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Selective Intramolecular [N]CH Activation in Bis(1-ethenylamino-Cp)zirconium−Butadiene Complexes and Related Systems

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Treatment of 6-(dimethylamino)-6-methylpentafulvene (**2a**) with methyllithium in ether at −40 °C leads to CH_3 addition to the C6-fulvene carbon atom to yield the $[C_5H_4{-}CMe_2{-}NMe_2]Li$ reagent **3a**, whereas treatment of **2a** with MeLi in THF at −78 °C results in deprotonation with formation of $[C_5H_4{-}C({=}CH_2){-}NMe_2]Li$ (**4a**). In contrast, treatment of 6-diethylamino-6-methylfulvene (**2b**) with methyllithium under any of these conditions leads only to H^+-abstraction to give $[C_5H_4{-}C({=}CH_2){-}NEt_2]Li$ (**4b**). Treatment of the reagents **4** with $CpZrCl_3$ yields the enamino-Cp-substituted bent metallocenes $[\eta^5\text{-}C_5H_4{-}C({=}CH_2){-}NR_2]\text{-}CpZrCl_2$ **5a** ($R = CH_3$) and **5b** ($R = C_2H_5$), respectively. Analogous treatment of **4b** with zirconium tetrachloride gave the doubly functionalized zirconocene complex $[\eta^5\text{-}C_5H_4{-}C({=}CH_2){-}NEt_2]_2ZrCl_2$ (**6b**). The complexes **5a**, **5b**, and **6b** were characterized by X-ray diffraction. Treatment of **3a** with $CpZrCl_3$ gave $[\eta^5\text{-}C_5H_4{-}CMe_2{-}NMe_2]CpZrCl_2$ (**8a**); the analogous reaction with $ZrCl_4$ gave $[\eta^5\text{-}C_5H_4{-}CMe_2{-}NMe_2]_2ZrCl_2$ (**8b**). Both complexes **8** reacted with (butadiene)magnesium with replacement of both chloride ligands at zirconium. The probably generated (η^4-butadiene)zirconocene complexes were, however, not stable under the applied reaction conditions, but reacted further by C−H activation at the $N{-}CH_3$ group with intramolecular hydrogen transfer to the butadiene ligand to yield the cyclometalated products $[\eta^5\text{-}C_5H_4{-}CMe_2{-}N(CH_3){-}CH_2{-}]Zr(L)(CH_2CHCHCH_3)$ **13a** (L = Cp) and **13b** ($L = [\eta^5\text{-}C_5H_4{-}CMe_2{-}NMe_2]$), respectively. Complex **5a** reacts analogously with (butadiene)magnesium to yield the C−H activation product $[\eta^5\text{-}C_5H_4{-}C({=}CH_2){-}N(CH_3){-}CH_2{-}]ZrCp(CH_2CHCHCH_3)$ **14**. The 1-diethylaminoethenyl-Cp-substituted systems **5b** and **6b** react differently with (butadiene)magnesium. They form the stable η^4-butadiene complexes *s-trans*-**15** and *s-cis*-**15A/B** (from **5b**) and *s-trans*-**17** and *s-cis*-**17** (from **6b**), respectively. [N]CH activation was not observed in these cases. Treatment of the cyclometalated products **13a**, **14**, and **15** with $B(C_6F_5)_3$ gave active homogeneous Ziegler−Natta catalysts for ethene polymerization, whereas the systems **13b**/$B(C_6F_5)_3$ and **17**/$B(C_6F_5)_3$ were close to inactive under comparable conditions.

Introduction

Group 4 bent metallocene complexes have a rather low tolerance toward functional group substituents at their Cp ligands.[1,2] Dialkylaminomethyl substituents and their derivatives play a special role in this respect. They can readily be introduced by means of fulvene routes,[3,4] and their respective zirconocene dichloride complexes can readily be prepared.[5] However, the methyl zirconocene cation complexes that contain the $\eta^5\text{-}Cp{-}CR_2{-}NMe_2$ ligand system have turned out to be quite unstable with regard to a rapid CH activation at $N{-}CH_3$. This results in the liberation of methane with concomitant formation of the organometallic α-metalation products (see Chart 1).[6] This reaction type is of importance since it may interfere with the formation of the respective methylmetallocene cations during typical Ziegler−Natta catalyst activation procedures of such systems[7−9] (see Chart 1).

We have, therefore, looked for experimentally feasible structural variations of the $Cp{-}CR_2{-}NMe_2$ ligand system that could make this complicating [N]CH activa-

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[§] X-ray crystal structure analyses.

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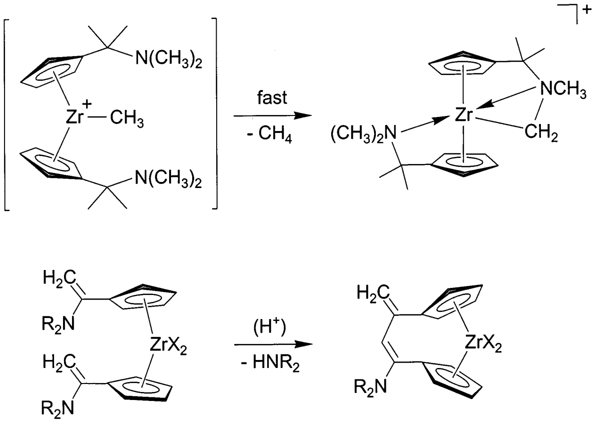
Chart 1



tion process less favorable. Introduction of an enamino substituent instead of the dialkylamino group might be a possibility since the resulting CH-activated (i.e., α-metalated) product would be more strained and thus its formation might be energetically less likely to occur. Such systems were prepared but showed another serious chemical instability: in the presence of trace amounts of acid (or Lewis acid) they undergo a rapid intramolecular Mannich-type coupling reaction to yield an interesting novel *ansa*-metallocene system (see Chart 1).[10,11]

We have now found that the [N]CH activation features as well as the tendency of such systems to undergo intramolecular catalyzed Mannich condensation is quite dependent on the alkyl substituents at the nitrogen atom. We here report about the synthesis and some characteristic properties of the corresponding diethylamino-substituend group 4 metallocene complexes (and their catalytic features) that go far beyond a simple homologous substituent variation when compared with their respective dimethylamino derivatives.

Results and Discussion

Synthesis and Characterization of the Metallocene Dichloride Complexes. Both the *tert*-enamino-Cp and the substituted dialkylaminomethyl-Cp group 4 metallocenes used in this study were prepared by means of variations of a fulvene route.[12,13] Treatment of *N*,*N*-dimethylacetamide (**1a**) or *N*,*N*-diethylacetamide (**1b**) with dimethyl sulfate followed by the reaction with sodium cyclopentadienide resulted in the formation of the 6-dialkylamino-substituted pentafulvenes, analogous with that described by Hafner et al.[3] The product 6-diethylamino-6-methylfulvene (**2b**) was characterized by X-ray diffraction (see Figure 1). It shows the presence of a cross-conjugated system of three C=C double bonds. The bond lengths of the exocyclic C=C bond in **2b** amounts to 1.395(4) Å. The adjacent C−N bond is slightly shortened at 1.340(3) Å, which indicates some conjugation of the electron lone pair at nitrogen with the fulvene π-system.

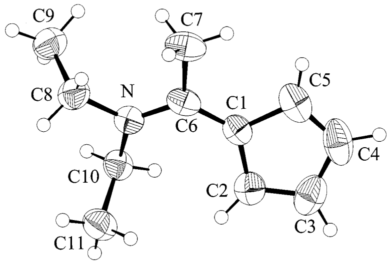


Figure 1. Molecular structure of the fulvene **2b**. Selected bond lengths (Å) and angles (deg): C1−C2 1.433(4), C1−C5 1.445(4), C1−C6 1.395(4), C2−C3 1.365(4), C3−C4 1.412(5), C4−C5 1.349(5), C6−C7 1.510(4), C6−N 1.340(3), N−C8 1.471(3), N−C10 1.462(3); C1−C6−C7 118.8(3), C1−C6−N 126.0(3), C7−C6−N 115.2(3), C6−N−C8 123.4(3), C6−N−C10 123.4(3), C8−N−C10 113.1(3).

Treatment of the dimethylamino-substituted fulvene (**2a**) with 1 molar equiv of methyllithium in diethyl ether at −40 °C resulted in a clean addition of the methyl carbon nucleophile to the fulvene C6-carbon atom with formation of the corresponding [(1-(dimethylamino)-1-methylethyl)cyclopentadienyl]lithium reagent (**3a**, see Scheme 1).[4−6] In contrast, methyllithium acted solely as a base toward the fulvene **2a**, when the reaction was carried out in tetrahydrofuran solution at −78 °C. Under these conditions the enamino-substituted cyclopentadienide (**4a**) was obtained as the only product (85% isolated). The product **4a** shows characteristic ^{1}H NMR signals at δ 6.34 and 6.13 (C_5H_4), δ 4.30 and 3.89 ($=CH_2$), and δ 2.78 (NMe_2) in a d_6-benzene/d_8-thf (1:1) solvent mixture (^{13}C NMR signals of the $C=CH_2$ unit at δ 158.3 and 80.7).

The reaction of methyllithium with the diethylaminofulvene **2b** is different in that under all reaction conditions applied only deprotonation was achieved to yield the enamino-substituted cyclopentadienide **4b**. Scheme 1 shows typical reaction conditions of the preparation of this compound.

