Synthesis and Dynamic Features of (Chloro)zirconocene Cations Stabilised by Pendant (Diarylphosphanyl)alkyl and (Dimethylamino)alkyl Substituents at Their Cyclopentadienyl Ring Systems

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Treatment of the substituted (diarylphosphanyl)methyl group-4 metallocene complexes $[(C_5H_4–CR^1R^2–PAr_2)_2ZrCl_2]$ (**2**: R^1/R^2 = CH_3/CH_3, H/CH_3, H/aryl) with $Li[B(C_6F_5)_4]$ in dichloromethane solution results in chloride ligand abstraction (with LiCl precipitation) to yield the complexes $[(C_5H_4–CR^1R^2–PAr_2)_2Zr–Cl^+]$ (**5**), with both phosphanyl groups internally coordinated to the metal centre. Three possible diastereoisomers are observed in the case of **5c** (R^1 = H; R^2 = CH_3), while bulkier R^2 substituents give higher selectivities. The thermally induced (reversible) cleavage of the Zr–phosphane linkage results in dynamic NMR behaviour. Gibbs activation energies of $\Delta G^{\neq}$(298 K) = 14.8 ± 0.5 and 14.5 ± 0.5 kcal/mol were obtained for these intramolecular equilibration processes in the complexes *trans*-**5d** (R^1 = H; R^2 = Ph) and *trans*-**5e** (R^1 = H; R^2 = ferrocenyl), respectively. Treatment of the substituted (dimethylamino)methyl metallocene complexes $[(C_5H_4–CR^1R^2–NMe_2)_2ZrCl_2]$ (**6a**, **6b**) with $Li[B(C_6F_5)_4]$ proceeds analogously to yield the cation systems $[\{C_5H_4–C(CH_3)_2–NMe_2\}_2ZrCl^+]$ (**12a**) and $[\{C_5H_4–CH(CH_3)–NMe_2\}_2ZrCl^+]$ (**12b**, three possible diastereoisomers). Both complexes have their pairs of amino groups coordinated to the metal centre. The complexes exhibit dynamic NMR spectra. Selective equilibration of the diastereotopic $N(CH_3)^A(CH_3)^B$ resonances of complex **12a** is observed [$\Delta G^{\neq}$(233 K) = 11.5 ± 0.2 kcal/mol], whereas the adjacent $C(CH_3)^A(CH_3)^B$ methyl groups remain diastereotopic. The dynamic equilibration of the latter was observed at a markedly higher temperature [$\Delta G^{\neq}$(333 K) = 17.3 ± 0.2 kcal/mol]. Treatment of $[\{C_5H_4–C(CH_3)_2–NMe_2\}CpZrCl_2]$ (**10**) with $Li[B(C_6F_5)_4]$ resulted in the formation of complex $[\{C_5H_4–C(CH_3)_2–NMe_2\}CpZr–Cl^+]$ (**11**), which shows the internal $–N(CH_3)^A(CH)^B$ equilibration proceeding with a markedly higher activation barrier [$\Delta G^{\neq}$(333 K) = 17.6 ± 0.2 kcal/mol] than in **12a**, and a stereochemical memory effect indicative of solvent coordination to the metal centre of the resulting highly electrophilic chlorozirconocene cation intermediate. Complex **11** was characterised by an X-ray crystal structure analysis, which shows the internal Zr←amine coordination.

Introduction

Alkylzirconocene cations are regarded as the active species in homogeneous Ziegler−Natta olefin polymerisation.[1a−1e] Some of such complexes can very easily be prepared, a typical example being the parent compound $[Cp_2ZrCH_3^+]$ (**1**), readily available from the neutral precursor $[Cp_2Zr(CH_3)_2]$ by a variety of methods.[2a,2b,3−5] The cation **1** is stabilised by tight ion pair formation with its anion.[6] Alternatively, it adds a variety of simple neutral donor ligands such as tetrahydrofuran to form pseudotetrahedral adducts (e.g., $[Cp_2ZrCH_3(THF)^+]$ or its respective "outer-sphere" or "solvent-separated" ion pair).[7,8] $[^RCp_2ZrCl^+]$ complexes are much less stable. Their syntheses are often less straightforward and they require stronger donor ligand stabilisation. A typical example is shown in Scheme 1. Treatment of the (diarylphosphanyl)alkyl-substituted $[^RCp_2Zr(CH_3)_2]$ derivatives with $B(C_6F_5)_3$ as a suitable methyl anion abstractor[9,10] results in the clean formation of the corresponding $[^RCp_2ZrCH_3^+]$ cation (**3**).[11] Treatment of this in turn with a second equivalent of $B(C_6F_5)_3$ in the presence of a chloride source then gives rise to subsequent formation of the doubly internally phosphane-stabilised $[^RCp_2ZrCl^+]$ cation derivative **5** (via **4**, see Scheme 1).[11,12]

It would be interesting to have the corresponding (dimethylamino)alkyl-substituted Cp systems available in order to study the stabilising influence of the tertiary amine donor ligands relative to the stabilising phosphanes. However, their synthesis from **6** by an analogous pathway is precluded by a preferred internal C−H activation process that rapidly takes place at the stage of the intermediate **8** (see Scheme 2).[13−16] We therefore had to devise an alternative pathway to make the (dimethylamino)alkyl−Cp-containing

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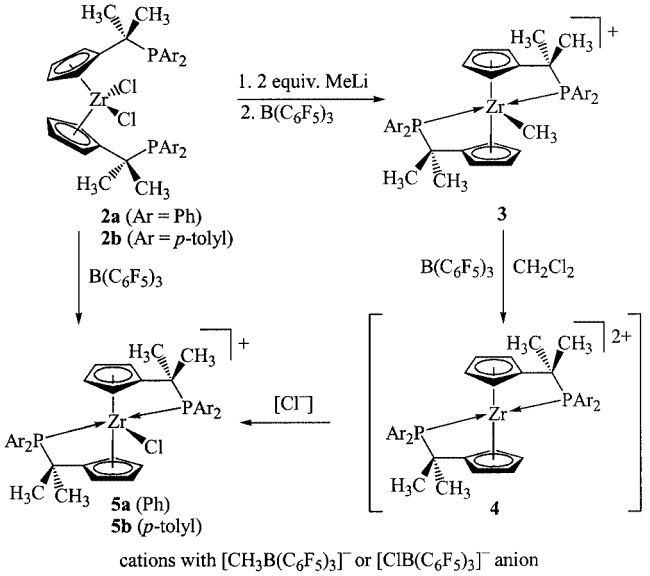
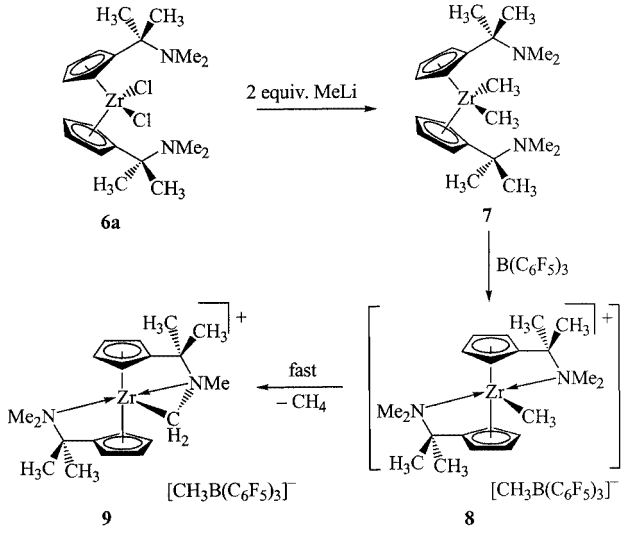


Scheme 1

[$^{R}Cp_2Zr-Cl^+$] cation systems synthetically available. Such a selective preparative route is described in this paper. The dynamic NMR behaviour of the resulting complexes allowed for an estimate of the internal stabilisation of such strongly electrophilic group-4 metallocene cations by tertiary amine donor ligands.

