot 2\text{THF}$ gave a 1:1 mixture of *meso*-**10b** and *rac*-**10b** (36% combined yield). In this case it was also possible to obtain the pure *rac*-**10b** diastereomer separated and isolated (~15% yield).

Alkylzirconocene cations were later to be generated from the zirconocene systems **10a** and *rac*-**10b**. Therefore, the respective metallocene dichloride complexes were converted to the dimethylmetallocenes by treatment with methylolithium. The corresponding complexes **11a** and *rac*-**11b** were isolated in 82% and 75% yield, respectively. The dimethylmetallocene complex **11b** was characterized by X-ray diffraction (see below).

X-ray Crystal Structure Analyses. Single crystals of isomerically pure **9b** samples were obtained by the diffusion method. In this case a clear solution of the pure diastereomer *rac*-**9b** in dichloromethane was prepared, into which pentane was allowed to diffuse during a period of several weeks at ambient temperature. Large crystals formed quite reproducibly in this way. It turned out that the chiral bent metallocene complex *rac*-**9b** crystallized under these conditions with spontaneous enantiomeric separation. Several crystals from the same as well as different crystallizations were investigated by X-ray diffraction. In each case the crystal scanned contained a single enantiomer of the chiral **9b** diastereomer, with its experimental disclosure apparently being statistical. The structure depicted in Figure 1 is of the *R,R*-configured enantiomer.

The remarkable feature about the structure of (*R,R*)-**9b** is that it is not distinguished in its most characteristic structural parameters from the majority of known 16-electron zirconium(IV) bent metallocene complexes. That means that, the tertiary amino groups present at the side chains that are attached to the Cp rings do not at all interact directly with the electron-deficient early transition metal center, neither intra- nor intermolecularly. In the crystal the zirconium center of (*R,R*)-**9b** has attained a pseudotetrahedral coordination geometry. The molecular symmetry is C_2 . The Zr–Cl bond distance is 2.4529(5) Å, the Cl–Zr–Cl angle 97.70(3)°. The average Zr–C(Cp) distance amounts to 2.510 Å, and the corresponding Cp(centroid)–Zr–Cp(centroid) angle

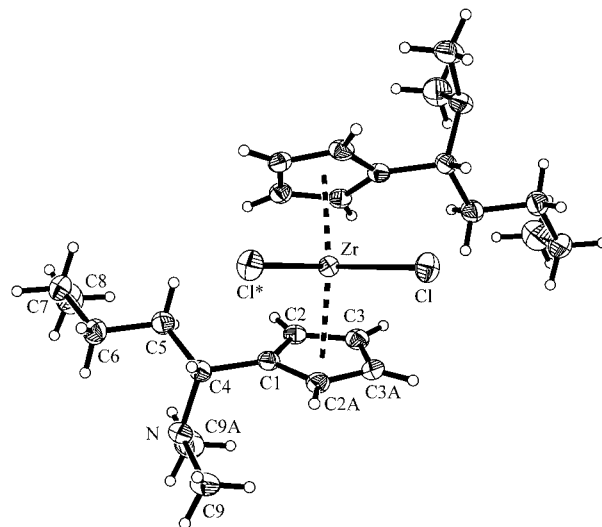


Figure 1. View of the molecular geometry of the metallocene enantiomer (*R,R*)-**9b** with nonsystematic atom-numbering scheme. Selected bond lengths (Å) and angles (deg): Zr–Cl 2.4529(5), Zr–Cl 2.542(2), Zr–C2 2.496(2), Zr–C2a 2.522(2), Zr–C3 2.477(2), Zr–C3a 2.515(2), C1–C4 1.518(3), C4–N 1.477(3), C4–N–C9 113.7(2), C4–N–C9a 114.6(2), C9–N–C9a 111.4(2), torsional angles C2–C1–C4–N 96.2(2), C2–C1–C4–C5 –29.8(3), C1–C4–N–C9 66.1(3).

is 131.7°. The 1-(*N,N*-dimethylamino)pentyl side chains are found in a relative conformational arrangement that places the two $\text{N}(\text{CH}_3)_2$ groups at the utmost intramolecular distance from the zirconium center. The side chains themselves are both oriented in the lateral positions at the bent metallocene wedge.⁹ The overall metallocene conformation is bis-lateral:anti.¹⁰ Taken together the torsional arrangement of the groups at the bent metallocene backbone indicates that the characteristic structural appearance of (*R,R*)-**9b** seems to be governed primarily by steric factors. The tertiary amino group does not appear to interact as a specific functional group with the formally electron-deficient zirconium center in its immediate vicinity.

The orientation of the amino groups away from the 16-electron zirconium center seems to be a general

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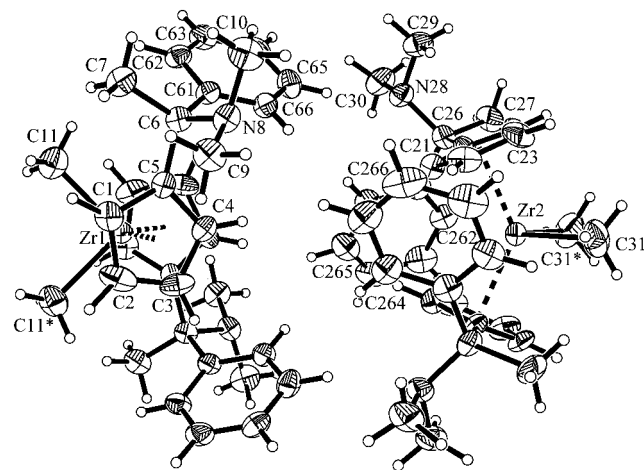


Figure 2. Projections of the independent molecules of **11b** as found in the crystal. Selected bond lengths (Å) and angles (deg): Zr1–C11 2.272(7), Zr2–C31 2.274(7), Zr1–C1 2.562(6), Zr1–C2 2.490(6), Zr1–C3 2.480(6), Zr1–C4 2.547(5), Zr1–C5 2.603(5), Zr2–C21 2.541(6), Zr2–C22 2.478(6), Zr2–C23 2.498(7), Zr2–C24 2.552(6), Zr2–C25 2.612(6), C5–C6 1.516(8), C25–C26 1.515(8), C6–N8 1.505(7), C26–N28 1.503(8), C11–Zr1–C11* 91.3(4), C31–Zr2–C31* 91.2(5), centroid(C1–C5)–Zr1–centroid(C1*–C5*) 132.6, centroid(C21–C25)–Zr2–centroid(C21*–C25*) 132.9, torsional angles C1–C5–C6–N8 104.0(6), C21–C25–C26–N28 60.3(7), C4–C5–C6–N8 –61.3(6), C24–C25–C26–N28 –105.9(6).