We have then reacted the [Cp-C(=CH_2)NMe_2]Li reagent **4a** with $CpZrCl_3$.[14] The reaction proceeded

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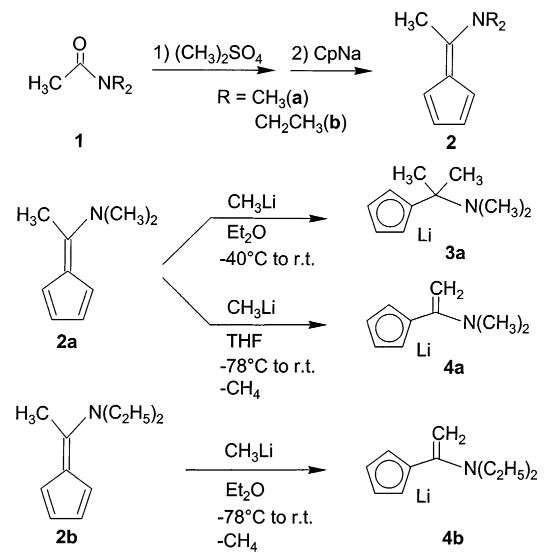
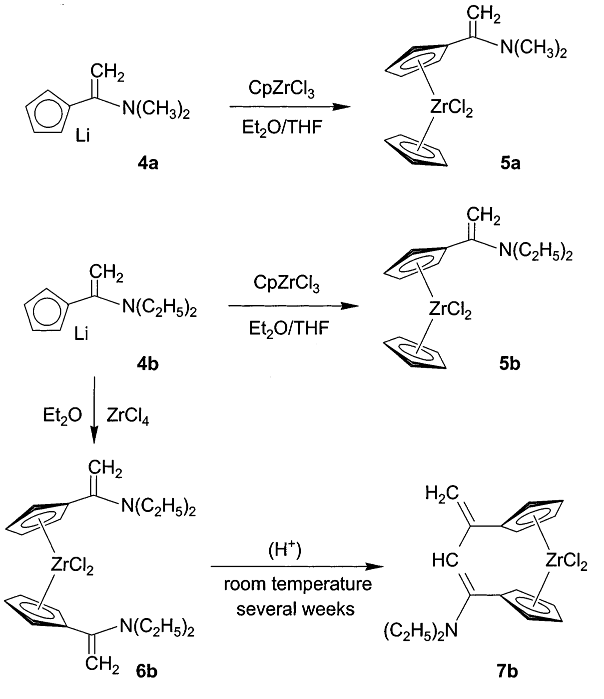
Scheme 1



Scheme 2



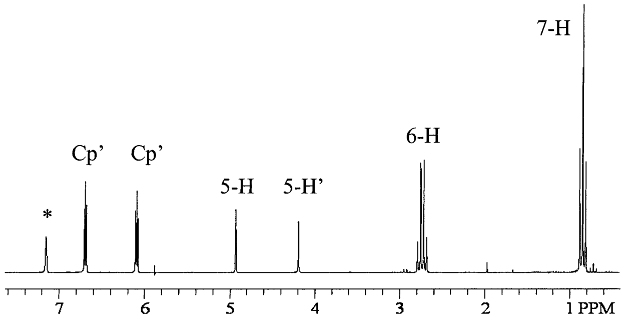


Figure 2. ^1H NMR spectrum of complex **6b** (d_6-benzene, 200 MHz, 300 K)

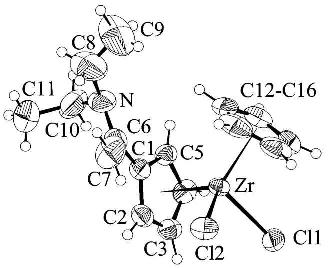


Figure 3. View of the molecular structure of the enamino-functionalized zirconocene chloride complex **5b**. Selected bond lengths (Å) and angles (deg): Zr−Cl1 2.430(1), Zr−Cl2 2.441(1), C1−C6 1.487(5), C6−C7 1.315(6), C6−N 1.387(5), N−C8 1.468(6), N−C10 1.483(7); Cl1−Zr−Cl2 93.65(4), C1−C6−C7 121.0(4), C1−C6−N 113.5(4), C7−C6−N 125.3(4), C6−N−C8 117.2(5), C6−N−C10 116.2(4), C8−N−C10 113.6(5). For additional values see the text.

smoothly in a diethyl ether/THF solvent mixture and gave the metallocene complex **5a** in >70% yield. Complex **5a** is characterized by ^1H NMR signals at δ 6.08 (s, 5H, Cp), δ 6.38 and 6.00 (C_5H_4), δ 4.70 and 4.11 (=CH_2), and δ 2.19 (NMe_2). The reaction of $CpZrCl_3$ with the reagent **4b** proceeded analogously to yield the corresponding metallocene dichloride complex **5b** (63% isolated, see Scheme 2). We had previously found that the reaction of **4a** with zirconium tetrachloride in a 2:1 molar ratio was hard to stop at the stage of the salt metathesis product (**6a**) because of a facile subsequent Mannich-type condensation reaction to the respective *ansa*-metallocene[10] (see Chart 1). We have now observed that treatment of $ZrCl_4$ with 2 molar equiv of the diethylaminoethenyl-substituted cyclopentadienide reagent **4b** at 0 °C in diethyl ether cleanly gave the nonbridged doubly functionalized bent metallocene system. The compound **6b** was eventually isolated as a yellow solid in 57% yield. Figure 2 shows the ^1H NMR spectrum of complex **6b**. This enamino-functionalized nonbridged bent metallocene is rather stable at ambient conditions, but it is not completely resistant to intramolecular Mannich-type CC coupling. A very slow Mannich-type reaction was in fact observed upon storage of the complex for weeks at room temperature. After 4 weeks ca. 50% of a sample had converted to the *ansa*-metallocene **7b** with loss of diethylamine. We assume that this occurred by the typical acid-catalyzed CC coupling process that we had previously described.[10]

The functionalized metallocene dichloride complexes **5a**, **5b**, and **6b** were characterized by X-ray diffraction. Single crystals were obtained from all three compounds from pentane solutions. The molecular geometry of complex **5b** is depicted in Figure 3. It exhibits a typical pseudotetrahedral bent metallocene type structure with bond angles around the central zirconium atom of Cl1−Zr−Cl2 93.65° and Cp(centroid)−Zr−Cp(centroid) 128.9°. These are typical values of zirconocene complexes.[15] Both cyclopentadienyl rings are rather uniformely η^5-coordinated to the central group 4 metal center. The Zr−C(Cp) bond lengths of the substituted η^5-Cp−Zr unit are found in a range between 2.477(3) and 2.526(4) Å. The bond distances of the zirconium atom to the carbon atoms of the unsubstituted C_5H_4 ring are in a very similar range between 2.471(4) and 2.509(4) Å. The enamino substituent is oriented close to coplanar with its adjacent cyclopentadienyl ring (dihedral angles θ

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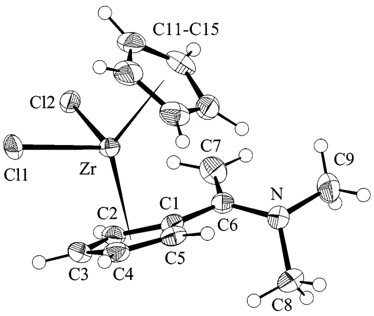

Figure 4. Molecular structure of complex **5a**. Selected bond lengths (Å) and angles (deg): Zr−Cl1 2.505(2), Zr−Cl2 2.558(2), C1−C6 1.491(8), C6−C7 1.328(9), C6−N 1.401(8), N−C8 1.473(8), N−C9 1.449(8); Cl1−Zr−Cl2 95.88(5), C1−C6−C7 121.3(6), C1−C6−N 113.8(5), C7−C6−N 124.8(6), C6−N−C8 117.2(5), C6−N−C9 116.7(5), C8−N−C9 111.5(5).

C2−C1−C6−C7 32.8(6)°, C5−C1−C6−N 28.3(5)°). The connecting C1(Cp)−C6 bond length amounts to 1.487(5) Å. The C6−C7 bond (1.315(6) Å) is in the typical C=C range.[16,17] The bond angles around C6 are 121.0(4)° (C1−C6−C7), 125.3(4)° (C7−C6−N), and 113.5(4)° (C1−C6−N). The sum of bonding angles at nitrogen is 347.0°. The bent metallocene conformation is such that the enamino substituent is oriented in a gauche-type position between a lateral and a backside orientation (“10 o'clock position”). Inside the Cp/enamino substituent plane the C(6)=C(7) double bond is oriented such that it points toward the open front side of the bent metallocene wedge.

The structures of the complexes **5a** and **5b** are similar. The monofunctionalized system **5a** shows a similar conformational arrangement of the substituent that is attached to the η^5-C_5H_4 ring system (see Figure 4). In **5a** the enamino C=C double bond length amounts to 1.328(9) Å (C6−C7). The C6−N bond length is found at 1.401(8) Å, and the connecting bond to the Cp ring (C1−C6) is 1.491(8) Å.

The Cl1−Zr−Cl2 angle of complex **6b** amounts to 96.28(6)°; the Cp(centroid) −Zr−Cp(centroid) angle to 128.8°. Both enamino-substituted Cp rings are uniformely η^5-coordinated. The corresponding Zr−C1 to C5 bond distances are in a narrow range between 2.476(5) Å (Zr−C5) and 2.528(6) Å (Zr−C2) (see Figure 5). The corresponding values of the second ring are found between 2.485(6) (Zr−C14) and 2.535(6) Å (Zr−C16). Both enamino-substituents show similar characteristic structural features: both the C6−C7 (1.327(9) Å) and the C17−C18 (1.315(7) Å) distances are in the typical C=C double bond range. Each single enamino-Cp conformation is similar to that found in **5b**, i.e., with the C(6)=C(7) and the C(17)=C(18) double bonds located practically in the Cp ring planes.