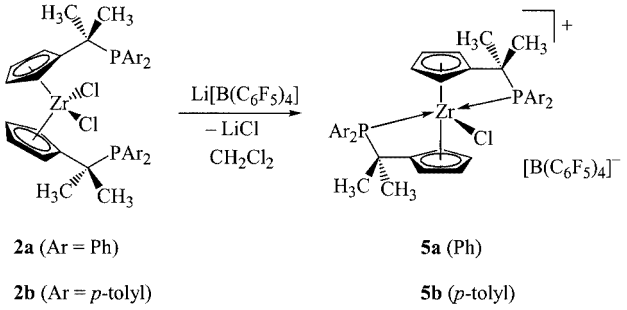


Scheme 2

Results and Discussion

Synthesis and Characterisation of [Chlorobis{[(diarylphosphanyl)alkyl]cyclopentadienyl}zirconium] Cation Complexes

We had previously prepared a series of [{(Ar_2PCMe_2)C_5H_4}$_2$$ZrCl^+$] cation systems by a three-step synthesis via the dication intermediate **4**, as outlined in Scheme 1 [**5a**′: Ar = Ph; **5b**′: Ar = *p*-tolyl, with [$CH_3B(C_6F_5)_3^-$] anion; **5a**′′: Ar = Ph, with [$ClB(C_6F_5)_3^-$] anion].[11] In one case (**5a**′′) we succeeded in preparing the substituted chlorozirconocene cation directly by means of chloride abstraction by the strong organometallic Lewis acid $B(C_6F_5)_3$.[11,12] This result indicated to us that chloride abstraction by more powerful reagents, such as $Li[B(C_6F_5)_4]$,[17,18] might provide a suitable direct route to this general class of internally donor ligand stabilised chlorozirconocene cation systems. Initial tests were therefore carried out with the substituted [{[(diarylphosphanyl)methyl]C_5H_4}$_2$$ZrCl_2$] systems **2a** (Ar = Ph) and **2b** (Ar = *p*-tolyl), which were each treated with 1 mol-equiv. of the $Li[B(C_6F_5)_4]$ reagent in dichloromethane solution at room temperature. After ca. 1 h, the chloride abstraction was complete. The resulting LiCl precipitate was removed by filtration and the corresponding chlorometallocene cation products **5a** and **5b** were isolated in 55 and 67% yields, respectively (both with [$B(C_6F_5)_4^-$] anion, see Scheme 3).

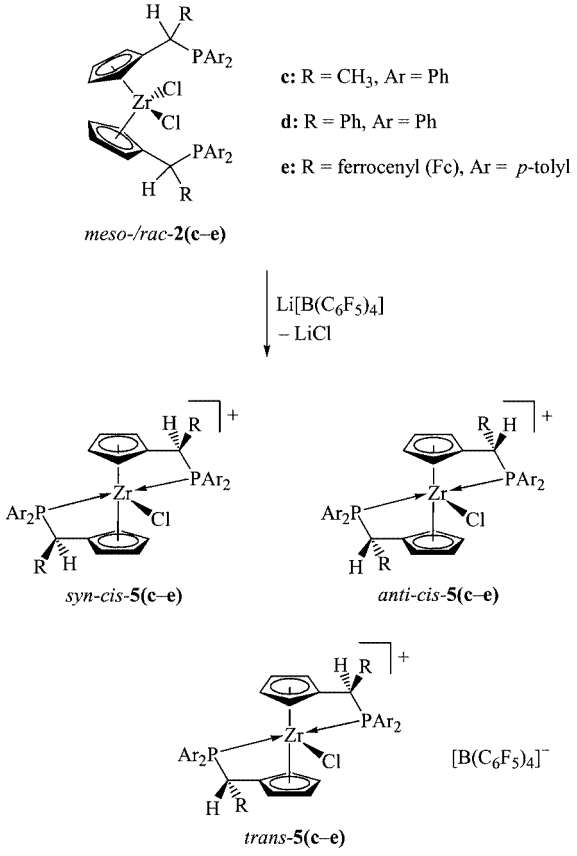


Scheme 3

We have also used the previously described complexes [($C_5H_4-CHR-PAr_2$)$_2$$ZrCl_2$] **2c** (R = CH_3; Ar = Ph), **2d** (R = Ph; Ar = Ph) and **2e** (R = ferrocenyl; Ar = *p*-tolyl)[11,12,30] as neutral substrates for the chloride abstraction reaction with $Li[B(C_6F_5)_3]$ to give the new metallocene cation complexes **5c**−**e** (see Scheme 4).

The complexes **2c**−**e** each contain two stereogenic carbon centres and were each employed in the Cl^- abstraction reaction as ca. 1:1 *meso*-/*rac*-**2(c−e)** mixtures of diastereoisomers. The doubly phosphorus-coordinated products **5c**−**e** can each form three diastereoisomers: two complexes in which the substituents at the pair of stereogenic metallacyclic ring carbon centres are oriented *cis* (*syn*- or *anti*-oriented relative to the Zr−Cl vector,[19] thus giving rise to the formation of compounds *syn-cis*-**5c**−**e** and *anti-cis*-**5c**−**e**, respectively), together with the *trans* diastereoisomers (*trans*-**5c**−**e**) (see Scheme 4).

In the case of **5c** (R = CH_3; Ar = Ph) a near to statistical mixture of the three diastereoisomers was actually obtained (isolated in 54% yield). This is evident from inspection of typical NMR spectra of the organometallic salt **5c**. The ^{31}P NMR spectrum (at 253 K) shows singlets at δ = −36.2 and −45.9 ppm corresponding to the pairs of symmetry-equivalent phosphorus nuclei of the complexes *syn-cis*-**5c** and *anti-cis*-**5c** (no absolute assignment was achieved) and an AB pattern at δ = −38.1 ppm and δ = −47.2 ppm with a $^2J_{P,P}$



Scheme 4

coupling constant of 110 Hz, attributable to the *trans*-**5c** diastereoisomer (see Figure 1).

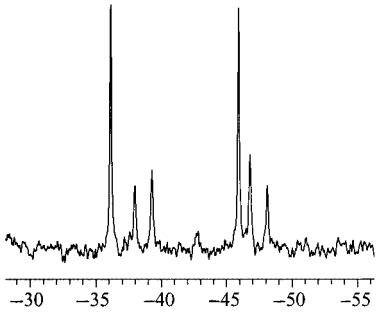
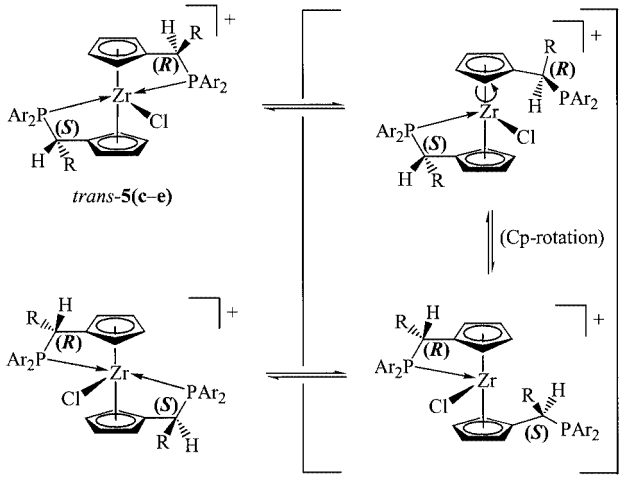


Figure 1. $^{31}P\{^{1}H\}$ NMR spectrum of the close to statistical mixture of the *syn-cis*-**5c**, *anti-cis*-**5c** and *trans*-**5c** diastereomers (in CD_2Cl_2 solution)

As would be expected, each *cis*-**5c** isomer exhibits a set of four methine $^{1}H/^{13}C$ NMR signals of the pair of symmetry-equivalent C_5H_4 ligand units. In contrast, the (C_5H_4−CHMe−[P]) ligands of the *trans*-**5c** isomer are diastereotopic. Consequently, complex *trans*-**5c** shows a set of eight Cp signals of equal intensity (for numerical values see the Exp. Sect.), a pair of C_α−*H* multiplets (δ = 4.21 and 4.47 ppm), each of 1 H relative intensity, and two methyl ^{1}H NMR resonances at δ = 1.25 and 1.50 ppm.

Treatment of complex [(C_5H_4−CHPh−PPh_2)$_2ZrCl_2$] (**2d**) with the Li[$B(C_6F_5)_4$] reagent cleanly resulted in the formation of the chlorozirconocene cation complex **5d**. Again, diastereomeric complexes are formed, but the ^{31}P NMR spectrum of **5d** shows the presence only of the *trans*-**5d** isomer (AB system at δ = −18.4 and −41.8 ppm, $^{2}J_{P,P}$ = 108 Hz) and of *one* of the *cis*-**5d** isomers, in a ca. 1:1 ratio.