structural feature of this class of compounds. A very similar arrangement of the $\text{C}(\text{CH}_3)_2[\text{N}(\text{CH}_3)_2]\text{Ph}$ substituents is found for the dimethylzirconocene complex **11b**. Single crystals of **11b** were formed when the pure *rac*-**11b** diastereomer was slowly crystallized from dichloromethane. Again, the large substituents at the Cp rings are arranged anti to each other in opposite lateral sectors at the bent metallocene backbone with the $\text{N}(\text{CH}_3)_2$ groups both oriented toward the outside, away from the bent metallocene core (see Figure 2). There are two independent molecules of **11b** in the crystal, both being chemically equivalent. Their characteristic structural parameters are very similar (see Figure 2).

We conclude that it appears that there is no direct interaction between the 16-electron zirconium center and the substituted (*N,N*-dimethylamino)methyl substituents attached to the Cp ligands of these specific zirconocene complexes.¹¹ This seems to hold for the zirconocene dichlorides **9** and **10** and for the probably slightly more electrophilic dimethylzirconocene complexes **11**, as well. The situation changes drastically when a methyl anion becomes abstracted from the zirconium center in **11**, initially generating a cationic zirconium complex with a formal 14-electron count.¹²

Zirconocene Cation Systems Derived from 11. The dimethylzirconocene complex **11a** was suspended in toluene and treated with 1 molar equiv of tris-

(pentafluorophenyl)borane¹³ at -20°C . A rapid reaction was observed to take place that proceeds with the evolution of a gas (probably methane, see below).¹⁴ A single organometallic product is formed that separates from the reaction mixture as an oil. Workup, including prolonged stirring with pentane, eventually led to isolation of a solid product (84% yield). The product was identified as **13a**. The asymmetric spiro-metallocene complex **13a** shows very characteristic NMR spectra. In the ^1H NMR spectrum of the cationic spiro-metallocene the signals of the eight pairwise diastereotopic cyclopentadienyl methine hydrogen atoms appear (at 253 K in dichloromethane- d_2 solution) at δ 6.56, 6.51, 6.25, 5.95, 5.93, 5.75 (double intensity), and 5.54 [corresponding ^{13}C NMR Cp resonances (dichloromethane- d_2 , 208 K) at δ 113.0, 112.0, 110.0, 109.3, 106.5, 104.1, 99.5, 99.2 (CH) and δ 123.6, 115.2 (ipso-C of Cp), respectively]. As a result of the spiro-metallocene structure both $\text{C}(\text{CH}_3)_2$ methyl pairs ($^1\text{H}/^{13}\text{C}$ NMR signals at δ 1.60, 1.50, 1.49, 1.36/17.3, 24.6, 24.0, 24.2) and the $\text{N}(\text{CH}_3)_2$ methyl pair are diastereotopic. Together with the signal of the remaining single $\text{N}-\text{CH}_3$ group consequently three resonances due to methyl groups at nitrogen are observed for **13a** in both the ^1H and ^{13}C NMR spectrum (δ 2.30, 2.31, 2.44/43.3, 47.1, 47.6). The remaining methylene group that bridges between zirconium and nitrogen ($\text{Zr}-\text{CH}_2-\text{N}$) gives rise to a single ^{13}C NMR resonance at δ 48.8. The corresponding pair of hydrogen atoms is again diastereotopic due to the chiral spirocyclic ring structure of the metallacyclic system. It gives rise to an AX pair of ^1H resonances at δ 2.27 and 1.57 ($^2J = 9.6$ Hz) at 253 K in dichloromethane- d_2 . In addition, the characteristic NMR signals of the $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3$ anion were monitored (see Experimental Section for further details).

The specific chirality information contained in complex **13a** is not completely persistent, though. Raising the temperature from 253 to 303 K (i.e., the highest temperature chosen in dichloromethane- d_2 solution) rapidly leads to a (reversible) broadening and coalescence of the $\text{Zr}-\text{CH}_2-\text{N}$ AX system in the ^1H NMR spectrum. At the same time the four $\text{C}(\text{CH}_3)_2$ signals get broad as do the $\text{N}(\text{CH}_3)_2$ pair of resonances and also the Cp-methine signals. Only the single $\text{N}-\text{CH}_3$ ^1H NMR signal at δ 2.48 ppm appears to remain unaffected by the dynamic NMR behavior of complex **13a**; it remains a sharp singlet at all temperatures.

A brief investigation of the dynamic ^1H NMR spectra of complex **13a** in bromobenzene at 200 MHz has confirmed the pairwise coalescence of the diastereotopic