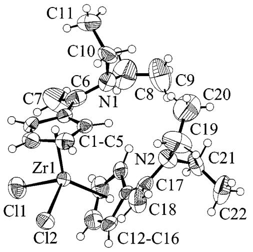

Figure 5. Molecular structure of complex **6b** (values from molecule 1). Selected bond lengths (Å) and angles (deg): Zr−Cl1 2.426(2), Zr−Cl2 2.436(2), C1−C6 1.471(8), C12−C17 1.477(8), C6−C7 1.327(9), C17−C18 1.315(7), C6−N1 1.395(8), C17−N2 1.384(7), N1−C8 1.455(8), N2−C19 1.482(8), N1−C10 1.446(7), N2−C21 1.473(7); Cl1−Zr−Cl2 96.28(6), C1−C6−C7 120.0(7), C12−C17−C18 121.1(6), C1−C6−N1 114.7(5), C12−C17−N2 113.9(5), C7−C6−N1 125.1(7), C18−C17−N2 124.8(6), C6−N1−C8 115.6(6), C17−N2−C19 114.8(5), C6−N1−C10 114.5(5), C17−N2−C21 115.5(5), C8−N1−C10 115.1(6), C19−N2−C21 116.1(6).

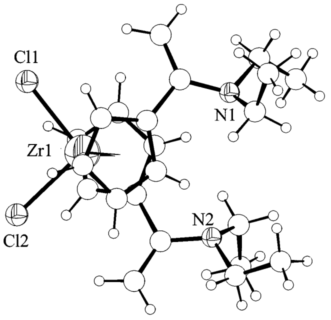

Figure 6. Top projection of the structure of complex **6b** showing the typical conformational arrangement of the pair of enamino substituents at the bent metallocene framework

The C12−C17 and the C1−C6 vectors are oriented in the “10 o'clock” and “2 o'clock” positions. They are thus pointing to different hind lateral sectors of the bent metallocene wedge in a close to C_2-symmetrical overall conformational arrangement (see Figure 6).[18,19] Both nitrogen atoms are again close to trigonally planar coordinated (the sums of the bonding angles at N1 and N2 are 345.2° and 346.4°, respectively).

(Butadiene)metallocene Complexes. We had recently converted the zirconocene dichloride **8a** to the corresponding dimethyl zirconium compound **9a** by treatment with 2 equiv of methyllithium. Subsequent treatment with $B(C_6F_5)_3$ resulted in transfer of a methyl anion equivalent from zirconium to boron. However, the probably resulting methylmetallocene cation (**10a**) was not stable under the reaction conditions due to a rapid subsequent methane elimination with formation of the internal η^2-iminium salt complex **11a** (see Chart 2).[6] The unique three-membered metallacyclic structure of **11a** was identified by X-ray diffraction. In addition it gave rise to very characteristic NMR features, especially the [N]CH_2 ^{13}C NMR resonance at δ 45.6, with a coupling constant $^1J_{CH} = 152$ Hz, which is typical of a three-membered ring structure, including metallacyclic three-membered rings.[20]

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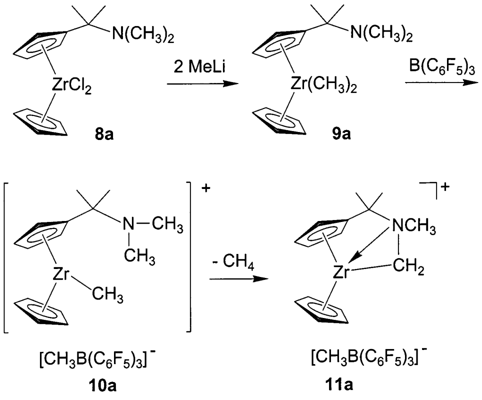
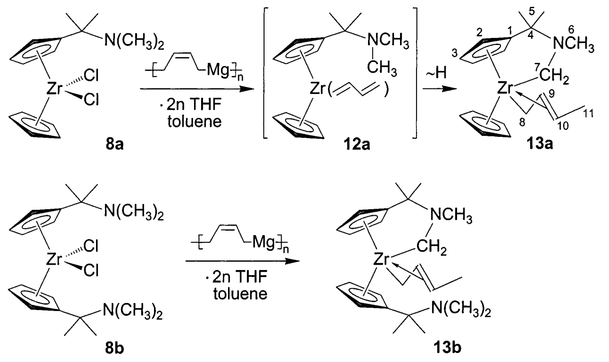
Chart 2



Scheme 3



Treatment of **8a** with (butadiene)magnesium[21] gives a similar result. The reaction probably proceeds by formation of the respective (butadiene)metallocene complex,[22] which is, however, unstable under the applied reaction conditions with respect to C–H activation[23] at the adjacent nitrogen-activated N–CH_3 methyl group. Only in this case the intramolecular H transfer does not require an electrophilic activation, but the H atom is directly transferred from the N–CH_3 unit to a terminal carbon atom of the butadiene ligand in the alleged intermediate. We have isolated the corresponding neutral C–H activation product (**13a**) as a brown oil in 87% yield (see Scheme 3).

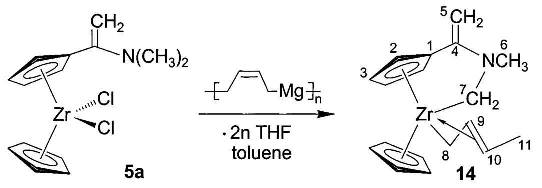
The substituted η^5-C_5H_4–R ring of the product **13a** exhibits four methine ^{1}H NMR signals at δ 5.36, 5.14, 4.86, and 4.36 due to the chirality of the system. There is a η^5-Cp resonance at δ 4.99, representing five hydrogens and two signals (each 3H) of the diastereotopic CMe_2 methyl groups. A single N–CH_3 group has remained (δ 2.36), and there is a new N–CH_2–Zr pair of ^{1}H NMR signals at δ 2.44 and 1.95 (^2J = 10.8 Hz). In contrast to the previously reported related cationic system **11a** (see Chart 2), the neutral product **13a** probably is devoid of a direct N→Zr interaction. This is deducted from the observed ^{13}C NMR resonance of the C7 (i.e., N–CH_2–[Zr]) carbon atom (δ 62.8) that shows a pair of $^1J_{CH}$ coupling constants of 120 and 129 Hz. This is a clear indication of the absence of a three-membered metallacyclic (ZrNC) substructure in **13a** (see Scheme 3). The open structure of **13a** is probably stabilized by the presence of a σ,π-type allyl coordination[24] of the C_4H_7 ligand at zirconium, which shows typical ^{1}H NMR features at δ 1.67/1.49 (8-H/H′), 4.43 (9-H), 3.26 (10-H), and 1.64 (10-CH_3).

Table 1. Selected ^{1}H and ^{13}C NMR Data of the CH Activation Products 13 and 14[a]

	5-H	6-H	7-H	C7	8-H	9-H	10-H	11-H
13a	1.18, 1.14	2.36	2.44, 1.95	62.8	1.67, 1.49	4.43	3.26	1.64
13b	1.20, 1.14	2.35	2.42, 1.94	64.9	1.62, 1.44	4.48	3.54	1.70
14	3.88, 3.27	2.73	2.62, 2.12	61.7	1.72, 1.41	4.39	3.12	1.48

[a] In [D_8]toluene at 246 K (**13a**), 233 K (**13b**), 300 K (**14**), 600 (^{1}H)/150 (^{13}C) MHz.

Scheme 4



Treatment of the related complex **8b** with (butadiene)magnesium results in an analogous formation of the CH activation product **13b** (69% isolated). Complex **13b** shows ^{1}H NMR spectroscopic features very similar to **13a** for the bridged Cp–CMe_2–NMe(CH_2) ligand and the σ,π-crotyl group in addition to an intact Cp-CMe_2–NMe_2 moiety (see Table 1 and Scheme 3).

A similar reaction took place when the 1-dimethylaminoethenyl-Cp-substituted metallocene dichloride complex **5a** was treated with the (butadiene)magnesium reagent. Again we could not isolate the respective conjugated diene zirconocene intermediate. When formed under the applied reaction conditions, it rapidly reacts further by a subsequent H-abstraction of the butadiene ligand from the N–CH_3 group to yield the α-metalated product **14** (see Scheme 4). The product shows the typical NMR features of the σ,π-crotyl ligand at zirconium (see Table 1). Again, the characteristic ^{13}C NMR features of the [Zr]–CH_2–[N] unit indicate that the nitrogen atom is *not* coordinated to the metal center (δ (CH_2) = 61.7, $^1J_{CH}$ = 128 and 130 Hz; the adjacent N–CH_3 group shows ^{13}C NMR features of δ (N–CH_3) = 45.3 with $^1J_{CH}$ = 133 Hz).