Complex *trans*-**5d** shows two ^{1}H NMR Cp−C*H*R signals at δ = 5.65 and 5.57 ppm. An increase in the temperature results in coalescence of the signals of pairwise diastereotopic groups of *trans*-**5d**, including these Cp−C*H*R resonances with a Gibbs activation energy of $\Delta G^{\neq}$(298 K) = 14.8 ± 0.5 kcal/mol.[11,20,21] The NMR signals of the *cis*-**5d** isomers remain unaffected by the dynamic behaviour of *trans*-**5d**. We therefore assign a process as depicted in Scheme 5 to account for this characteristic behaviour, in which a consecutive dissociation of *both* Zr←P linkages takes place in *trans*-**5d**, followed by rotation around the Zr−Cp vector and reformation of the stabilising intramolecular Zr←phosphane interactions.



Scheme 5

Complex **5c** shows similar dynamic NMR features at elevated temperatures. We have found indications for an intramolecular equilibration process of *trans*-**5c**, analogous to that described above for **5d**, *and* a separate equilibration between the two *cis*-**5c** isomers. Unfortunately, the coalescence temperatures could not be reached cleanly in this case because of a rapid thermal decomposition of the systems.

Complex **5e** was obtained as a similar mixture of a single *cis*-**5e** diastereomer and the *trans*-**5e** diastereomer. Complex *trans*-**5e** exhibits a total of eight C_5H_4 resonances [at δ = 7.18, 6.92, 6.17, 6.06 ppm (ring A), and δ = 6.65, 6.06, 6.00, 5.94 ppm (ring B)] and a pair of CpC*H*R ^{1}H NMR resonances at δ = 5.06 and 5.12 ppm. From the coalescence of these last two signals at T_c = 298 K, a Gibbs activation energy of $\Delta G^{\neq}(T_c)$ = 14.5 ± 0.5 kcal/mol was obtained. Again, the *cis*-**5e** isomer is not involved in this dynamic process. It shows a single ^{31}P NMR resonance (δ = −18.2

ppm) and four C_5H_4−R ^{1}H NMR multiplets at δ = 7.15, 6.42, 6.35, and 6.22 ppm.

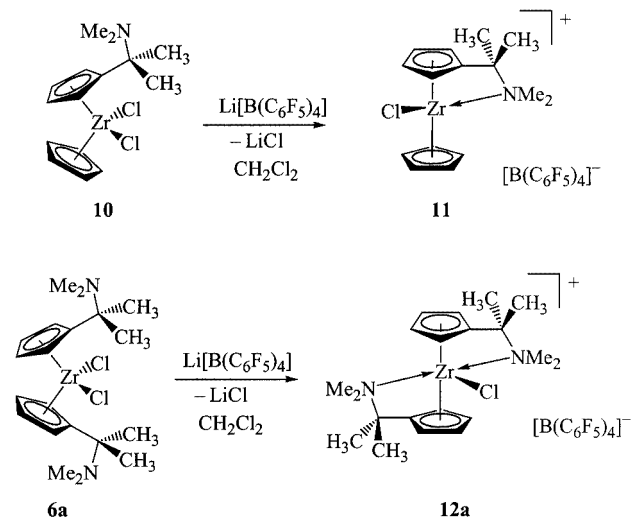
Synthesis and Characterisation of [Chlorobis{[(dimethylamino)alkyl]cyclopentadienyl}zirconocene] Cation Complexes

The starting materials for the preparation of the related [(dimethylamino)alkyl−C_5H_4]zirconium complexes (**6a**,**b** and **10**) were also prepared by a fulvene route,[22] as described previously by us.[14−16] The synthesis started from 6-(dimethylamino)-6-methylfulvene.[23] Hydride addition gave the Li[C_5H_4−CHMe−NMe_2] reagent,[24] which was then transmetallated with zirconium to yield a *meso*/*rac* mixture of [$(C_5H_4$−CHMe−$NMe_2)_2ZrCl_2$] (**6b**). Methyllithium addition to 6-(dimethylamino)-6-methylfulvene[25] gave Li[C_5H_4−CMe_2−NMe_2]. Transmetallation by treatment with [$ZrCl_4(THF)_2$] [26] furnished [$(C_5H_4$−CMe_2−$NMe_2)_2ZrCl_2$] (**6a**), whereas treatment with $CpZrCl_3$ [27] gave [$(C_5H_4$−CMe_2−$NMe_2)CpZrCl_2$] (**10**).

Complex **10** was treated with 1 mol-equiv. of Li[$B(C_6F_5)_4$] in dichloromethane to yield the cation complex **11** (> 70% isolated) (see Scheme 6). Single crystals of **11** suitable for an X-ray crystal structure analysis were obtained when liquid pentane was allowed to diffuse slowly into a CH_2Cl_2 solution of the organometallic salt. Cations and anions of **11** are independent in the solid state. The zirconium atom in **11** is pseudotetrahedrally coordinated by two η^5-cyclopentadienyl rings, the chloride ligand and the nitrogen atom of the pendant −CMe_2−NMe_2 group attached to one of the C_5H_4 ligands (Figure 2). The resulting N−Zr−Cl angle is fairly large at 106.0(1)°, whereas the Zr−N bond length is short at 2.369(3) Å [the respective Zr−N(Me_2) distance in **9**, for example (see Scheme 2), amounts to 2.469(1) Å].[14−16] The framework of the metallacyclic ring system in complex **11** is reasonably unstrained, with bond angles C1−C6−N = 100.7(3)° and C6−N−Zr = 99.6(2) [bond lengths C1−C6 1.528(5) Å, C6−N 1.541(5) Å]. The C1−C6 vector at the C1 to C5 Cp ring is oriented slightly out of the C_5H_4 ring plane toward the zirconium centre (161.5°).

The internal (dimethylamino)alkyl coordination to the electron-deficient zirconium centre also shows up in the ^{15}N NMR shift of **11**.[28] The cation complex **11** exhibits a ^{15}N NMR resonance at δ = −359.8 ppm, which is Δδ > −20 as compared to its neutral precursor **10**,[14−16] for which an open, noncoordinating geometry of the −CMe_2−NMe_2 substituent was found by X-ray diffraction.[14−16]

The *meso*-**6b**/*rac*-**6b** mixture also reacts cleanly with Li[$B(C_6F_5)_4$] in dichloromethane at ambient temperature to yield **12b** (Scheme 7). The NMR spectra at room temperature are quite complicated, due to the dynamics of the system and some signal overlap. At 213 K a clean separation of most resonances is achieved, and it was shown that a ca. 1:2:1 mixture of three diastereoisomers was obtained. These show the same overall characteristics as seen earlier for the related phosphorus complexes (see above). Consequently, it should also be assumed here that two *cis*-configured cation complexes have been obtained, namely *syn*-*cis*-**12b** and *anti*-*cis*-**12b**, and their diastereoisomer *trans*-**12b**. Each of the *cis* complexes shows four ^{1}H/^{13}C NMR methine resonances of their symmetry-equivalent pairs of C_5H_4 ligands, whereas the C_5H_4 ligands of *trans*-**12b** are diastereotopic and hence give rise to the observation of eight respective methine NMR signals. Similarly, we have observed a total of four −C*H*Me− signals in the mixture (one each of *syn*- and *anti*-*cis*-**12b** and two of *trans*-**12b**) as well as four −CH(CH_3)− ^{1}H NMR doublets. Both nitrogen centres in the complexes **12b** are coordinated to the zirconium atom. This follows from the observed ^{1}H and ^{13}C NMR patterns, *and* is clearly demonstrated by the observed *four* ^{15}N NMR resonances[28] (again, two for the pair of *cis*-**12b** isomers and the remaining pair originating from *trans*-**12b**), all of which are charac-