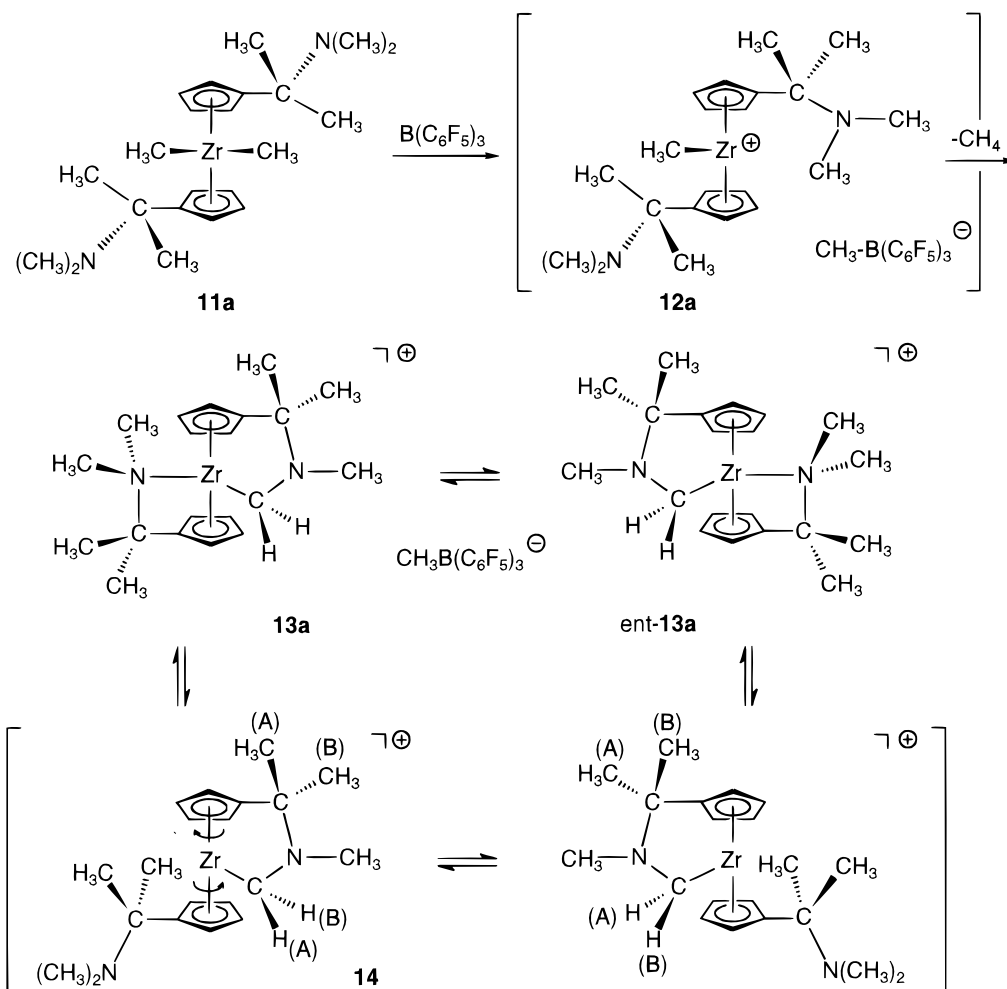
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Scheme 2



$\text{C}(\text{CH}_3)_2$ and $\text{N}(\text{CH}_3)_2$ pairs at higher temperatures. Thus, complex **13a** undergoes a thermally induced reversible symmetrization process that is rapid on the NMR time scale. Most likely this is to be explained by a process initiated by rupture of the $\text{Zr}-\text{N}$ bond in **13a** leading to a monocyclic organometallic intermediate (**14a**) that can easily undergo conformational equilibration^{9,10,15} before the reverse reaction takes place by the electrophilic cationic zirconium center capturing and coordinating to the $\text{N}(\text{CH}_3)_2$ group close by to re-form the thermodynamically favored spiro-metallocene structure **13a** (see Scheme 2).

The stereochemical situation is altered if persistent chirality centers at carbon are introduced. This has been the case when *rac*-**11b** was employed as the starting material. Its reaction with $\text{B}(\text{C}_6\text{F}_5)_3$ also proceeds very cleanly to generate the respective spiro-metallocene complex **13b** with loss of methane. In this case two diastereomers (**13b**, **13b'**) (both with relative configurations *R**,*R** at carbon and *S** or *R** at zirconium, respectively) could in principle occur, but only a single diastereomer was observed within the accuracy of the NMR analysis. It remains to be revealed which of the two possible diastereomers is the thermodynamically preferred one that is obtained, but it is clear that the $\text{Cp}-\text{CMePh}[\text{N}]$ substituent pattern chosen here has shifted the equilibrium situation depicted in Scheme 3

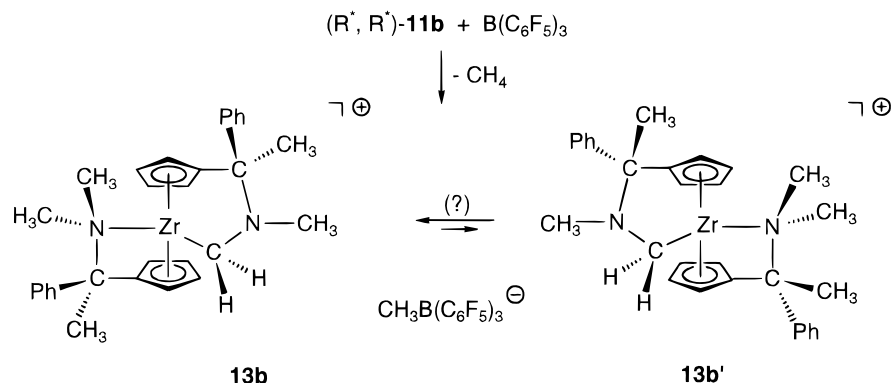
so far to one side that this spiro-metallocene product appears as being static on the NMR time scale.

Although a thorough mechanistical investigation has still to come, the following description of the reaction course taken in the formation of the spiro-metallocenes **13** involving a CH-activation step appears likely. Obviously, the reaction sequence is initiated by the abstraction of a methyl group from the zirconium center in **11** by the $\text{B}(\text{C}_6\text{F}_5)_3$ Lewis acid.^{6,14} The resulting methylzirconocene cation (**12**) seems to be extremely reactive with regard to an intramolecular CH-activation reaction.¹⁶ All attempts to at least observe the intermediate **12** by carrying out the methyl transfer reaction under direct NMR control at low temperature have not proven successful so far. We thus conclude that the methylzirconocene cation **12** encounters a situation set up for a very favorable subsequent reaction due to the presence of the substituted (dimethylamino)methyl substituents attached to the Cp ligands. Undoubtedly, the essential step of this reaction sequence involves CH activation. In view of the electronic situation present at the d^0 -configured zirconium center¹⁷ in **12** the most commonly observed pathway for CH activation by means of oxidative addition of the C-H bond to the metal center¹⁸ is very unlikely to occur.