The reaction of the corresponding 1-diethylaminoethenyl-Cp zirconocene dichloride complex **5b** with the (butadiene)magnesium reagent leads to different prod-

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Scheme 5

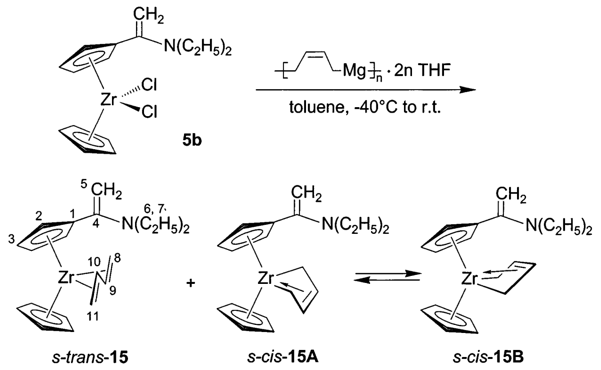
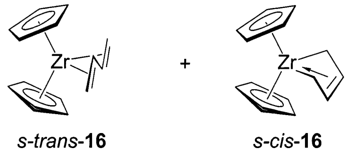


Table 2. Selected NMR Data of the (*s-trans-* and *s-cis-*Butadiene)zirconium Complexes 15−17[a]

complex	Cp-H	8-H/H′	11-H/H′	9-H,10-H	C8,C11	C9,C10
*s-trans-***15**	4.92	3.28	3.23	3.10	61.9	97.6
		1.36	1.13	2.85	60.4	97.3
*s-cis-***15A**	5.50	3.37	−0.67	4.83	51.8	112.6
*s-cis-***15B**	4.97	3.37	−0.51	4.73	51.8	112.4
*s-trans-***16**	4.80	3.20	2.90	1.20	59.0	96.0
*s-cis-***16**	4.78	2.15	−0.70	4.85	49.0	112.0
*s-trans-***17**		3.32	1.31	3.20	62.5	98.6
*s-cis-***17**		3.38	−0.46	4.82	49.2	112.6

[a] ^{1}H (600 MHz), ^{13}C (150 MHz) NMR spectra in [D$_8$]toluene at 233 K (**15**), 213 K (**17**), or 298 K (**16**). Data of **16** from refs 25 and 26.

Chart 3



ucts. In this case the corresponding (butadiene)metallocene complexes have turned out to be resistant to the intramolecular C−H activation. They are stable under the reaction conditions and were isolated as a mixture of one (η^4-*s-trans*-butadiene)[Zr] complex (*s-trans*-**15**) and two diastereoisomeric (η^4-*s-cis*-butadiene)[Zr] complexes (*s-cis*-**15A** and *s-cis*-**15B**) in a ca. 7:8:5 ratio. The latter two interconvert rapidly on the NMR time scale at ambient temperature,[25] but their interconversion was sufficiently slow at 233 K in toluene solution that their static ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectra could be monitored. Selected characteristic NMR data of the chiral complex *s-trans*-**15** and the two *s-cis*-**15A/B** systems (see Scheme 5) are listed in Table 2 [with the data of the parent (η^4-*s-trans*- and η^4-*s-cis*-butadiene)ZrCp$_2$ complexes (**16**) as a comparison[26] (see Chart 3)].

The bis(1-diethylaminoethenyl-Cp)ZrCl$_2$ complex **6b** reacts analogously with (butadiene)magnesium to yield a ca. 2:5 mixture of the (η^4-*s-trans*-) and (η^4-*s-cis*-butadiene)metallocene isomers *s-trans*-**17** and *s-cis*-**17** (see Scheme 6). C−H activation in the α-position to nitrogen was not observed.

Scheme 6

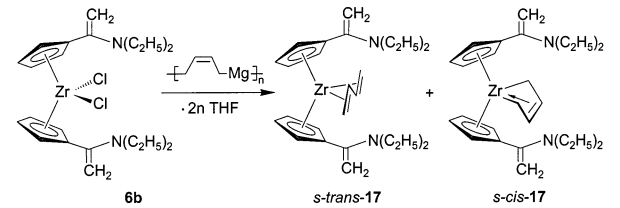


Table 3. Ethene Polymerization with Catalyst Derived from B(C$_6$F$_5$)$_3$ Activation of the Complexes 13, 14, 15, and 17

metallocene complex	equiv activator	*T* (°C)	act.[a]	mp (°C)
13a	1.1	25	314	128
	2.1	25	817	127
	5.1	25	478	127
	1.1	60	22	127
	1.1	10	511	126
	1.1	0	201	126
14	1.1	25	351	128
	2.1	25	573	127
	5.1	25	321	127
	1.1	60	367	129
	1.1	10	33	127
	1.1	0	167	127
15	1.1	25	581	126
	2.1	25	666	127
	5.1	25	478	126
	1.1	60	62	126
	1.1	10	172	126
	1.1	0	11	126
13b	1.1	25		
	5.1	25		
17	1.1	25		
	5.1	25	25	129

[a] Catalyst activities in kg (polymer) mol^{-1} (cat)·h^{-1}·bar^{-1}.

Catalytic Ethene Polymerization. The (crotyl)-zirconocene complexes **13**, **14**, **15**, and **17** were used as precursors for the generation of homogeneous Ziegler−Natta ethene polymerization catalysts. They were all activated by treatment with the strong organometallic Lewis acid B(C$_6$F$_5$)$_3$.[27,28] Between 1.1 and 5.1 molar equiv of the activator component was used.

The polymerization reactions were carried out in toluene at 2 bar ethene pressure, and the solutions contained some triisobutylaluminum as an internal moisture scavanger. The polymerization experiments were carried out at several temperatures in the range between 0 and 60 °C. Typical results are listed in Table 3.

It turns out that both α-metalated C−H activation products **13a** and **14** show reasonable ethene polymerization activities at room temperature. The same holds for the (butadiene)metallocene **15**, which generates an active homogeneous Ziegler−Natta system upon treatment with B(C$_6$F$_5$)$_3$. The polymerization activities of these three systems are similar, as are the qualitative temperature profiles of the polymerization process at these catalysts. The presence of a single amino functionality at the metallocene framework apparantly does not hinder the polymerization features, even if only 1

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Table 4. Ethene Polymerization with the 13a/Tris(pentafluorphenyl)borane Catalyst

no.	m_{cat} (n_{cat})/mg (μmol)	equiv activator	m_{act} (n_{act})/mg (μmol)	T/°C	weight of PE/g	activity *a*	mp/°C
1	13 (36.0)	1.1	20 (39.0)	25	11.29	314	128
2	13 (36.0)	2.1	40 (78.1)	25	29.40	817	127
3	13 (36.0)	5.1	100 (195.0)	25	17.20	478	127
4	13 (36.0)	1.1	20 (39.0)	60	0.79	22	127
5	13 (36.0)	1.1	20 (39.0)	10	18.4	511	126
6	13 (36.0)	1.1	20 (39.0)	0	7.24	201	126

Table 5. Ethene Polymerization with the 14/Tris(pentafluorphenyl)borane Catalyst

no.	m_{cat} (n_{cat})/mg (μmol)	equiv activator	m_{act} (n_{act})/mg (μmol)	T/°C	weight of PE /g	activity *a*	mp/°C
1	13 (37.7)	1.1	21 (41.0)	25	13.24	351	128
2	9 (26.1)	2.1	28 (54.6)	25	14.96	573	127
3	9 (26.1)	5.1	70 (136.7)	25	8.38	321	127
4	9 (26.1)	1.1	15 (29.3)	60	9.58	367	129
5	9 (26.1)	1.1	15 (29.3)	10	0.86	33	127
6	9 (26.1)	1.1	15 (29.3)	0	4.35	167	127

Table 6. Ethene Polymerization with the 15/Tris(pentafluorphenyl)borane Catalyst

no.	m_{cat} (n_{cat})/mg (μmol)	equiv activator	m_{act} (n_{act})/mg (μmol)	T/°C	weight of PE/g	activity *a*	mp/°C
1	13 (34.9)	1.1	20 (39.1)	25	20.29	581	126
2	13 (34.9)	2.1	40 (78.1)	25	23.23	666	127
3	13 (34.9)	5.0	100 (195.3)	25	16.68	478	126
4	13 (34.9)	1.1	20 (39.1)	60	2.15	62	126
5	13 (34.9)	1.1	20 (39.1)	10	6.20	178	126
6	13 (34.9)	1.1	20 (39.1)	0	0.40	11	126

Table 7. Ethene Polymerization with the 13b/Tris(pentafluorphenyl)borane Catalyst

no.	m_{cat} (n_{cat})/mg (μmol)	equiv activator	m_{act} (n_{act})/mg (μmol)	T/°C	weight of PE /g	activity *a*	mp/°C
1	13 (29.2)	1.1	16 (31.3)	25	0		
2	13 (29.2)	5.1	85 (166.0)	25	0		

Table 8. Ethene Polymerization with the 17/Tris(pentafluorphenyl)borane Catalyst

no.	m_{cat} (n_{cat})/mg (μmol)	equiv activator	m_{act} (n_{act})/mg (μmol)	T/°C	weight of PE/g	activity *a*	mp/°C
1	13 (27.7)	1.1	15 (29.3)	25	0		
2	13 (27.7)	5.1	80 (156.3)	25	0.70	25	129

molar equiv of the $B(C_6F_5)_3$ activator component was used (see Table 3). This becomes different when an additional amino group is present at the metallocene framework: the additional donor substituents in the complexes **13b** and **17** apparently are able to block the active zirconocene cation species quite effectively. The **13b**-derived system shows no catalyst activity, and the less basis enamino-substituted system **17** shows only a marginal ethene polymerization activity at high metallocene/activator ratios.

Conclusions

Our study has revealed pronounced differences in the chemical behavior of the 1-diethylaminoethenyl and the 1-dimethylaminoethenyl substituents at the Cp rings of the respective (butadiene)zirconocene frameworks. The latter undergo very rapid C−H activation at the nitrogen-bound methyl groups. Intramolecular H transfer leads to the formation of the cyclometalated complex **14**. In contrast, α-CH activation at the *N*-ethyl groups was not observed so far. The respective functionalized (butadiene)zirconocenes (**15**, **17**) are stable and can easily be isolated and handled at room temperature.