Scheme 6

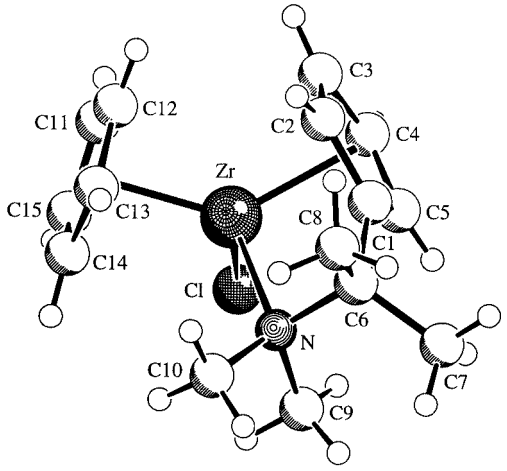
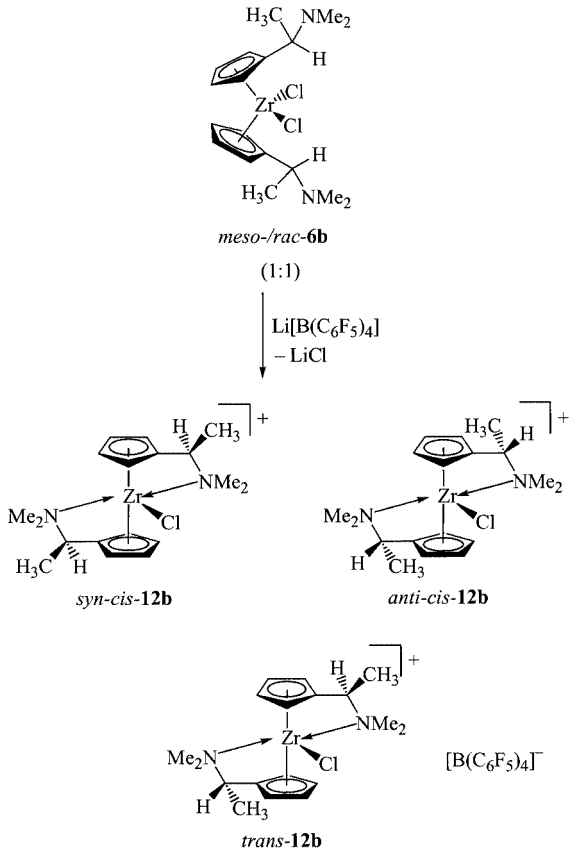


Figure 2. A view of the molecular geometry of **11** in the crystal (only the cation is depicted); selected bond lengths [Å] and angles [°]: Zr−N 2.369(3), Zr−Cl 2.426(1), Zr−C 2.398(4) to 2.502(4), C1−C6 1.528(5), C6−N 1.541(5), C6−C7 1.527(6), C6−C8 1.527(6), N−C9 1.491(5), N−C10 1.480(5); N−Zr−Cl 106.0(1), Zr−N−C6 99.6(2), Zr−N−C9 101.0(2), Zr−N−C10 123.5(2), C9−N−C6 112.8(3), C10−N−C6 115.1(4), C9−N−C10 104.2(3), N−C6−C1 100.7(3), N−C6−C7 112.6(3), N−C6−C8 111.0(4), C7−C6−C1 112.7(4), C8−C6−C1 109.8(4), C7−C6−C8 109.7(4)

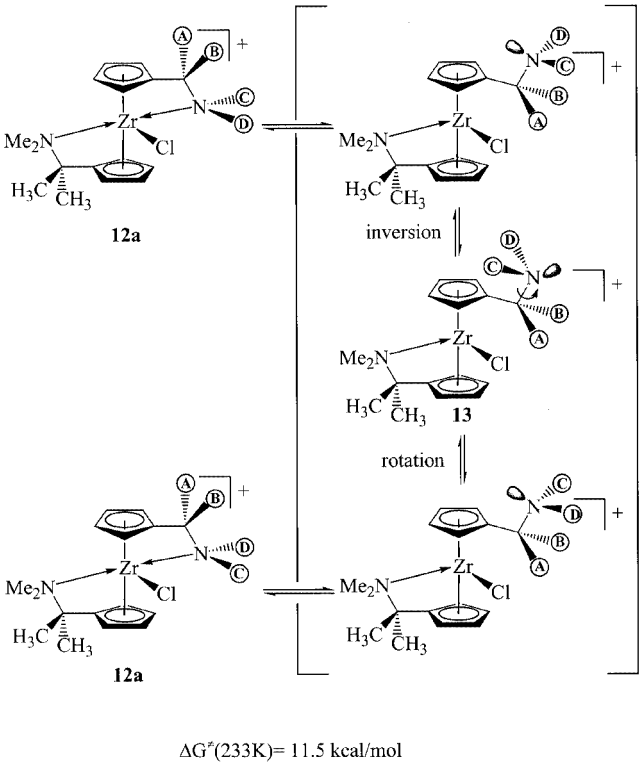
teristically shifted to more negative δ values (by $\Delta\delta \approx -30$) relative to the open, noncoordinated amino groups of the starting material **6b** (^{15}N NMR: **12b**: δ = −369.6, −369.3, −364.7, −367.1 ppm vs. **6b**: δ = −337.6 ppm). Because of the complexity of the system, with many overlapping NMR resonances at higher temperature, the dynamic NMR features of the metallocene cation isomers of **12b** were not further analysed.



Scheme 7

Treatment of $[(C_5H_4{-}CMe_2{-}NMe_2)_2ZrCl_2]$ (**6a**) with $Li[B(C_6F_5)_4]$ cleanly resulted in chloride abstraction with formation of the complex **12a** (Scheme 6; 78% yield, isolated). Again, the ^{15}N NMR spectra indicate that both $-NMe_2$ groups were coordinated to the central zirconium atom (^{15}N NMR: **12a**: δ = −358.6 vs. **6a**: δ = −337.4 ppm).

The dynamic features of complex **12a** are slightly different from those of the phosphorus-containing cations **5**. At 298 K the ^{1}H NMR spectrum of **12a** shows a 1:1 pair of signals for the $Cp{-}C(CH_3)_2$ methyl groups, indicating their chemical differentiation into *syn*- and *anti*-CH_3 substituents relative to the central Zr−Cl vector. At the same time we observe only a double intensity ^{1}H NMR singlet of the $-N(CH_3)_2$ groups of **12a** at ambient temperature. This indicates that, at room temperature, a rapid equilibration of the diastereotopic methyl groups of the amino function (marked C and D in Scheme 8) is taking place in a process that does not involve a similar exchange of the corresponding (A and B) methyl groups at the adjacent α-carbon atom. This indicates that a rapid dynamic process involving cleavage of the $Zr{-}N(Me)_2$ linkage, inversion at the nitrogen atom, rotation around the $N{-}C(Me_2)$ vector and ring closure by reformation of the Zr−N bond is taking place in the complexes **12**; this process must take place *without* concomitant rotation around the Zr−Cp vector, since no CMe^AMe^B interconversion is observed under these conditions.



Scheme 8

This isolated dynamic process of the $Zr{-}NMe_2$ moiety in **12a** can be slowed on the ^{1}H NMR timescale and eventually frozen (see Figure 3). Below a decoalescence temperature of T_c = 243 K, a 1:1 pair of $N(CH_3)_2$ ^{1}H NMR resonances is observed, and a Gibbs activation energy of $\Delta G^{\neq}(233\ K) = 11.5 \pm 0.2$ kcal/mol was calculated[20,21] for this characteristic dynamic process of **12a**, which probably involves a rate-determining (reversible) rupture of the zirconium−nitrogen linkage (Scheme 9).

A considerable increase in the monitoring temperature eventually also results in a broadening of the pair of CMe^AMe^B ^{1}H NMR signals and subsequently in their coalescence (see Figure 3). In 1,2-dideuteriotetrachloroethane solvent a Gibbs activation energy of $\Delta G^{\neq}(333\ K) = 17.3 \pm 0.2$ kcal/mol was obtained for this second dynamic process of **12a**. Unlike the "low-temperature" NMe^CMe^D exchange in **12a** (see above), this "high-temperature" intramolecular CMe^AMe^B equilibration requires rupture of *both* Zr−N linkages to take place at some time. We therefore have to assume the involvement of a chlorozirconocene intermedi-