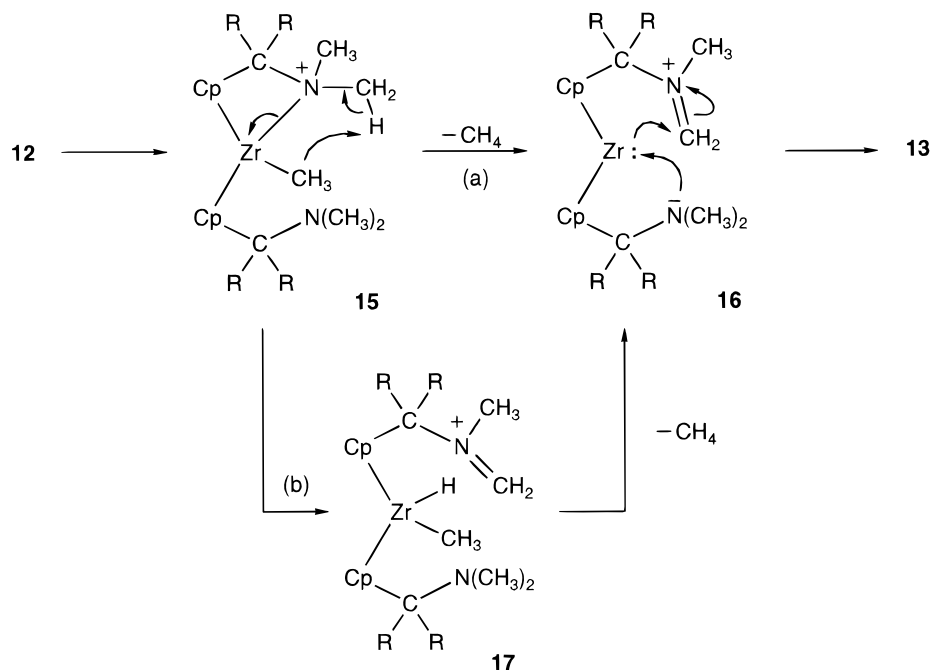
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Scheme 3

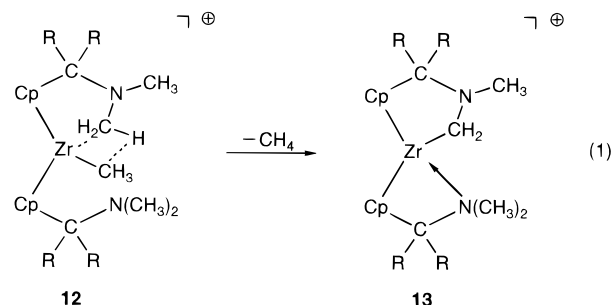


Scheme 4



It is, however, possible that a direct C–H activation at the N–CH₃ group is taking place, involving a four-centered transition state (see eq 1). Similar “ σ -metathesis” reactions have been observed to occur in the reactions of very electrophilic Cp*₂ScR reagents.¹⁹ But it should be noted that such processes often prefer activation of σ -bonds that exhibit high s-character.²⁰ Also, in the reaction of **12** we note a very specific C–H activation selectivity as only the CH₃ groups adjacent to nitrogen and not to carbon are involved.

A specific mechanistic involvement of the amino nitrogen of **12** in the observed C–H activation process



could take place by either of two effects. Intramolecular coordination of the tertiary amino functionality to the cationic zirconium center could be involved. This would simply bring the N–CH₃ group into the vicinity of the Zr–CH₃ base, and this might open up a viable pathway of a concerted methane elimination (**15** → **16**). Alternatively one might also consider a stepwise process leading from **15** to **16** via **17**, followed by a classical reductive coupling step (pathway b, see Scheme 4).

All it requires to form the final product is the intramolecular attack of the zirconium(II) center of the

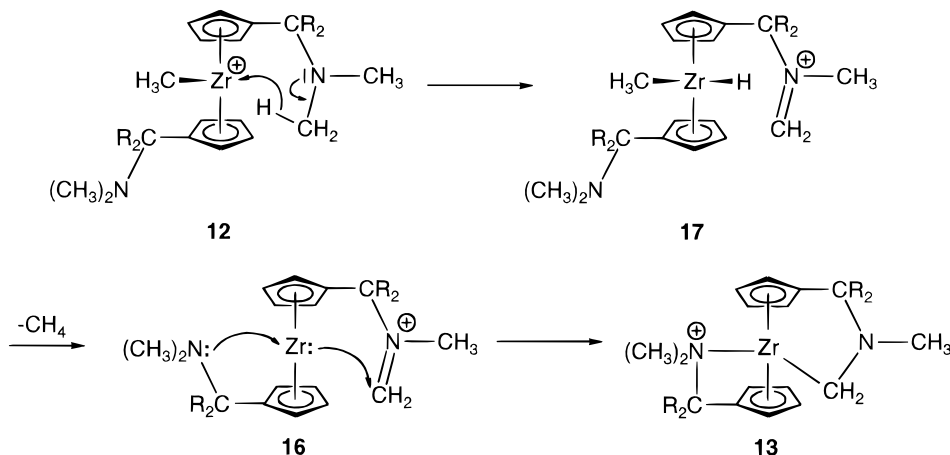
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Scheme 5



resulting complex **16** with its electron pair serving as a nucleophile to the electrophilic carbon center of the adjacent iminium ion functional group that is attached to the Cp-ring system.²¹ This reaction bears a great similarity to the central step of the Mannich reaction and may just be regarded as an analogously proceeding organometallic aminomethylation reaction. It just employs an organometallic nucleophile instead of the typical organic nucleophilic reagents used in the common Mannich reaction.²²

But it should also be noted that non-ligand-stabilized alkylzirconocene cations bear a great similarity to reactive carbenium ions: they are very electrophilic reagents, and their respective σ -bonds, the zirconium-carbon and zirconium-hydrogen bond, respectively, are thermodynamically very strong.²³ Therefore, it is possible that donor-ligand free methylzirconocene cations such as **12** have a tendency for hydride abstraction²⁴ from mildly activated C-H linkages, especially when such a bond is brought into close spatial contact with the electrophilic metal center, as is the case here. The hydride abstraction reaction consequently leads to the formation of the hydrido(methyl)zirconocene species **17**, which is now ideally set up for reductive elimination of methane to generate **16**, which is then converted to the final product **13** as outlined above (Scheme 5).

The metallocene cation system **12** encountered in this study admittedly is of a rather special constitution as

it brings a C-H bond that is activated toward hydride abstraction into the close vicinity of the electrophilic zirconium cation center. Nevertheless, the observed very rapid hydride transfer from carbon to zirconium, which is followed by methane formation, indicates that CH activation may be another important reaction type that is induced by group 4 bent metallocene cations. This reaction appears to point to some essential similarity between the 14-electron bent metallocene cation systems and the carbenium ions. It would be tempting to try to use this related reactivity to uncover novel catalytic reaction pathways other than the well-studied insertion reactions of the bent metallocene cations that involve CH activation.^{3b} Doing this stoichiometrically seems to be unproblematic, as shown by the organometallic aminomethylation reaction observed in this study, as long as a thermodynamically favorable reaction is found to close the overall reaction cycle. Catalytically this can potentially be done by combining the CH-activation reaction of a suitable organic substrate, induced by the electrophilic zirconocene cation, with one of the established insertion reactions at such electrophilic metallocene catalyst species.²⁵ Studies aimed at developing such novel catalytic reaction patterns of alkylzirconocene cation systems are currently being carried out in our laboratory.