The Lewis acid $B(C_6F_5)_3$ probably adds to the (butadiene)ligands of the systems **15** and **17** to generate active zwitterionic single-component metallocene Ziegler−Natta catalysts.[9,29,30] Treatment of the cyclometalated systems (**13**, **14**) with $B(C_6F_5)_3$ could either remove the σ,π-crotyl ligand or lead to cleavage of the $Zr-CH_2$-[N] bond. Either pathway would eventually lead to an active α-olefin polymerization process. However, it seems that the subsequent alkene insertion process is hindered considerably in the cases of the doubly functionalized systems **13b** and **17**. Amino groups seem to be tolerated in homogeneous Ziegler−Natta chemistry if they can be sterically kept away from the active metallocene cation center. This seems to be the case in the systems **13a/**$B(C_6F_5)_3$ and **14**/$B(C_6F_5)_3$ and even in the betaine systems derived from $B(C_6F_5)_3$ addition to the (butadiene)metallocenes **15**. In contrast, the pendant dialkylamino groups in the **13b**/$B(C_6F_5)_3$ and **17**/$B(C_6F_5)_3$ systems seem to be positioned such as to effectively interact with the in situ generated metal cation center to interfere with the reaction of the added alkene.

Experimental Section

Reactions were carried out under an argon atmosphere using Schlenk-type glassware or in a glovebox. Solvents (including the deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior use. NMR spectra

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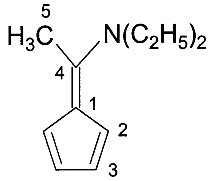
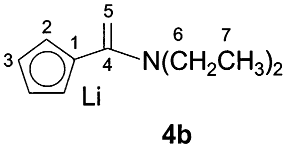
were recorded on a Bruker AC 200 P NMR spectrometer (^{1}H, 200 MHz; ^{13}C, 50 MHz) at 300 K, a Bruker AMX 400 (^{1}H, 100.6 MHz; ^{13}C, 400.1 MHz) at 300 K, or a Varian Unity Plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 150 MHz) at 298 K and lower temperatures. (η^5-Cyclopentadienyl)trichlorozirconium,[14] 6-(dimethylamino)-6-methylfulvene (**2a**),[2,31] [(1-(dimethylamino)-1-methylethyl)cyclopentadienyl]lithium (**3a**),[5,6] [(1-dimethylaminoethenyl)cyclopentadienyl]lithium (**4a**),[6] [η^5-(1-(dimethylamino)-1-methylethyl)cyclopentadienyl](η^5-cyclopentadienyl)dichlorozirconium (**8a**),[6] bis[η^5-(1-(dimethylamino)-1-methyl-ethyl)cyclopentadienyl]dichlorozirconium (**8b**),[6] and (*cis*-2-buten-1,4-diyl)magnesiumbis(tetrahydrofuran) ("(butadiene)-magnesium") [21] were prepared according to literature procedures. Most of the compounds were characterized by additional GCOSY, GHSQC, and GHMBC NMR experiments;[32] for details see the Supporting Information. The assignments in the spectra follow unsystematical numbering schemes (shown in the graphics).

6-Diethylamino-6-methylfulvene (2b). Dimethylsulfate (35.6 mL, 47.2 g, 0.37 mol) was slowly added at 50−60 °C to dimethylformamide (46.5 mL, 43.0 g, 0.37 mol). After heating the reaction mixture for 2 h at 70−80 ° C it was cooled to room temperature. The resulting reaction mixture was added at −10 °C to a stirred solution of sodium cyclopentadienide (40.3 g, 0.54 mol) in 500 mL of THF. After the resulting sodium methyl sulfate was filtered off, the solvent was removed in vacuo and the residue was solved in 300 mL of cyclohexane. The solution was refluxed with charcoal (5 g) and filtered. After removal of the solvent 31.0 g of the yellow product **2b** (0.19 mol, 51%) was obtained. Mp: 44 °C. Anal. Calcd for $C_{11}H_{17}N$ (163.3): C, 80.93; H, 10.50; N, 8.58. Found: C, 80.79; H, 10.92; N, 8.55. IR (KBr): $\tilde{\nu}$ 3094 (w), 3071 (w), 2981 (m), 2933 (m), 2878 (w), 1705 (w), 1663 (w), 1555 (vs), 1472 (m), 1452 (m), 1404 (m), 1380 (m), 1353 (s), 1277 (m), 1195 (w), 1154 (w), 1086 (m), 1073 (m), 1050 (s), 1013 (m), 890 (s), 813 (m), 736 (s), 651 (m). ^{1}H NMR (benzene-d_6): δ 6.87, 6.76, 6.70 (3 m, 4H, 2-H, 2-H′, 3-H, 3-H′), 2.95 (q, 4H, 6-H, $^3J_{HH}$ = 7.0 Hz), 1.98 (s, 3H, 5-H), 0.74 (t, 6H, 7-H, $^3J_{HH}$ = 7.0 Hz). ^{13}C{^{1}H} NMR (benzene-d_6): δ 155.2 (C4), 123.6, 122.0, 120.0, 116.4 (C2, C2′, C3, C3′), 118.3 (C1), 46.1 (C6), 19.8 (C5), 12.9 (C7).



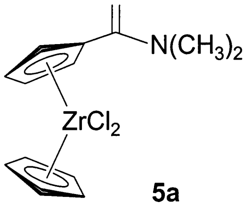
2b

X-ray Crystal Structure Analysis of 2b: formula $C_{11}H_{17}N$, M = 163.26, yellow crystal 0.45 × 0.10 × 0.05 mm, a = 8.783(4) Å, b = 10.845(4) Å, c = 10.935(3) Å, β = 107.46(3)°, V = 993.6(6) Å^3, ρ_{calc} = 1.091 g cm^{-3}, μ = 4.72 cm^{-1}, empirical absorption correction via ψ-scan data (0.816 ≤ T ≤ 0.977), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 2156 reflections collected ($-h$, $+k$, $\pm l$), [(sin θ)/λ] = 0.62 Å^{-1}, 2025 independent (R_{int} = 0.061) and 783 observed reflections [$I \geq 2\,\sigma(I)$], 113 refined parameters, R = 0.056, wR_2 = 0.109, max. residual electron density 0.16 (−0.17) e Å^{-3}, hydrogens calculated and refined as riding atoms.



4b

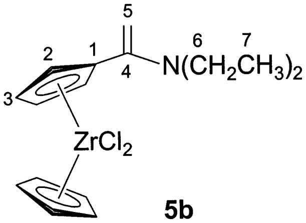
[(1-Diethylaminoethenyl)cylopentadienyl]lithium (4b). Methyllithium (22.0 mL, 32.0 mmol, 1.6 M in diethyl ether) was slowly added at −78 ° C to a stirred solution of 6-diethylamino-6-methylfulvene **2b** (5.00 g, 30.6 mmol) in 150 mL of diethyl ether. The reaction mixture was allowed to warm to room temperature overnight. The resulting solid was collected by filtration and washed with pentane (20 mL) to yield 4.77 g (92%) of the product **4b**. Mp: 120 °C. IR (KBr): $\tilde{\nu}$ 3094 (w), 3074 (w), 2983 (m), 2937 (w), 1557 (vs), 1473 (m), 1454 (m), 1405 (m), 1380 (m), 1357 (s), 1279 (w), 1088 (m), 1052 (s), 1015 (s), 892 (m), 814 (m), 737 (s), 652 (m). ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8, 2:1): δ 6.11 (m, 2H, Cp′), 5.91 (m, 2H, Cp′), 4.15 (d, 1H, 5-H, $^2J_{HH}$ = 1.6 Hz), 3.78 (d, 1H, 5-H′, $^2J_{HH}$ = 1.6 Hz), 3.16 (q, 4H, 6-H, $^3J_{HH}$ = 6.9 Hz), 1.00 (t, 6H, 7-H, $^3J_{HH}$ = 6.9 Hz). ^{13}C{^{1}H} NMR (benzene-d_6/tetrahydrofuran-d_8, 2:1): δ 155.8 (C4), 119.9 (Cp$_{ipso}$), 104.7, 103.6 (Cp′), 82.4 (C5), 43.9 (C6), 12.4 (C7).



5a

[η^5-(1-Dimethylaminoethenyl)cyclopentadienyl](η^5-cyclopentadienyl)dichlorozirconium (5a). A suspension of (η^5-cyclopentadienyl)trichlorozirconium (1.12 g, 4.26 mmol) in 100 mL of diethyl ether was cooled to −60 °C. At this temperature [(1-dimethylaminoethenyl)cyclopentadienyl]lithium (**4a**) (600 mg, 4.75 mmol) in 50 mL of tetrahydrofuran/diethyl ether (1:1) was added to the stirred suspension. After the reaction mixture was warmed to room temperature and stirred for an additional 1 h, the formed LiCl was filtered off. The solvent was removed, and the residue was suspended in pentane. A 1.12 g (73%) amount of the brown product **5a** was obtained by filtration. Mp: 121° C (dec). Anal. Calcd for $C_{14}H_{17}Cl_2NZr$ (361.4): C, 46.53; H, 4.74; N, 3.88. Found: C, 46.75; H, 5.39; N, 3.45. IR (KBr): $\tilde{\nu}$ 3092 (w), 2963 (m), 2855 (w), 2373 (w), 1703 (w), 1634 (m), 1560 (w), 1440 (w), 1363 (m), 1262 (s), 1098 (s), 1020 (vs), 810 (vs). ^{1}H NMR (benzene-d_6): δ 6.39, 6.01 (2m, 4H, Cp′), 6.09 (s, 5H, Cp), 4.70 (d, 1H, 5-H, $^1J_{HH}$ = 1.0 Hz), 4.12 (d, 1H, 5-H′, $^1J_{HH}$ = 1.0 Hz), 2.21 (s, 6H, 6-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 151.2 (C4), 123.3 (Cp′$_{ipso}$), 118.4, 115.6 (Cp′), 117.2 (Cp), 94.7 (C5), 42.0 (C6).