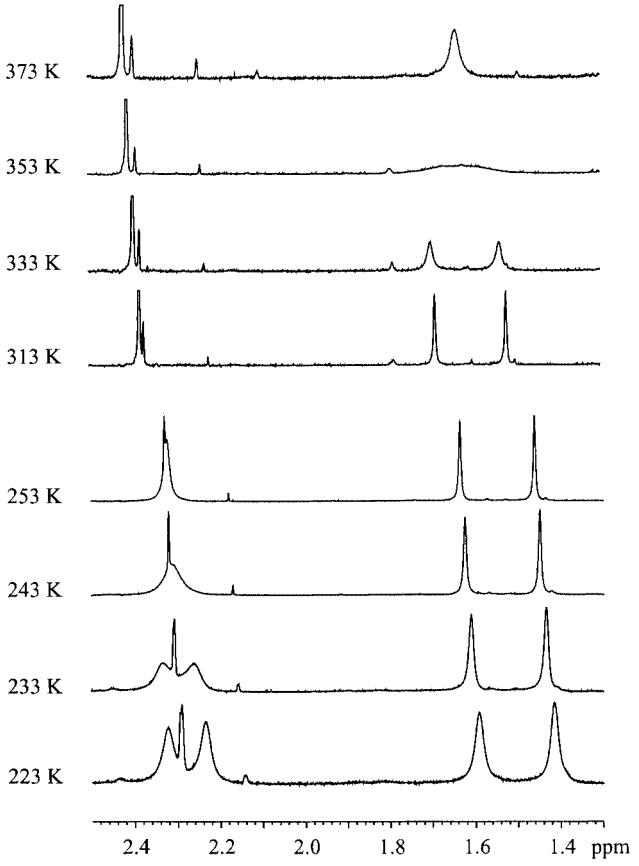
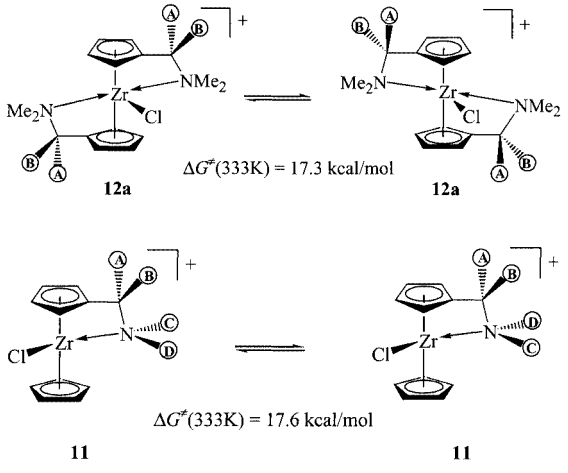


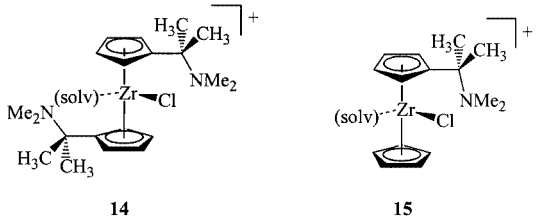
Figure 3. Dynamic ^{1}H NMR spectra of **12a** (600 MHz, $C_2D_2Cl_4$) showing the rapid equilibration of the diastereotopic $-NMe_2$ methyl resonances (left) followed by a markedly slower diastereotopic signal exchange at the adjacent $-CMe_2-$ moieties (right)



Scheme 9

ate (such as **14**, see Scheme 10) that lacks any favourable internal amine donor stabilisation.

Analogous dynamic behaviour is observed for complex **11**, which at *low* temperature (223 K) shows two $-C(CH_3)-$ ^{1}H NMR singlets (in CD_2Cl_2, 600 MHz) at δ = 1.60 and 1.55 ppm *and* a pair of $-N(CH_3)_2$ singlets (δ = 2.61, 2.33 ppm), of which only the latter displays coalescence with increasing NMR monitoring temperature. This again indicates that rapid (on the NMR timescale) breaking of the Zr−N bond takes place, followed by inversion at the nitrogen atom without equilibration of the remaining groups of signals, but that the activation barrier of this process is substantially higher [**11**: $\Delta G^{\neq}$(333 K) = 17.6 ± 0.2 kcal/mol] than in **12**.



Scheme 10

It is remarkable that the internal NMe^CMe^D equilibration of **11** is observed without a concomitant equilibration of the adjacent CMe^AMe^B moiety. We must assume that the $-NMe_2$ group in the respective intermediate (e.g., **15**; see Scheme 10) is not coordinated to the zirconium atom. Nevertheless, a complete rotation of the $C_5H_4-CMe_2NMe_2$ ligand around the Zr−Cp vector cannot be operative, since this would result in an inversion at the stereogenic zirconium centre,[19] which would be registered as a CMe^AMe^B interconversion on the NMR timescale. This is not observed by dynamic NMR spectroscopy in the experimentally accessible temperature range: the dynamic cation system **11** shows a remarkable stereochemical memory effect. We assume that stereoselective solvent coordination at the reactive intermediate stage (e.g., **15** in Scheme 10) might account for this observation. A similar stabilising solvent coordination of the intermediate **14** derived from the "more symmetrical" system **12a** would in principle also be in accord with the observed dynamic features of that system.

The systems **5a**[11] and **12a** are suitable for comparison of the stabilising features of $-PAr_2$ and $-NMe_2$ groups in a chlorozirconocene cation system, since these two complexes exhibit the same type of dynamic CMe^AMe^B equilibration process requiring rupture of *both* Zr−N/P linkages. Our experiments show that $-NMe_2$ and $-PAr_2$ stabilisation in these [Zr]−Cl^+ systems are about equal, as judged from the respective enantiomerisation barriers of the two systems [$\Delta G^{\neq}_{enant}$(358 K) = 17.5 ± 0.5 kcal/mol (**5a**[11]), $\Delta G^{\neq}_{enant}$(298 K) = 17.3 ± 0.5 kcal/mol (**12a**)]. In addition, comparison of the two nitrogen-stabilised chlorozirconocene cation systems **12a** and **11** shows a fairly substantial difference in the $\Delta G^{\neq}$ values of their internal $-NMe^CMe^D$ equilibration processes. As would be expected, the corresponding activation barrier of **11** is markedly higher because the chloro zirconocene cation resulting from Zr←NR_2- dissociation now lacks any internal stabilisation (but probably benefits from some solvent or anion interaction). In this case, the observed $\Delta G^{\neq}$(**12a**)/$\Delta G^{\neq}$(**11**) differ-

ence of $\Delta\Delta G^{\neq} \approx 6$ kcal/mol for internal $-NMe^{C}Me^{D}$ equilibration should probably be regarded as a lower limit of the stabilisation energy of such an electrophilic zirconocene cation by an amine donor ligand.

Experimental Section

General Remarks: Reactions were carried out under argon in Schlenk-type glassware or in a glovebox. Solvents (including the deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. The following instruments were used for characterisation of the synthesised compounds: Bruker AC 200 P NMR spectrometer (^{1}H 200 MHz, ^{13}C 50 MHz) at 298 K or a Varian Unity Plus NMR spectrometer (^{1}H 600 MHz, ^{13}C 150 MHz) at variable temperature (most NMR assignments were secured by 2D NMR experiments);[29] a Nicolet 5 DXC FT-IR spectrometer; a Micromass Quattro LC-Z mass spectrometer; elemental analyses were carried out with a Fross−Heraeus CHN-rapid elemental analyser or a Vario El III micro elemental analyser. $[\{C_5H_4(CMe_2)PPh_2\}_2ZrCl_2]$ (**2a**),[11] $[\{C_5H_4(CMe_2)P(tolyl)_2\}_2ZrCl_2]$ (**2b**),[11] $[\{C_5H_4(CHMe)PPh_2\}_2ZrCl_2]$ (**2c**),[12] $[\{C_5H_4(CHPh)PPh_2\}_2ZrCl_2]$ (**2d**),[12] $[\{C_5H_4(CHFc)P(tolyl)_2\}_2ZrCl_2]$ (**2e**),[30] $[\{C_5H_4(CMe_2)NMe_2\}_2ZrCl_2]$ (**6a**),[14−16] $[\{C_5H_4(CHMe)NMe_2\}_2ZrCl_2]$ (**6b**),[14−16] $[\{C_5H_4(CMe_2)NMe_2\}\{Cp\}ZrCl_2]$ (**10**),[14−16] tris(pentafluorophenyl)borane $[B(C_6F_5)_3,]$[9,10] lithium [tetrakis(pentafluorophenyl)borate] $[Li\{B(C_6F_5)_4\}]$[17a][17b,18] were prepared by literature methods.