Experimental Section

All reactions involving organometallic reagents or substrates were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds. Bruker AC 200 P, Bruker ARX 300, and Varian Unity Plus 600 NMR spectrometers; Nicolet 5 DXC FT-IR spectrometer; DuPont 2910 (STA Instruments) DSC. Elemental analyses: Foss-Heraeus CHN-O-Rapid. X-ray crystal structure analy-

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ses: Enraf-Nonius CAD4 diffractometer (programs used include SHELX 86, SHELX 93, and XP). The organic starting materials 6-(*N,N*-dimethylamino)fulvene (**5**) and 6-(*N,N*-dimethylamino)-6-methylfulvene (**6**) were prepared according to the procedures published by Hafner et al.⁸

[1-(*N,N*-Dimethylamino)ethyl]cyclopentadienyl]lithium (7a**).** Etheral methyllithium (51 mL of a 1.6 M solution, 77.0 mmol) was added dropwise with stirring to a solution of 9.3 g (77.0 mmol) of 6-(*N,N*-dimethylamino)fulvene (**5**) in 120 mL of ether at -40°C . The reaction mixture was allowed to warm to room temperature overnight with stirring. A light brown suspension was obtained. The product (**7a**) was simply collected by filtration to give 9.8 g (89%) of **7a**, that was characterized by NMR spectroscopy. ^1H NMR (benzene-*d*₆/THF-*d*₈, 5:1): δ 5.81, 5.74 (m, each 2H, Cp), 3.59 (q, $^3J = 6.8$ Hz, 1H, CH), 2.14 (s, 6H, NMe₂), 1.39 (d, $^3J = 6.8$ Hz, 3H, CH₃). ^{13}C NMR (benzene-*d*₆/THF-*d*₈, 5:1): δ 120.9 (quat. C of Cp), 110.2, 103.8 (CH of Cp), 60.7 (CH), 41.8 (NMe₂), 17.2 (CH₃).

[1-(*N,N*-Dimethylamino)pentyl]cyclopentadienyl]lithium (7b**).** *n*-Butyllithium (1.6 M solution in hexane, 26.1 mL, 41.8 mmol) was added dropwise with stirring to a solution of 6-(*N,N*-dimethylamino)fulvene (**5**, 5.1 g, 41.7 mmol) in 40 mL of tetrahydrofuran at -40°C . The reaction mixture was allowed to warm to room temperature overnight. Solvent was removed in vacuo from the resulting clear brown colored solution to give a highly viscous oil. Pentane (30 mL) was added and the mixture stirred for 12 h to give a precipitate of solid **7b**. Pentane was decanted and the remaining solid dried in vacuo to give 7.3 g (95%) of **7b** as a light brownish colored powder, which was characterized by NMR spectroscopy. ^1H NMR (benzene-*d*₆/THF-*d*₈, 3:1): δ 5.92, 5.80 (m, each 2H, Cp), 3.52 (m, 1H, CH), 2.18 (s, 6H, NMe₂), 1.92, 1.68, 1.43 (m, 2H each), and 0.89 (br t, 3H, *n*-butyl). ^{13}C NMR (benzene-*d*₆/THF-*d*₈, 3:1): δ 117.5 (quat. C of Cp), 104.7, 102.5 (CH of Cp), 65.4 (CH), 41.7 (NMe₂), 34.0, 31.0, 23.2, 14.7 (*n*-butyl).

[1-(*N,N*-Dimethylamino)-1-methylethyl]cyclopentadienyl]lithium (8a**).** Analogously as described for the synthesis of **7a** above, the fulvene **6** (7.72 g, 57.2 mmol), dissolved in 120 mL of ether, was treated with 33.2 mL of a 1.72 M etheral methyllithium solution (57.2 mmol) to yield **8a** (7.3 g, 82%) as a light brown colored powder. The product **8a** was characterized by NMR spectroscopy. ^1H NMR (benzene-*d*₆/THF-*d*₈, 10:1): δ 6.00, 5.94 (m, each 2H, Cp), 2.19 (s, 6H NMe₂), 1.53 [s, 6H, C(CH₃)₂]. ^{13}C NMR (benzene-*d*₆/THF-*d*₈, 10:1): δ 124.5 (quat. C of Cp), 103.3, 102.5 (CH of Cp), 57.1 (CMe₂), 39.8 [N(CH₃)₂], 26.2 [C(CH₃)₂].

[1-(*N,N*-Dimethylamino)-1-methylbenzyl]cyclopentadienyl]lithium (8b**).** Analogously as described above, the fulvene **6** (solution of 2.9 g, 21.2 mmol, in 50 mL of ether) was treated with phenyllithium (20.1 mmol) to yield 3.9 g (84%) of **8b** as a slightly brownish colored powder, characterized by NMR spectroscopy. ^1H NMR (benzene-*d*₆/THF-*d*₈, 3:1): δ 7.84, 7.15, 7.00 (m, 5H, Ph), 5.92, 5.86 (m, each 2H, Cp), 2.25 (s, 6H, NMe₂), 1.78 (s, 3H, CH₃). ^{13}C NMR (benzene-*d*₆/THF-*d*₈, 3:1): δ 153.8 (ipso-C of Ph), 128.5, 127.3, 124.9 (CH of Ph), 129.2 (ipso-C of Cp), 103.8, 102.4 (CH of Cp), 64.4 (quat. C-NMe₂), 40.3 (NMe₂), 27.2 (CH₃).