X-ray Crystal Structure Analysis of 5a: formula $C_{14}H_{17}NCl_2Zr$, M = 361.41, yellow crystal 0.50 × 0.08 × 0.03 mm, a = 9.657(1) Å, b = 12.872(1) Å, c = 12.053(1) Å, β = 95.42(1)°, V = 1491.5(2) Å^3, ρ_{calc} = 1.609 g cm^{-3}, μ = 10.77 cm^{-1}, empirical absorption correction via SORTAV (0.615 ≤ T ≤ 0.968), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 8845 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.65 Å^{-1}, 3270 independent (R_{int} = 0.048) and 2554 observed reflections [$I \geq 2\sigma(I)$], 165 refined parameters, R = 0.060, wR_2 = 0.149, max. residual electron density 1.66 (−1.07) e Å^{-3} close to the chlorine atoms, hydrogens calculated and refined as riding atoms.



5b

[η^5-(1-Diethylaminoethenyl)cyclopentadienyl](η^5-cyclopentadienyl)dichlorozirconium (5b). Analogously as

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(31) Meerwein, H.; Florian, W.; Schön, N.; Stopp, G. *Liebigs Ann. Chem.* **1961**, *641*, 1. Hafner, K.; Vöpel, K. H.; Ploss, G.; König, C. *Liebigs Ann. Chem.* **1963**, *661*, 52.

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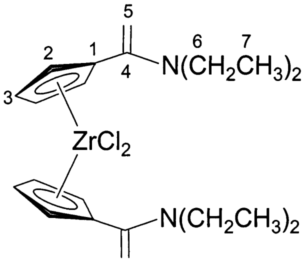
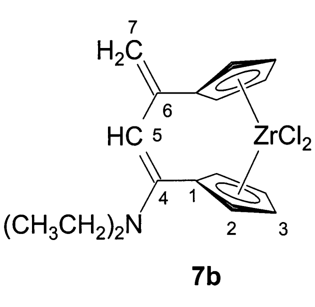
described above, a solution of 1.49 g (8.80 mmol) of (η^5-cyclopentadienyl)trichlorozirconium in 150 mL of diethyl ether was reacted with a suspension of 2.32 g (8.80 mmol) of [(1-dimethylaminoethenyl)cyclopentadienyl]lithium (**4b**) in 50 mL of diethyl ether/tetrahydrofuran (1:1). After workup 2.14 g (63%) of the product **5b** was obtained as a beige-colored solid. Mp: 90 °C. Anal. Calcd for $C_{16}H_{21}Cl_2NZr$ (389.5): C, 49.34; H, 5.43; N, 3.60. Found: C, 48.93; H, 5.37; N, 3.56. IR (KBr): $\tilde{\nu}$ 3079 (w), 2967 (m), 2933 (w), 2364 (m), 1617 (m), 1594 (m), 1551 (vs), 1473 (m), 1380 (m), 1351 (s), 1279 (m), 1262 (m), 1053 (m), 1018 (s), 813 (vs). ^{1}H NMR (benzene-d_6): δ 6.41 (m, 2H, Cp′), 5.99 (m, 2H, Cp′), 6.12 (s, 5H, Cp), 4.87 (ps, 1H, 5-H), 4.17 (ps, 1H, 5-H′), 2.67 (q, 4H, 6-H, $^3J_{HH}$ = 7.0 Hz), 0.80 (t, 6H, 7-H, $^3J_{HH}$ = 7.0 Hz). ^{13}C{^{1}H} NMR (benzene-d_6): δ 146.5 (C4), 122.4 (Cp′$_{ipso}$), 116.9, 114.5 (Cp′), 115.3 (Cp), 95.6 (C5), 42.5 (C6), 11.6 (C7).

X-ray Crystal Structure Analysis of 5b: formula $C_{16}H_{21}NCl_2Zr$, $M = 389.46$, yellow crystal 0.10 × 0.10 × 0.05 mm, $a = 11.387(1)$ Å, $b = 13.210(1)$ Å, $c = 11.802(1)$ Å, $\beta = 107.04(1)°$, $V = 1697.3(2)$ Å^3, $\rho_{calc} = 1.524$ g cm^{-3}, $\mu = 9.53$ cm^{-1}, empirical absorption correction via SORTAV ($0.911 \leq T \leq 0.954$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 11580 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.65$ Å^{-1}, 3899 independent ($R_{int} = 0.056$) and 2759 observed reflections [$I \geq 2\sigma(I)$], 183 refined parameters, $R = 0.046$, $wR_2 = 0.084$, max. residual electron density 0.47 (−0.49) e Å^{-3}, hydrogens calculated and refined as riding atoms.



6b

Bis[η^5-(1-diethylaminoethenyl)cyclopentadienyl]dichlorozirconium (6b). At 0 °C solid zirconiumtetrachloride (1.03 g 4.40 mmol) was added to a suspension of [(1-dimethylaminoethenyl)cyclopentadienyl]lithium (**4b**) (1.49 g, 8.81 mmol) in 100 mL of diethyl ether. The reaction mixture was stirred for an additional 1 h, and the formed LiCl was filtered off. The solvent was removed in vacuo, and the residue was suspended in pentane. The filtration yielded 1.21 g (57%) of the yellow solid product **6b**. Mp: 142° C. Anal. Calcd for $C_{22}H_{32}Cl_2N_2Zr$ (486.6): C, 54.30; H, 6.63; N, 5.76. Found: C, 54.02; H, 7.19; N, 5.91. IR (KBr): $\tilde{\nu}$ 3093 (m), 2971(s), 2932 (m), 2873 (m), 1595 (m), 1552 (vs), 1470 (m), 1452 (m), 1403 (m), 1381 (s), 1352 (vs), 1281 (m), 1073 (m), 1054 (s), 1034 (m), 891 (m), 805 (s), 734 (s), 649 (m). ^{1}H NMR (benzene-d_6): δ 6.69 (m, 4H, Cp′), 6.09 (m, 4H, Cp′), 4.92 (ps, 2H, 5-H), 4.20 (ps, 2H, 5-H), 2.75 (q, 4H, 6-H, $^3J_{HH}$ = 7.1 Hz), 0.86 (t, 6H, 7-H, $^3J_{HH}$ = 7.1 Hz). ^{13}C{^{1}H} NMR (benzene-d_6): δ 146.9 (C4), 122.8 (Cp′$_{ipso}$), 117.8, 115.0 (Cp′), 95.1 (C5), 44.9 (C6), 10.4 (C7).

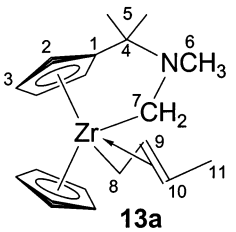


7b

After three weeks at room temperature 50% of **6b** had rearranged to the product **7b**. ^{1}H NMR (benzene-d_6): δ 6.52 (m, 4H, Cp′), 5.83 (m, 4H, Cp′), 5.44 (ps, 1H, 5-H), 4.83 (m, 1H, 7-H), 4.75 (m, 1H, 7-H′), 2.55 (q, 4H, 8-H, $^3J_{HH}$ = 7.1 Hz), 0.71 (t, 6H, 9-H, $^3J_{HH}$ = 7.1 Hz).

X-ray Crystal Structure Analysis of 6b: formula $C_{22}H_{32}N_2Cl_2Zr$, $M = 486.62$, yellow crystal 0.40 × 0.30 × 0.05 mm, $a = 13.987(2)$ Å, $b = 20.351(4)$ Å, $c = 16.981(3)$ Å, $\beta = 103.46(1)°$, $V = 4700.9(14)$ Å^3, $\rho_{calc} = 1.375$ g cm^{-3}, $\mu = 7.04$ cm^{-1}, empirical absorption correction via ψ-scan data ($0.766 \leq T \leq 0.966$), $Z = 8$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 9906 reflections collected ($-h$, $+k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 9511 independent ($R_{int} = 0.058$) and 4275 observed reflections [$I \geq 2\sigma(I)$], 495 refined parameters, $R = 0.051$, $wR_2 = 0.094$, max. residual electron density 0.44 (−0.58) e Å^{-3}, two almost identical molecules in the asymmetric unit, hydrogens calculated and refined as riding atoms.

Data sets were collected with Enraf Nonius CAD4, Nonius MACH3, and KappaCCD diffractometers, the latter two equipped with a rotating anode generator Nonius FR591. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MolEN (K. Fair, Enraf-Nonius B.V., 1990) and Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction for CCD data SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37; Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics DIAMOND (Brandenburg, K. Universität Bonn, 1997).