$[C_5H_4(CHFc)P(tolyl)_2]Li(THF)$:[30] This compound was obtained from (p-tolyl)$_2$PH (2.8 g, 13.0 mmol), nBuLi (8.0 mL, 13.0 mmol) and 6-ferrocenylfulvene (3.9 g, 14.8 mmol), 5.4 g (75%) isolated. ^{1}H NMR (200.1 MHz, C_6D_6/[D$_8$]THF, 298 K): δ = 1.07 (m, 4 H, THF), 1.94, 2.01 (s, each 3 H, Me of p-tolyl), 2.05 (m, 4 H, THF), 3.60, 3.84, 4.05 (m, 4 H, C_5H_4 of Fc), 4.09 (s, 5 H, C_5H_4 of Fc), 4.62 (d, $^2J_{PH}$ = 6.1 Hz, 1 H, CHFc), 6.24 (br. s, 2 H of C_5H_4), 6.30, 6.58 (br. s, each 1 H of C_5H_4), 6.82, 6.89 (m, each 2 H, p-tolyl), 7.31 (m, 2 H, p-tolyl), 7.65 (m, 2 H, p-tolyl) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6/[D$_8$]THF, 298 K): δ = −0.9 ppm.

$[\{C_5H_4(CHFc)P(tolyl)_2\}_2ZrCl_2]$ (2e):[30] **2e** was obtained from $[C_5H_4(CHFc)P(tolyl)_2]Li(THF)$ (5.0 g, 9.0 mmol) and $[ZrCl_4(THF)_2]$ (1.69 g, 4.5 mmol), and isolated as a yellow solid (4.3 g, 81%) as a 1:1 mixture of diastereoisomers. IR (KBr): $\tilde{\nu}$ = 3111, 3091, 2918, 2850, 1595, 1497, 1468, 1456, 1394, 1266, 1185, 1105, 1090, 1039, 1027, 1018, 998, 813, 734, 512, 503, 500, 486, 423 cm^{-1}. ^{1}H NMR (200.1 MHz, C_6D_6, 298 K): δ = 2.02, 2.06 (s, each 6 H, Me of p-tolyl), 3.83 (m, 2 H, Fc), 3.92−3.93 (m, 4 H, Fc), 4.33 (d, J_{PH} = 0.5 Hz, 10 H, Fc), 4.47 (m, 2 H, Fc), 5.04 (d, $^2J_{PH}$ = 1.5 Hz, 2 H, C*H*Fc), 4.65, 4.82, 5.73, 6.32 (m, each 2 H, C_5H_4), 6.83 (pd, $J_{H,H}$ = 8 Hz, 4 H, p-tolyl), 6.93 (pd, $J_{H,H}$ = 7 Hz, 4 H, p-tolyl), 7.10 (pt, $J_{H,H}$ = 8 Hz, 4 H, p-tolyl), 7.46 (dd, $J_{H,H}$ = 6, 8 Hz, 4 H, p-tolyl) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 298 K): δ = 21.1, 21.3 (Me of p-tolyl), 42.2 (d, $J_{P,C}$ = 28.9 Hz, *C*HFc), 66.3 (d, $J_{P,C}$ = 2.2 Hz, Fc), 68.2 (Fc), 69.6 (d, $^3J_{P,C}$ = 6.1 Hz, Fc), 70.1 (d, $J_{P,C}$ = 4.4 Hz, Fc), 71.1 (d, $J_{P,C}$ = 5.4 Hz, Fc), 89.9 (d, $J_{P,C}$ = 15.7 Hz, Fc), 105.8, 110.9, 113.8, 125.7 (C, C_5H_4), 129.1 (d, $J_{P,C}$ = 8.8 Hz, p-tolyl), 129.7 (d, $J_{P,C}$ = 4.4 Hz, C, p-tolyl), 131.8 (d, $J_{P,C}$ = 23 Hz, p-tolyl), 131.9 (d, $J_{P,C}$ = 16.6 Hz, C, p-tolyl), 135.7 (d, $J_{P,C}$ = 17.5 Hz, p-tolyl), 137.3 (d, $J_{P,C}$ = 24.5 Hz, p-tolyl), 137.7 (p-tolyl), 138.0 (d, $J_{P,C}$ = 8.8 Hz, C_5H_4), 140.0 (p-tolyl) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 298 K): δ = 12.1, 12.8 ppm.

General Procedure for the Preparation of $[\{C_5H_4(CR^1R^2)PAr_2\}_2ZrCl]^+[B(C_6F_5)_4]^-$, $[\{C_5H_4(CR^1R^2)NMe_2\}_2ZrCl]^+[B(C_6F_5)_4]^-$ or $[\{C_5H_4(CMe_2)NMe_2\}\{Cp\}ZrCl]^+[B(C_6F_5)_4]^-$: Dichloromethane (or CD_2Cl_2 or $C_2D_2Cl_4$) was added at room temperature to a mixture of equimolar amounts of the cyclopentadienyl complex (**2a−e, 6a−b, 10**) and the chloride anion abstractor $Li[B(C_6F_5)_4]$. The reaction mixture was stirred for 1 h. The precipitated LiCl was removed by filtration. The filtrate was concentrated in vacuo or used directly. The product was washed twice with pentane and dried in vacuo.

$[\{C_5H_4(CMe_2)PPh_2\}_2ZrCl]^+[B(C_6F_5)_4]^-$ (5a): 5a was obtained from **2a** (3.72 g, 5.0 mmol) and $Li[B(C_6F_5)_4]$ (3.43 g, 5.0 mmol), and isolated as a yellow-brown solid (3.82 g, 55%). IR (KBr): $\tilde{\nu}$ = 3015, 2919, 2856, 1601, 1497, 1443, 1184, 1094, 1018, 802, 514, 492 cm^{-1}. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 300 K): δ = 1.55−2.19 (br. s, 12 H, CH_3), 6.15−6.47 (br. m, 8 H, C_5H_4), 7.32−7.60 (m, 20 H, Ph) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 300 K): δ = −29.1 ppm. ^{11}B{^{1}H } NMR (64.2 MHz, CD_2Cl_2, 300 K): δ = −16.6 ($w_{1/2}$ = 32 Hz) ppm. $C_{64}H_{40}BClF_{20}P_2Zr$ (1388.42): calcd. C 55.37, H 2.90; found C 55.33, 3.36.

$[\{C_5H_4(CMe_2)P(tolyl)_2\}_2ZrCl]^+[B(C_6F_5)_4]^-$ (5b): 5b was obtained from **2b** (4.0 g, 5.0 mmol) and $Li[B(C_6F_5)_4]$ (3.43 g, 5.0 mmol), and isolated (2.68 g, 67%) as a beige solid. IR (KBr): $\tilde{\nu}$ = 3030, 3005, 2939, 1621, 1507, 1451, 1287, 1200, 1105, 802, 534 cm^{-1}. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 300 K): δ = 1.55, 1.76 (m, each 6 H, CH_3), 2.41 (s, 12 H, CH_3 of p-tolyl), 6.13, 6.22 (m, each 4 H, C_5H_4), 7.25−7.55 (m, 16 H, p-tolyl) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 300 K): δ = −31.0 ppm. ^{11}B{^{1}H} NMR (64.2 MHz, CD_2Cl_2, 300 K): δ = −13.6 ($w_{1/2}$ = 48 Hz) ppm. $C_{68}H_{48}BClF_{20}P_2Zr$ (1444.53): calcd. C 56.54, H 3.35; found C 56.34, 3.72.