Bis[η^5 -[1-(*N,N*-dimethylamino)ethyl]cyclopentadienyl]zirconium Dichloride (*rac*/*meso*-9a** Mixture).** A cooled (0°C) suspension of $\text{ZrCl}_4 \cdot 2\text{THF}$ (2.50 g, 10.7 mmol) in 20 mL of ether was added in several portions to a suspension of 3.25 g (22.6 mmol) of the cyclopentadienyllithium reagent **7a** in 50 mL of ether at 0°C . The mixture was stirred for 15 min at 0°C and then filtered. The etheral solution contained only very much contaminated product and was, therefore, discarded. The solid was extracted with dichloromethane until the liquid remained colorless. Solvent was removed from the dichloromethane extract to yield 2.03 g (44%) of the *rac*-**9a**/*meso*-**9a** 1:1 mixture, mp 180°C (dec, DSC). Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{ZrCl}_2$ (434.6): C, 49.75; H, 6.49; N, 6.45. Found: C, 49.08; H, 6.68; N, 6.47. ^1H NMR (benzene-*d*₆): δ 6.2 (br m, 8H) and 5.8 (br m, 8H, Cp), 4.1 (two overlapping quartets, 4H, CH), 2.0 (s,

24H, NMe₂), 1.24, 1.26 (each d, $^3J = 6.8$ Hz, 12H, CH₃). ^1H NMR (CDCl_3): δ 6.42, 6.25 (m, each 4H, Cp), 3.93 (m, 4H, CH), 2.12, 2.13 (s, each 12H, NMe₂), 1.28, 1.29 (d, $^3J = 6.8$ Hz, each 6H, CH₃). ^{13}C NMR (benzene-*d*₆): δ 134.6, 134.2 (ipso-C of Cp), 118.3, 118.1, 116.1, 116.0, 113.1, 112.9, 110.6, 109.8 (CH of Cp), 58.3 (CH), 40.4 (NMe₂), 12.2 (CH₃).

Bis[η^5 -[1-(*N,N*-dimethylamino)pentyl]cyclopentadienyl]zirconium Dichloride (*rac*/*meso*-9b** Mixture).** A solution of $\text{ZrCl}_4 \cdot 2\text{THF}$ (1.45 g, 3.83 mmol) in 30 mL of tetrahydrofuran was slowly added to a stirred suspension of **7b** (1.42 g, 7.67 mmol) in 150 mL of ether at 0°C . The mixture was stirred for 5 min at 0°C and then the solvent removed in vacuo. The brown viscous residue was dissolved in chloroform and then kept at -30°C overnight to precipitate the lithium chloride. The precipitate was removed by filtration. Solvent was then removed from the clear filtrate in vacuo to yield 0.69 g (35%) of the ca. 90% pure *rac*-**9b**/*meso*-**9b** 1:1 mixture. ^1H NMR (CDCl_3): δ 6.48, 6.36, 6.17, 6.08 (m, each 4H, Cp), 3.73, 3.68 (m, each 2H, CH), 2.06, 2.07 (s, each 12H, NMe₂), 1.9–1.1 (br m, 24H) and 0.9 (br t, 12H, *n*-butyl). ^{13}C NMR (CDCl_3): δ 132.7, 132.2 (ipso-C of Cp), 117.7, 116.9, 116.4, 115.7, 114.9, 114.7, 108.6, 107.7 (CH of Cp), 62.6 (CH-NMe₂), 40.7 (NMe₂), 30.7, 30.1 (CH-CH₂-), 22.6, 29.1 (CH₂-CH₂-), 14.1 (CH₃).

***rac*-Bis[η^5 -[1-(*N,N*-dimethylamino)pentyl]cyclopentadienyl]zirconium Dichloride (*rac*-**9b**).** A cooled (0°C) suspension of ZrCl_4 (1.96 g, 8.4 mmol) in 40 mL of toluene was added to a stirred solution of the cyclopentadienyllithium reagent **7b** (4.63 g, 25 mmol) in 100 mL of toluene at 0°C . The mixture was stirred overnight. Lithium chloride was filtered off through Celite and the residue washed with dichloromethane. Solvent was removed from the combined organic phases. The resulting oil was dissolved in pentane. During 2 weeks a precipitate was formed at $+6^{\circ}\text{C}$, and it was collected by filtration to yield 0.35 g (8%) of the *rac*-**9b** isomer as a solid. Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{N}_2\text{Cl}_2\text{Zr}$ (518.7): C, 55.57; H, 7.77; N, 5.40. Found: C, 54.15; H, 7.54; N, 5.14. ^1H NMR (benzene-*d*₆): δ 6.08, 6.02, 5.89, 5.61 (m, each 2H, Cp), 3.94 (m, 2H, CH), 2.00 (s, 12H, NMe₂), 1.3–1.9 (br m, 12H) and 0.97 (br t, 6H, *n*-butyl). ^{13}C NMR (CDCl_3): δ 132.7 (ipso-C of Cp), 117.0, 116.4, 114.9, 107.4 (CH of Cp), 62.6 (CH-NMe₂), 40.8 (NMe₂), 30.1, 29.1, 22.6, 14.1 (*n*-butyl).

X-ray Crystal Structure Analysis of the **9b Enantiomers.** The pure *rac*-**9b** diastereomer was dissolved in dichloromethane. Pentane was allowed to diffuse slowly into this solution at ambient temperature. Over a period of several weeks, long colorless needles of the product were obtained. The chiral **9b** diastereomer crystallized with spontaneous resolution of enantiomers. Several samples checked by X-ray diffraction revealed that single crystals contained the pure enantiomers (*R,R*)-**9b** or (*S,S*)-**9b**, respectively: formula $\text{C}_{24}\text{H}_{40}\text{N}_2\text{ZrCl}_2$, $M = 518.70$, $0.5 \times 0.3 \times 0.25$ mm, $a = 13.767(1)$ Å, $b = 14.207(1)$ Å, $c = 6.471(1)$ Å, $V = 1265.6(2)$ Å³, $\rho_{\text{calc}} = 1.361$ g cm⁻³, $\mu = 6.58$ cm⁻¹, no absorption correction, $Z = 2$, orthorhombic, space group $P2_12_12$ (No. 18), $\lambda = 0.710$ 73 Å, $\omega/2\theta$ scans, 2189 reflections collected ($\pm h, +k, -l$), $[(\sin \theta)/\lambda]_{\text{max}} = 0.62$ Å⁻¹, 2062 independent and 1990 observed reflections [$I \geq 2\sigma(I)$], 136 refined parameters, $R = 0.023$, $wR^2 = 0.060$, Flack parameter $-0.03(4)$, maximum residual electron density 0.58 (-0.69) e Å⁻³, hydrogens calculated and riding.