13a

Reaction of 8a with "(Butadiene)magnesium"; Formation of 13a. A 600 mg (1.59 mmol) sample of **8a** and (butadiene)magnesium (370 mg, 1.66 mmol) were mixed as solids in a 100 mL Schlenk flask. At −40 °C cold toluene (40 mL, −40 °C) was added. After the stirred mixture was warmed to room temperature overnight, the precipitated magnesium chloride was filtered off. The solvent was removed in vacuo from the organic filtrate, and the product was obtained as a brown oil. Yield of **13a**: 498 mg (87%). Anal. Calcd for $C_{19}H_{27}NZr$ (360.7): C, 63.28; H, 7.55; N, 3.88. Found: C, 62.19; H, 7.42; N, 3.75. IR (NaCl): $\tilde{\nu}$ 3090 (w), 2967 (vs), 2932 (s), 2819 (m), 2777 (m), 2654 (vw), 1576 (vw), 1443 (s), 1372 (m), 1355 (m), 1283 (m), 1075 (m), 1017 (s), 969 (m), 799 (vs), 696 (m) cm^{-1}. ^{1}H NMR (toluene-d_8, 246 K): δ 5.36 (m, 1H, Cp′), 5.14 (m, 1H, Cp′), 4.99 (s, 5H, Cp), 4.86 (m, 1H, Cp′), 4.43 (dt, 1H, 9-H, $^3J_{HH,\ trans}$ = 16.0 Hz, $^3J_{HH}$ = 10.5 Hz), 4.36 (ps, 1H, Cp′), 3.26 (dq, 1H, 10-H, $^3J_{HHtrans}$ = 16.0 Hz, $^3J_{HH}$ = 6.0 Hz), 2.44 (d, $^2J_{HH}$ = 10.8 Hz, 1H, 7-H), 2.36 (s, 3H, 6-H), 1.95 (d, 1H, 7-H′, $^2J_{HH}$ = 10.8 Hz), 1.67 (dd, 1H, 8-H, $^2J_{HH}$ = 4.0 Hz, $^3J_{HH}$ = 10.5 Hz), 1.64 (d, 3H, 11-H, $^3J_{HH}$ = 6.0 Hz), 1.49 (dd, 1H, 8-H′, $^2J_{HH}$ = 4.0 Hz, $^3J_{HH}$ = 10.5 Hz), 1.18 (s, 3H, 5-H), 1.14 (s, 3H, 5′-H). ^{13}C NMR (toluene-d_8, 246 K): δ 144.7 (Cp′$_{ipso}$), 121.1 (C9, $^1J_{CH}$ = 146 Hz), 108.1 (Cp′, $^1J_{CH}$ = 174 Hz), 104.9 (Cp, $^1J_{CH}$ = 173 Hz), 101.2 (Cp′, $^1J_{CH}$ = 172 Hz), 97.9 (Cp′, $^1J_{CH}$ = 173 Hz), 97.4 (Cp′, $^1J_{CH}$ = 173 Hz), 92.5 (C10, $^1J_{CH}$ =

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(32) Braun, S.; Kalinowski, H.-O.; Berger, S. in *150 and More Basic NMR Experiments*, VCH: Weinheim, **1998** and references therein.

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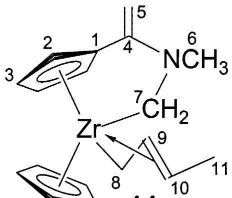
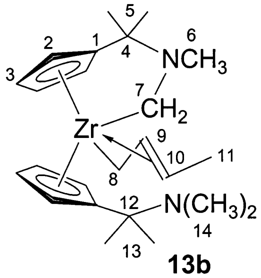
148 Hz), 62.8 (C7, $^1J_{CH} = 120$ Hz, $^1J_{CH} = 129$ Hz), 55.9 (C4), 46.6 (C6, $^1J_{CH} = 132$ Hz), 38.3 ($^1J_{CH} = 151$ Hz, C8, $^1J_{CH} = 150$ Hz), 26.7 (C5′, $^1J_{CH} = 126$ Hz), 18.0 (C5, $^1J_{CH} = 127$ Hz), 17.9 (C11, $^1J_{CH} = 130$ Hz).



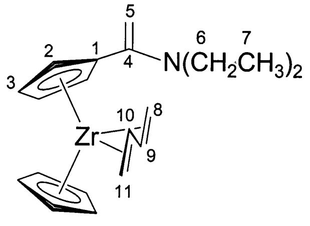
14

Reaction of 5a with "(Butadiene)magnesium"; Formation of 14. Analogously as described above, 700 mg (2.03 mmol) of **5a** was reacted with 460 mg (2.06 mmol) of (butadiene)magnesium in 40 mL of toluene to yield 496 mg (71%) of **14** as a brown oil. Anal. Calcd for $C_{18}H_{23}NZr$ (344.6): C, 62.74; H, 6.73; N, 4.06. Found: C, 62.60; H, 7.48; N, 3.56. IR (NaCl): $\tilde{\nu}$ 2965 (m), 2382 (m), 1699 (w), 1652 (m), 1635 (w), 1559 (s), 1457 (m), 1262 (s), 1102 (w), 1019 (s), 806 (vs), 730 (m) cm^{-1}. ^{1}H NMR (toluene-d_8): δ 5.31 (m, 1H, Cp′), 5.21 (m, 1H, Cp′), 4.99 (m, 1H, Cp′), 4.95 (s, 5H, Cp), 4.43 (m, 1H, Cp′), 4.39 (dt, 1H, 9-H, $^3J_{HH,trans} = 16.2$ Hz, $^3J_{HH} = 10.3$ Hz), 3.88 (s, 1H, 5-H), 3.27 (s, 1H, 5-H′), 3.12 (m, 1H, 10-H, $^3J_{HH,trans} = 16.2$ Hz, $^3J_{HH} = 5.8$ Hz), 2.73 (s, 3H, 6-H), 2.62 (d, 1H, 7-H, $^2J_{HH} = 9.6$ Hz), 2.12 (d, 1H, 7-H′, $^2J_{HH} = 9.6$ Hz), 1.72 (dt, 1H, 8-H, $^2J_{HH} = 4.2$ Hz, $^3J_{HH} = 10.3$ Hz), 1.48 (d, 1H, 11-H, $^3J_{HH} = 5.8$ Hz), 1.41 (dt, 1H, 8-H′, $^2J_{HH} = 4.2$ Hz, $^3J_{HH} = 10.3$ Hz). ^{13}C NMR (toluene-d_8): δ 152.1 (C4), 133.7 (Cp′$_{ipso}$), 120.8 (C9, $^1J_{CH} = 158$ Hz), 106.8 (Cp′, $^1J_{CH} = 173$ Hz), 105.2 (Cp, $^1J_{CH} = 170$ Hz), 104.9 (Cp′, $^1J_{CH} = 176$ Hz), 100.9 (Cp′, $^1J_{CH} = 170$ Hz), 100.0 (Cp′, $^1J_{CH} = 173$ Hz), 93.5 (C10, $^1J_{CH} = 153$ Hz), 79.6 (C5, $^1J_{CH} = 161$ Hz, $^1J_{CH} = 157$ Hz), 61.7 (C7, $^1J_{CH} = 128$ Hz, $^1J_{CH} = 130$ Hz), 45.3 (C6, $^1J_{CH} = 133$ Hz), 39.4 (C8, $^1J_{CH} = 154$ Hz, $^1J_{CH} = 147$ Hz), 17.8 (C11, $^1J_{CH} = 128$ Hz).

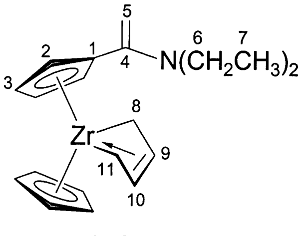


13b

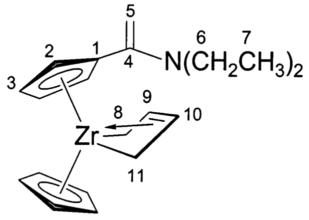
Reaction of 8b with "(Butadiene)magnesium"; Formation of 13b. Analogously as described above, 110 mg (0.24 mmol) of **8b** was reacted with 60 mg (0.27 mmol) (butadiene)-magnesium in 20 mL of toluene to yield 76.0 mg (69%) of **13b** as a brown oil. Anal. Calcd for $C_{24}H_{38}N_2Zr$ (445.8): C, 64.66; H, 8.59; N, 6.28. Found: C, 64.51; H, 7.86; N, 6.28. IR (NaCl): $\tilde{v}$ 2972 (s), 2935 (s), 2863 (m), 2819 (m), 2777 (m), 1604 (vw), 1495 (m), 1460 (w), 1375 (m), 1357 (m), 1259 (m), 1159 (m), 1133 (m), 1079 (m), 1046 (s), 969 (w), 855 (w), 801 (vs), 731 (s), 695 (m) cm^{-1}. ^{1}H NMR (toluene-d_8, 233K): δ 5.35 (m, 1H, Cp′), 5.26 (m, 2H, Cp′), 5.21 (m, 1H, Cp′), 5.15 (m, 1H, Cp′), 4.97 (m, 1H, Cp′), 4.66 (m, 1H, Cp′), 4.48 (m, 1H, Cp′), 4.48 (dd, 1H, 9-H, $^3J_{HH} = 16.2$ Hz, $^3J_{HH} = 10.8$ Hz), 3.54 (m, 1H, 10-H, $^3J_{HH} = 6.5$ Hz, $^3J_{HH} = 16.2$ Hz), 2.42 (d, 1H, 7-H, $^2J_{HH} = 10.8$ Hz), 2.35 (s, 3H, 6-H), 1.94 (d, 1H, 7-H′, $^2J_{HH} = 10.8$ Hz), 1.92 (s, 6H, 14-H), 1.70 (d, 1H, 11-H, $^3J_{HH} = 6.5$ Hz), 1.62, 1.44 (2dd, each 1H, 8-H and 8-H′, $^3J_{HH} = 10.8$ Hz, $^2J_{HH} = 5.0$ Hz), 1.24 (s, 3H, 13-H), 1.21 (s, 3H, 13′-H), 1.20 (s, 3H, 5-H), 1.14 (s, 3H, 5-H′). ^{13}C{^{1}H} NMR (toluene-d_8, 233 K): δ 142.6 (Cp′$_{ipso}$), 123.6 (Cp′$_{ipso}$), 120.2 (C9), 109.3 (Cp′), 107.7 (Cp′), 105.5 (Cp′), 103.9 (Cp′), 103.7 (Cp′), 101.8 (Cp′), 100.2 (C10), 99.2 (Cp′), 88.1 (Cp′), 64.9 (C7), 56.4 (C12), 55.8 (C4), 46.2 (C6), 39.1 (C14), 37.2 (C8), 27.5 (C13), 26.0 (C5′), 23.4 (C13′), 18.6 (C5), 17.95 (C11).