$[\{C_5H_4(CHMe)PPh_2\}_2ZrCl]^+[B(C_6F_5)_4]^-$ (5c): 5c was obtained from **2c** (3.58 g, 5.0 mmol) and $Li[B(C_6F_5)_4]$ (3.43 g, 5.0 mmol), and isolated (3.67 g, 54%) as a beige solid. IR (KBr): $\tilde{\nu}$ = 2965, 2810, 1621, 1479, 1453, 1110, 1088, 1015, 802, 685, 554 cm^{-1}. Mixture of three diastereoisomers. ***synlanti-cis*-5c:** ^{1}H NMR (599.9 MHz, CD_2Cl_2, 253 K): δ = 1.23, 1.51 (m, each 3 H, Me), 4.10, 4.33 (m, each 1 H, C*H*Me), 6.20, 6.27, 6.41, 6.88 (br. m, each 2 H, C_5H_4), 7.16−7.65 (m, 20 H, Ph) ppm. ^{13}C{^{1}H} NMR (150.8 MHz, CD_2Cl_2, 253 K): δ = 15.1, 19.6 (Me), 26.5, 38.9 (*C*HMe), 100.6, 102.0, 106.4, 109.0, 112.9, 113.2, 116.2, 120.2 (C_5H_4), 131.0, 133.0 (*ipso*-C of C_5H_4), 129.3−137.0 (Ph) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 300 K): δ = −45.9, −36.2 ppm. ***trans*-5c:** ^{1}H NMR (599.9 MHz, CD_2Cl_2, 253 K): δ = 1.25, 1.50 (m, 3 H, Me), 4.21, 4.47 (m, each 1 H, C*H*Me), 5.99, 6.27, 6.46, 6.94 (br. m, each 2 H, C_5H_4), 7.16−7.65 (m, 20 H, Ph) ppm. ^{13}C{^{1}H} NMR (150.8 MHz, CD_2Cl_2, 253 K): δ = 14.4, 19.3 (Me), 26.7, 28.2 (*C*HMe), 100.2, 101.0, 108.6, 108.8, 113.2, 115.3, 115.9, 116.5 (C_5H_4), 132.0, 133.0 (*ipso*-C of C_5H_4), 129.3−137.0 (Ph) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 300 K): δ = −47.2 (d, $^2J_{P,P}$ = 110 Hz), −38.1 (d, $^2J_{P,P}$ = 110 Hz) ppm. $[B(C_6F_5)_4]^-$ anion: ^{13}C{^{1}H} NMR (150.8 MHz, CD_2Cl_2, 253 K): δ = 124.0 (br. s, *ipso*-C of C_6F_5), 136.2 (dm, $J_{C,F}$ = 242 Hz, *m*-C_6F_5), 138.1 (dm, $J_{C,F}$ = 242 Hz, *p*-C_6F_5), 148.0 (dm, $J_{C,F}$ = 240 Hz, *o*-C_6F_5) ppm. ^{11}B{^{1}H} NMR (64.2 MHz, CD_2Cl_2, 300 K): δ = −16.6 ($w_{1/2}$ = 33 Hz) ppm. $C_{62}H_{36}BClF_{20}P_2Zr$ (1360.4): calcd. C 54.74, H 2.67; found C 55.34, 3.30.

$[\{C_5H_4(CHPh)PPh_2\}_2ZrCl]^+[B(C_6F_5)_4]^-$ (5d): 5d was obtained from **2d** (4.20 g, 5.0 mmol) and $Li[B(C_6F_5)_4]$ (3.43 g, 5.0 mmol), and isolated (2.74 g, 37%) as a light beige solid. Only the signals of the major *cis*-**5d** isomer are listed. ^{1}H NMR (599.9 MHz, CD_2Cl_2, 253 K): δ = 5.51 (br. m, 2 H, C*H*Ph), 6.38, 6.48, 6.59, 7.10 (m, each 2 H, C_5H_4), 7.2−7.5 (m, 30 H, Ph) ppm. ^{13}C{^{1}H} NMR (150.8 MHz, CD_2Cl_2, 253 K): δ = 39.1 (*C*HPh), 102.0, 109.5,

112.0, 118.0 (C_5H_4), 136.0 (dm, $J_{C,F}$ = 240 Hz, *m*-C_6F_5), 138.0 (*ipso*-C of Ph at P), 138.1 (dm, $J_{C,F}$ = 247 Hz, *p*-C_6F_5), 147.0 (dm, $J_{C,F}$ = 239 Hz, *o*-C_6F_5) ppm; *ipso*-C of C_6F_5, not observed, Ph resonances not listed. $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 300 K): δ = −41.8 (d, $^2J_{P,P}$ = 108 Hz), −18.4 (d, $^2J_{P,P}$ = 108 Hz, *trans* isomer), −15.0 (*cis* isomer) ppm. $^{11}B\{^1H\}$ NMR (64.2 MHz, CD_2Cl_2, 300 K): δ = −16.2 ($w_{1/2}$ = 37 Hz) ppm. $C_{72}H_{40}BClF_{20}P_2Zr$ (1484.5): calcd. C 58.25, H 2.72; found C 57.34, 3.48. The coalescence of the CHPh protons of the *trans* isomer was observed at 298 K [^1H NMR (200 MHz, CD_2Cl_2, 243 K): δ = 5.57 and 5.65 ppm; Δν = 17 Hz]: $\Delta G^{\neq}$ = 14.8 ± 0.5 kcal/mol.

[{C_5H_4(CHFc)P(tolyl)$_2$}$_2$ZrCl]$^+$[B(C_6F_5)$_4$]$^-$ (5e): 5e was obtained from **2e** (5.56 g, 5.0 mmol) and Li[B(C_6F_5)$_4$] (3.43 g, 5.0 mmol), and isolated as a beige solid (5.36 g, 61%). IR (KBr): ν̃ = 3019, 2856, 1621, 1491, 1443, 1188, 1088, 1027, 802, 625, 514, 492 cm^{-1}. Two diastereoisomers. ***cis*-5e:** ^1H NMR (599.9 MHz, CD_2Cl_2, 253 K): δ = 2.32 (s, 12 H, CH_3 of *p*-tolyl), 3.96 (s, 10 H, Fc), 3.39, 3.85, 4.07, 4.16 (m, each 2 H, Fc), 6.22, 6.35, 6.42, 7.15 (m, each 2 H, C_5H_4), 7.24−7.43 (m, 16 H, *p*-tolyl) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 253 K): δ = 35.6 (*C*HFc), 66.9, 67.8, 68.4, 68.7, 84.4 (Fc), 68.6 (Fc), 101.2, 108.2, 111.4, 116.4, 129.3 (C_5H_4), 129.5 (*p*-tolyl) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 300 K): δ = −18.2. ***trans*-5e:** ^1H NMR (599.9 MHz, CD_2Cl_2, 253 K): δ = 2.26, 2.35 (s, each 6 H, CH_3 of *p*-tolyl), 3.58, 3.88, 3.96, 3.98, 3.99 (s, each 5 H, Fc), 3.58, 3.88, 3.96, 3.99, 4.12, 4.14, 4.16, 4.21 (br. s, each 1 H, Fc), 5.06 (d, J_{PH} = 8.7 Hz, 1 H, C*H*Fc), 5.12 (d, J_{PH} = 5 Hz, 1 H, C*H*Fc), 5.94, 6.00 (m, each 1 H, C_5H_4), 6.06 (m, 2 H, C_5H_4), 6.17, 6.65, 6.92, 7.18 (m, each 1 H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 253 K): δ = 35.9, 36.6 (*C*HFc), 68.9 (2 × Fc), 67.3, 67.7, 68.0, 68.7, 69.0, 69.1, 69.4, 70.3, 83.4, 84.4 (Fc), 101.0, 103.2, 104.0, 109.4, 113.0, 115.6, 115.7, 116.4, 124.2, 129.5 (C_5H_4) ppm; tolyl resonances not listed. $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 300 K): δ = −36.1 (d, $^2J_{P,P}$ = 117 Hz), −24.1 (d, $^2J_{P,P}$ = 117 Hz) ppm. [B(C_6F_5)$_4$]$^-$ anion: $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 253 K): δ = 124.0 (br. s, *ipso*-C of C_6F_5), 136.6 (dm, $J_{C,F}$ = 240 Hz, *m*-C_6F_5), 138.2 (dm, $J_{C,F}$ = 245 Hz, *p*-C_6F_5), 148.0 (dm, $J_{C,F}$ = 253 Hz, *o*-C_6F_5) ppm. $^{11}B\{^1H\}$ NMR (64.2 MHz, CD_2Cl_2, 300 K): δ = −16.5 ($w_{1/2}$ = 34 Hz) ppm. ESI-MS: *m*/*z* (%) = 1077 (100) [$C_{60}H_{56}ClFeP_2Zr$]. $C_{84}H_{56}BClF_{20}Fe_2P_2Zr$ (1756.46): calcd. C 57.44, H 3.21; found C 56.73, 3.54. The coalescence of the C*H*Fc protons of *trans*-**5e** was observed at 298 K [^1H NMR (599.9 MHz, CD_2Cl_2, 253 K): δ = 5.06 and 5.12 ppm; Δν = 36 Hz]: $\Delta G^{\neq}$ = 14.5 ± 0.5 kcal/mol.