Bis[η^5 -[1-(*N,N*-dimethylamino)-1-methylethyl]cyclopentadienyl]zirconium Dichloride (10a**).** A cooled (0°C) suspension of $\text{ZrCl}_4 \cdot 2\text{THF}$ (6.82 g, 18.1 mmol) in 60 mL of ether was added in portions to a stirred suspension of 5.71 g (36.1 mmol) of the cyclopentadienyllithium reagent **8a** in 250 mL of ether at 0°C . The mixture was stirred for 15 min at 0°C . The precipitate was collected by filtration and washed with ether (3×20 mL). The solid residue was extracted with dichloromethane. Solvent was removed from the dichloromethane extracts to give 4.44 g (53%) of **10a** as a solid. The combined etheral phases were concentrated in vacuo to ca. 50% of their original volume and kept overnight at -30°C to precipitate additional **10a**, which was collected by filtration (1.51 g, 18%). Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{N}_2\text{Cl}_2\text{Zr}$

(462.2): C, 51.93; H, 6.97; N, 6.06. Found: C, 49.61; H, 6.75; N, 6.12. ^1H NMR (dichloromethane- d_2): δ 6.47, 6.37 (m, each 4H, Cp), 1.96 (s, 6H, NMe $_2$), 1.51 [s, 6H, C(CH $_3$) $_2$]. ^{13}C NMR (CDCl $_3$): δ 121.0 (ipso-C of Cp), 117.7, 111.8 (CH of Cp), 56.3 (C–NMe $_2$), 39.0 (NMe $_2$), 24.2 (CH $_3$).

Bis[η^5 -[1-(*N,N*-dimethylamino)-1-methylbenzyl]cyclopentadienyl]zirconium dichloride (*rac*/*meso*-10b** Mixture).** A cold (0 °C) suspension of ZrCl $_4$ ·2THF (3.59 g, 9.5 mmol) in 50 mL of ether was added in portions to a suspension of 4.18 g (19.0 mmol) of **8b** in 250 mL of ether at –30 °C. The mixture was stirred for an additional 2 h at –30 °C. The precipitate was collected by filtration, washed with ether (3 × 10 mL), and then extracted with dichloromethane. Solvent was removed from the extract. The residue was stirred for 15 min with 20 mL of a 1:1 ether/pentane mixture. The solid product was recovered by filtration and dried in vacuo to yield 2.00 g (36%) of the *rac*-**10b**/*meso*-**10b** 1:1 mixture, mp 174 °C, dec. Anal. Calcd for C $_{30}$ H $_{36}$ N $_2$ Cl $_2$ Zr (586.8): C, 61.41; H, 6.18; N, 4.77. Found: C, 59.44; H, 6.13; N, 4.20. ^1H NMR (dichloromethane- d_2): δ 7.5–7.3 (br m, 12H) and 7.77, 7.73 (m, each 4H, Ph), 6.26, 6.20 (m, each 4H), 6.40, 6.12, 5.01, 3.66 (m, each 2H, Cp), 1.78, 1.83 (s, each 12H, NMe $_2$), 1.77, 1.75 (s, each 6H, CH $_3$).

***rac*-Bis[η^5 -[1-(*N,N*-dimethylamino)-1-methylbenzyl]cyclopentadienyl]zirconium Dichloride (*rac*-**10b**).** To a cooled (–30 °C) suspension of 3.39 g (15.5 mmol) of **8b** in 50 mL of ether was added in portions a precooled (0 °C) suspension of 2.92 g (7.7 mmol) of ZrCl $_4$ ·2THF in 50 mL of ether. The mixture was then stirred for 2 h at –30 °C and the precipitate collected by filtration and washed with ether (3 × 10 mL). The remaining solid was extracted with dichloromethane until the extracts became colorless. Solvent was removed from the dichloromethane phase to give a brown solid. Pentane (15 mL) was added and the mixture stirred for 15 min. The solid was collected by filtration and dried in vacuo to yield 0.68 g (15%) of *rac*-**10b**, mp 182 °C dec. Anal. Calcd for C $_{30}$ H $_{36}$ N $_2$ Cl $_2$ Zr (586.8): C, 61.41; H, 6.18. Found: C, 60.93; H, 6.07. ^1H NMR (dichloromethane- d_2): δ 7.77, 7.39, 7.33 (m, 10H, Ph), 6.40, 6.27, 6.12, 3.66 (m, each 2H, Cp), 1.78 (s, 12H, NMe $_2$), 1.77 (s, 6H, CH $_3$). ^{13}C NMR (dichloromethane- d_2): δ 146.4 (ipso-C of Ph), 129.1, 128.3, 127.6 (CH of Ph) 140.5 (ipso-C of Cp), 126.2, 118.5, 114.1, 108.7 (CH of Cp), 63.2 (C–NMe $_2$), 39.3 (NMe $_2$), 12.0 (CH $_3$).

Bis[η^5 -[1-(*N,N*-dimethylamino)-1-methylethyl]cyclopentadienyl]dimethylzirconium (11a**).** A 4.0 mL volume of a 1.68 M ethereal methylolithium solution (6.7 mmol) was added dropwise with stirring to a suspension of 1.56 g (3.4 mmol) of **10a** in 250 mL of ether at –40 °C. The suspension was allowed to warm to –20 °C over a period of 2 h and then stirred for an additional 1 h at room temperature. The solid was removed by filtration through Celite. The clear filtrate was concentrated in vacuo until the solution became turbid. Precipitation of the product was then achieved at –30 °C. Complex **11a** (1.17g, 82%) was collected by filtration and dried in vacuo, mp 189 °C (dec, DSC). Anal. Calcd for C $_{22}$ H $_{38}$ N $_2$ Zr (421.8): C, 62.65; H, 9.08; N, 6.64. Found: C, 60.12; H, 8.65; N, 6.60. ^1H NMR (benzene- d_6): δ 5.89, 5.80 (m, each 4H, Cp), 2.00 (s, 12H, NMe $_2$), 1.25 [s, 12H, C(CH $_3$) $_2$], –0.01 [s, 6H, Zr-(CH $_3$) $_2$]. ^{13}C NMR (benzene- d_6): δ 131.6 (ipso-C of Cp), 110.2, 109.6 (CH of Cp), 56.7 (C–NMe $_2$), 39.3 (NMe $_2$), 32.1 (Zr–CH $_3$), 25.3 (C–CH $_3$).