s-trans-**15**



s-cis-**15a**



s-cis-**15b**

(Butadiene)[η^5-(1-diethylaminoethenyl)cyclopentadienyl](η^5-cylopentadienyl)zirconium, 15. Analogously as described above, 400 mg (1.03 mmol) of **5b** was reacted with 320 mg (1.44 mmol) of (butadiene)magnesium in 40 mL of toluene to yield 350 mg (90%) of **15** as a red-brown oil. The product was isolated as a mixture of three isomers (*s-trans*-**15**: *s-cis*-**15A**: *s-cis*-**15B** = 7:8:5, no absolute assignment of *s-cis*-**15A/B** was achieved). Anal. Calcd for $C_{20}H_{27}NZr$ (372.7): C, 64.46; H, 7.30; N, 3.76. Found: C, 62.80; H, 8.08; N, 3.56. IR (NaCl): $\tilde{\nu}$ 3087 (w), 2966 (s), 2928 (m), 2870 (m), 1699 (vw), 1598 (m), 1553 (m), 1495 (w), 1447 (m), 1378 (m), 1282 (m), 1261 (s), 1093 (s), 1019 (vs), 800 (vs), 731 (m) cm-^{1}. ^{1}H NMR (toluene-d_8, 233 K): *s-trans*-**15**: δ 5.48 (m, 1H, Cp′), 5.24 (m, 1H, Cp′), 5.10 (m, 1H, Cp′), 4.92 (s, 5H, Cp), 4.80 (s, 1H, 5-H), 4.18 (s, 1H, 5-H′), 3.72 (m, 1H, Cp′), 3.28, 3.23 (2m, 2H, 8-H,-11-H), 3.10, 2.85 (2m, 2H, 9-H, 10-H), 2.81 (m, 4H, 6-H), 1.36, 1.13 (2m, 2H, 8-H′, 11-H′), 0.86 (m, 6H, 7-H); *s-cis*-**15A/B**: δ 5.86 (m, 2H, Cp′), 5.50 (s, 5H, Cp$_A$), 5.05 (m, 4H, Cp′), 5.04 (s, 1H, 5-H$_A$), 4.97 (s, 5H, Cp$_B$), 4.95 (s, 1H, 5-H$_B$), 4.83 (m, 2H, 9-H$_A$, 10-H$_A$), 4.80 (m, 2H, Cp′), 4.73 (m, 2H, 9-H$_B$, 10-H$_B$), 4.28 (s, 1H, 5-H′$_A$), 4.27 (s, 1H, 5-H′$_B$), 3.37 (m, 4H, 8-H$_{A, B}$, 11-H$_{A, B}$), 2.81 (m, 8H, 6-H), 0.86 (m, 12H, 7-H), −0.51 (m, 2H, 8-H′$_B$, 11-H′$_B$), −0.67 (m, 2H, 11-H′$_A$, 8-H′$_A$). ^{13}C{^{1}H} NMR (toluene-d_8, 233 K): *s-trans*-**15**: δ 149.5 (C4), 115.4 (Cp′$_{ipso}$), 106.4 (Cp′), 101.2 (Cp), 99.5 (Cp′), 98.4 (Cp′), 97.6, 97.3 (C9, C10), 97.0 (Cp′), 94.2 (C5), 61.9, 60.4 (C8, C11), 43.8 (C6), 11.5 (C7); *s-cis*-**15A/B**: δ 150.6 (C4$_B$), 150.0 (C4$_A$), 120.7 (Cp′$_{ipso, A}$), 116.5 (Cp′$_{ipso, B}$), 112.6 (C9$_A$, C10$_A$), 112.4 (C9$_B$, C10$_B$), 108.3 (Cp′), 105.2 (Cp$_A$), 101.84 (Cp$_B$), 101.7 (Cp′), 100.0 (Cp′), 99.8 (Cp′), 95.1

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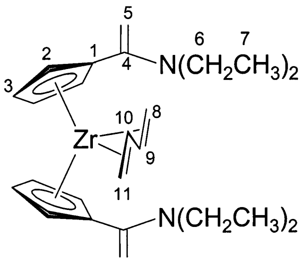
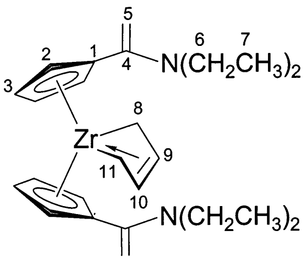
($C5_A$), 93.8 ($C5_B$), 51.8 ($C8_B$, $C11_B$), 51.8 ($C8_A$, $C11_A$), 43.8 (C6), 11.5 (C7).



s-trans-**17**



s-cis-**17**

(Butadiene)bis[η^5-(1-diethylaminoethenyl)cyclopentadienyl]zirconium, 17. Analogously as described above, 803 mg (1.65 mmol) of **6b** was reacted with 367 mg (1.65 mmol) of (butadiene)magnesium in 40 mL of toluene to yield 690 mg (89%) of **17** as a brown oil. The product was isolated as a mixture of two isomers (*s-trans*-**17**: *s-cis*-**15** = 2:5). Anal. Calcd for $C_{26}H_{38}N_2Zr$ (469.8): C, 66.47; H, 8.15; N, 5.96. Found: C, 66.60; H, 8.04; N, 5.45. IR (NaCl): $\tilde{\nu}$ 3086 (m), 3061 (m), 3027 (s), 2951 (m), 2921 (m), 2870 (m), 1942 (vw), 1858 (vw), 1604 (m), 1495 (s), 1460 (m), 1379 (w), 1258 (s), 1081 (s), 1030 (s), 801 (s), 729 (vs), 694 (s) cm^{-1}. ^1H NMR (toluene-d_8, 213 K): *s-trans*-**17**: δ 5.91, 5.34 (2m, 4H, Cp′), 5.13 (s, 2H, 5-H), 5.05 (m, 2H, Cp′), 4.34 (s, 2H, 5-H′), 3.61 (m, 2H, Cp′), 3.32 (m, 2H, 8-H, 11-H), 3.20 (m, 2H, 9-H, 10-H), 2.81, 2.99 (2m, 8H, 6-H, 6′-H), 1.31 (m, 2H, 8-H′, 11-H′), 0.97, 0.94 (2m, 12H, 7-H, 7′-H). *s-cis*-**17** : δ 6.22, 5.27 (2m, 4H, Cp′), 5.05 (s, 1H, 5-H), 4.91 (m, 2H, Cp′), 4.82 (m, 2H, 9-H, 10-H), 4.77 (s, 1H, 5-H), 4.75 (m, 2H, Cp′), 4.33 (s, 1H, 5-H′), 4.22 (s, 1H, 5-H′), 3.38 (m, 2H, 8-H, 11-H), 2.95, 2.80 (2m, 8H, 6-H, 6′-H), 0.94, 0.93 (m, 12H, 7-H, 7′-H), −0.46 (m, 2H, 8-H′, 11-H′). $^{13}C\{^1H\}$ NMR (toluene-d_8, 213 K): *s-trans*-**17**: δ 150.0 (C4), 124.9 (Cp'_{ipso}), 106.7 (Cp′), 101.5 (Cp′), 99.7 (Cp′), 99.6 (Cp′), 98.6 (C9, C10), 94.0 (C5), 62.5 (C8, C11), 43.4, 43.3 (C6, C6′), 11.7, 11.6 (C7, C7′). *s-cis*-**17**: δ 150.8 (C4), 149.4 (C4), 116.1 (Cp'_{ipso}), 116.0 (Cp'_{ipso}), 112.6 (C9, C10), 110.9 (Cp′), 102.4 (Cp′), 101.0 (Cp‘), 99.0 (Cp′), 93.1 (C5), 92.4 (C5), 49.2 (C8, C11), 43.2, 43.1 (C6, C6′), 11.8, 11.7 (C7, C7′).

Polymerization Reactions. All polymerizations were carried out in an 1 L glass autoclave charged with 150 mL of toluene and 0.5 mL of triisobutylaluminum. At the respective temperature the stirred (800 U/min) mixture was saturated for 30 min with ethene at a pressure of 2 bar. The catalyst precursor was activated with the according amount of tris(pentafluorphenyl)borane dissolved in toluene and injected into the autoclave. The polymerization reactions were carried out for 30 min under a constant pressure of 2 bar of ethene. The reaction mixture was hydrolyzed with a 1:1 mixture of methanol and 2 N HCl (20 mL), and water (100 mL) was added. The polyethylene was filtered off and dried in vacuo. The catalyst activity was calculated in units of *m*(kg polymer)/[*n*(mol cat.) *t*(h) *p* (bar ethene)].

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Supporting Information Available: Additional spectroscopic data and details of the X-ray crystal structure analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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