***rac*-Bis[η^5 -[1-(*N,N*-dimethylamino)-1-methylbenzyl]cyclopentadienyl]dimethylzirconium (*rac*-**11b**).** Analogously as described above, 0.34 g (0.6 mmol) of *rac*-**10b** was reacted with 0.7 mL of a 1.68 M ethereal methylolithium solution (1.2 mmol of CH $_3$ Li) in 60 mL of ether to yield 0.23 g (75%) of the product *rac*-**11b**, mp 176 °C (dec, DSC). Anal. Calcd for C $_{32}$ H $_{42}$ N $_2$ Zr (545.9): C, 70.40; H, 7.75; N, 5.13. Found: C, 68.23; H, 7.74; N, 4.80. ^1H NMR (benzene- d_6): δ 7.62, 7.14, 7.07 (m, 10 H, Ph), 6.33, 6.13, 5.16, 3.91 (m, each 2H, Cp), 1.83 (s, 12H, NMe $_2$), 1.55 (s, 6H, C–CH $_3$), –0.05 [s, 6H, Zr(CH $_3$) $_2$]. ^{13}C NMR (benzene- d_6): δ 147.5 (ipso-C of Ph), 127.7, 127.1 (CH of Ph, remaining signal under solvent), 135.2

(ipso-C of Cp), 115.5, 114.8, 107.8, 107.1 (CH of Cp), 62.9 (C–NMe $_2$), 39.4 (NMe $_2$), 32.4 (Zr–CH $_3$), 12.8 (C–CH $_3$).

X-ray Crystal Structure Analysis of **11b.** Single crystals of the chiral **11b** diastereomer were obtained from toluene- d_8 : formula C $_{32}$ H $_{42}$ N $_2$ Zr, M = 545.90, $1.2 \times 1.0 \times 0.7$ mm, a = 15.150(2) Å, b = 25.215(3) Å, c = 14.893(2) Å, β = 90.19(1)°, V = 5689.2(13) Å 3 , ρ_{calc} = 1.275 g cm $^{-3}$, μ = 4.08 cm $^{-1}$, empirical absorption correction via ψ -scan data ($0.810 \leq C \leq 0.998$), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 0.710 73 Å, $\omega/2\theta$ scans, 5993 reflections collected ($-h, +k, \pm l$), $[(\sin \theta)/\lambda]_{\text{max}}$ = 0.62 Å $^{-1}$, 5773 independent and 4143 observed reflections [$I \geq 2\sigma(I)$], 325 refined parameters, R = 0.084, wR^2 = 0.247, maximum residual electron density 0.243 (–2.28) e Å $^{-3}$, hydrogens calculated and riding. Accuracy is reduced due to absorption of the large sample crystal. Cutting leads to a great broadening of reflection profiles.

Reaction of **11a** with Tris(pentafluorophenyl)borane.

Formation of **13a.** A solution of 0.82 g (1.6 mmol) of tris(pentafluorophenyl)borane in 30 mL of toluene was added to a suspension of 0.68 g (1.6 mmol) of **11a** in 30 mL of toluene at –20 °C. Evolution of a gas was observed directly upon the addition. The mixture was stirred for 2 h at –20 °C. During this time a second oily phase separated. The toluene layer was decanted from the oil. Pentane (80 mL) was added to the oil and the mixture stirred for 2 days at ambient temperature to solidify the product. The solid product was collected by filtration and dried in vacuo to yield 1.2 g (84%) of the spiro-metallocene **13a**, mp 90 °C (dec DSC). Anal. Calcd for C $_{38}$ H $_{34}$ BN $_2$ F $_{15}$ Zr (905.7): C, 50.39; H, 3.78; N, 3.09. Found: C, 49.87; H, 3.79; N, 2.86. ^1H NMR (600 MHz, 223 K, dichloromethane- d_2): δ 6.53, 5.90, 5.73 (m, each 2H) and 6.23, 5.52 (m, each 1H, Cp), 2.41 (s, 3H, N–CH $_3$), 2.27 [s, 6H, N(CH $_3$) $_2$], 1.53, 2.21 (AX-system, 2J = 9.6 Hz, –CH $_2$ –N), 1.58, 1.47, 1.46, 1.32 [s, each 3H, C(CH $_3$) $_2$], 0.43 [br s, 3H, (C $_6$ F $_5$) $_3$ B–CH $_3$]. ^{13}C NMR (150 MHz, 223 K, dichloromethane- d_2): δ 148.8 ($^1J_{\text{CF}}$ = 237 Hz), 138.0 ($^1J_{\text{CF}}$ = 252 Hz), 136.9 ($^1J_{\text{CF}}$ = 244 Hz), 128.3 (C $_6$ F $_5$), 123.8, 115.4 (ipso-C of Cp), 113.1, 112.0, 110.2, 109.7, 106.7, 104.2, 99.7, 99.4 (CH of Cp), 60.6, 58.2 (CMe $_2$), 49.1 (CH $_2$), 47.7, 47.2 [N(CH $_3$) $_2$], 43.5 (N–CH $_3$), 24.8, 24.3, 24.1, 17.5 [C(CH $_3$) $_2$], 9.5 (B–CH $_3$).

Treatment of *rac*-**11b** with Tris(pentafluorophenyl)borane. Formation of **13b**.

Dichloromethane- d_2 (0.5 mL) was added to a mixture of the solid reagents *rac*-**11b** (27.3 mg, 0.5 mmol) and B(C $_6$ F $_5$) $_3$ (25.6 mg, 0.5 mmol) at ambient temperature. A rapid gas evolution was observed. The formation of the single **13b** diastereomer was quantitative as judged by NMR. ^1H NMR (600 MHz, 303 K, dichloromethane): δ 7.3–7.5 (m, 10H, Ph), 6.83, 6.58, 6.40, 6.23, 6.14, 5.97, 5.85, 5.80 (m, each 1H, Cp), 2.97 (s, 3H, N–CH $_3$), 2.55, 2.21 [s, each 3H, N(CH $_3$) $_2$], 2.51, 1.85 (AX-system, 2J = 9.6 Hz, N–CH $_2$ –), 1.845, 1.841 (s, each 3H, C–CH $_3$), δ 0.50 (br s, 3H, B–CH $_3$). ^{13}C NMR (150 MHz, 303 K, dichloromethane- d_2 , signals of the cation are given only): δ 141.7, 140.1 (ipso-C of Ph), 129.1, 128.3, 127.6, 127.3 (several signals overlapping, CH of Ph), 121.6, 117.0 (ipso-C of Cp), 121.4, 113.3, 112.6, 109.7, 107.0, 104.5, 104.0, 100.4 (CH of Cp), 67.5, 67.1 (C–CH $_3$), 56.6 (CH $_2$), 52.0 (N–CH $_3$), 49.2, 49.0 [N(CH $_3$) $_2$], 29.1, 28.6 [C(CH $_3$) $_2$].

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Supporting Information Available: Details of the X-ray crystal structure analyses of **9b** and **11b** and selected NMR spectra of complexes **9–11** and **13** (40 pages). Ordering information is given on any current masthead page.