[{C_5H_4(CMe$_2$)NMe$_2$}{Cp}ZrCl]$^+$[B(C_6F_5)$_4$]$^-$ (11): 11 was obtained from **10** (1.89 g, 5 mmol) and Li[B(C_6F_5)$_4$] (3.43 g, 5 mmol), and isolated as a beige solid (3.68 g, 72%). IR (KBr): ν̃ = 3054, 3027, 2985, 1684, 1525, 1464, 1273, 1104, 1020, 985, 805, 745, 590 cm^{-1}. ^1H NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 1.61, 1.68 (br. s, each 3 H, CMe_2), 2.52 (br. s, 6 H, NMe_2), 6.46, 6.60 (m, each 1 H, C_5H_4), 6.68 (s, 5 H, Cp), 6.75, 6.81 (m, each 1 H, C_5H_4) ppm. ^1H NMR (599.9 MHz, CD_2Cl_2, 223 K): δ = 1.55, 1.60 (br. s, each 3 H, CMe_2), 2.33, 2.61 (s, each 3 H, NMe_2), 6.50, 6.57 (m, each 1 H, C_5H_4), 6.64 (s, 5 H, Cp), 6.69, 6.77 (m, each 1 H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 223 K): δ = 23.0, 25.8 [C(*C*H$_3$)$_2$], 45.3, 47.5, [N(*C*H$_3$)$_2$], 61.1 (*C*Me$_2$), 102.5, 108.7, 114.2, 118.3 (C_5H_4), 120.1 (C_5H_5), 131.3 (*ipso*-C of C_5H_4), 135.7 (dm, $J_{C,F}$ = 245 Hz, *m*-C_6F_5), 137.5 (dm, $J_{C,F}$ = 251 Hz, *p*-C_6F_5), 146.3 (dm, $J_{C,F}$ = 245 Hz, *o*-C_6F_5) ppm, *ipso*-C of C_6F_5 not observed. $^{11}B\{^1H\}$ NMR (64.2 MHz, CD_2Cl_2, 300 K): δ = −16.5 (s, $w_{1/2}$ = 34 Hz) ppm. $C_{39}H_{21}BClF_{20}NZr$ (1021.1): calcd. C 45.88, H 2.07, N 1.37; found C 45.60, H 2.18, N 1.38.

X-ray Crystal Structure Analysis of 11: Empirical formula $C_{15}H_{21}NClZr{\cdot}BC_{24}F_{20}$, *M* = 1021.05, colourless crystal 0.35 × 0.35 × 0.15 mm, *a* = 10.744(1), *b* = 12.990(1), *c* = 13.823(1) Å, α = 96.49(1), β = 91.87(1), γ = 101.02(1)°, *V* = 1878.6(3) Å^3, $\rho_{calcd.}$ = 1.805 g cm^{-3}, μ = 4.97 cm^{-1}, empirical absorption correction by use of SORTAV (0.845 ≤ *T* ≤ 0.929), *Z* = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, *T* = 198 K, ω- and φ-scans, 19488 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.66 Å^{-1}, 8895 independent (R_{int} = 0.036) and 7149 observed reflections [$I \geq 2\sigma(I)$], 572 refined parameters, *R* = 0.050, wR^2 = 0.132, max. residual electron density 1.06 (−0.98) eÅ^{-3}, crystals seem to be partly hydrolysed, the one high peak in the final difference Fourier calculation is 1.90 Å away from Zr, the typical distance for Zr−H_2O, hydrogen atoms calculated and refined as riding atoms. Complex **11** seems to add HCl readily. From the mother liquor of a crystallisation experiment, the "open" HCl adduct [(C_5H_4−CMe$_2$−NHMe$_2$)CpZrCl$_2$] ("**11**+HCl") was characterised by single-crystal X-ray diffraction: Empirical formula $C_{15}H_{22}NCl_2Zr{\cdot}BC_{24}F_{20}$, *M* = 1057.51, colourless crystal 0.40 × 0.15 × 0.05 mm, *a* = 10.746(1), *b* = 13.877(1), *c* = 14.578(1) Å, α = 66.71(1), β = 86.97(1), γ = 85.91(1)°, *V* = 1991.0(3) Å^3, $\rho_{calcd.}$ = 1.764 g cm^{-3}, μ = 5.37 cm^{-1}, empirical absorption correction by SORTAV (0.814 ≤ *T* ≤ 0.974), *Z* = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, *T* = 243 K, ω- and φ-scans, 20597 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.66 Å^{-1}, 9350 independent (R_{int} = 0.031) and 7214 observed reflections [$I \geq 2\sigma(I)$], 585 refined parameters, *R* = 0.044, wR^2 = 0.101, max. residual electron density 0.65 (−0.59) eÅ^{-3}, hydrogen atoms calculated and refined as riding atoms. The data set was collected with a Nonius KappaCCD diffractometer, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., **1998**), data reduction Denzo-SMN[31], absorption correction SORTAV[32], structure solution SHELXS-97[33], structure refinement SHELXL-97[34], graphics SCHAKAL[35]. CCDC-184443 for (**11**) and -200138 ("**11**+HCl") contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[{C_5H_4(CMe$_2$)NMe$_2$}$_2$ZrCl]$^+$[B(C_6F_5)$_4$]$^-$ (12a): 12 was obtained from **6a** (2.31 g, 5 mmol) and Li[B(C_6F_5)$_4$] (3.43 g, 5 mmol), and isolated as a light beige solid (3.93 g, 71%). IR (KBr): ν̃ = 3031, 3010, 1613, 1520, 1444, 1260, 1101, 1016, 972, 822, 742, 606, 571 cm^{-1}. ^1H NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 1.53 (s, 6 H, CMe_2), 1.70, 2.40 (s, each 6 H, NMe_2), 6.30, 6.33, 6.35, 6.79 (m, each 1 H, C_5H_4) ppm. ^1H NMR (599.9 MHz, $C_2D_2Cl_4$, 298 K): δ = 1.48 (s, 6 H, CMe_2), 1.65, 2.34 (s, each 6 H, NMe_2), 6.21, 6.26, 6.43, 6.74 (m, each 1 H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 203 K): δ = 24.0, 24.8 [C(*C*H$_3$)$_2$], 45.0, 45.5 [N(*C*H$_3$)$_2$], 59.1 (*C*Me$_2$), 102.2, 107.7, 116.2, 122.1 (C_5H_4), 130.3 (*ipso*-C of C_5H_4Cp), 135.7 (dm, $J_{C,F}$ = 245 Hz, *m*-C_6F_5), 137.5 (dm, $J_{C,F}$ = 251 Hz, *p*-C_6F_5), 143.7 (dm, $J_{C,F}$ = 245 Hz, *o*-C_6F_5) ppm, *ipso*-C of C_6F_5 not observed. $^{11}B\{^1H\}$ NMR (64.2 MHz, CD_2Cl_2, 298 K): δ = −16.5 ($w_{1/2}$ = 33 Hz) ppm. ESI-MS: *m*/*z* (%) = 425 (100) [$C_{20}H_{32}ClN_2Zr$]. $C_{44}H_{32}BClF_{20}N_2Zr$ (1106.2): calcd. C 47.47, H 2.92, N 2.53; found C 47.46, C 3.19, N 2.50.

[{C_5H_4(CHMe)NMe$_2$}$_2$ZrCl]$^+$[B(C_6F_5)$_4$]$^-$ (12b): 12b was obtained from **6b** (2.17 g, 5 mmol) and Li[B(C_6F_5)$_4$] (3.43 g, 5 mmol), and isolated as a beige solid (3.50 g, 65%). IR (KBr): ν̃ = 3021, 2856, 1610, 1512, 1454, 1265, 1078, 1016, 972, 806, 740, 610 cm^{-1}. 1:2:1 mixture of three diastereoisomers: ^1H NMR (599.9 MHz, CD_2Cl_2,

298 K): δ = 1.43−1.54 (m, 24 H, CHCH_3), 2.39 (m, 48 H, NMe_2), 3.74 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CHCH$_3$), 3.88 (m, 2 H, CHCH$_3$), 4.06 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CHCH$_3$), 4.27 (m, 2 H, CHCH$_3$), 5.88−6.84 (m, 32 H, Cp) ppm. ^{1}H NMR (599.9 MHz, CD_2Cl_2, 213 K): δ = 1.37 (m, 18 H, CHCH_3), 1.46 (m, 6 H, CHCH_3), 2.26, 2.27, 2.35, 2.36 (s, each 12 H, NMe_2), 3.72 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CHCH$_3$), 3.83 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CHCH$_3$), 3.99 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CHCH$_3$), 4.00 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CHCH$_3$), 5.95, 6.11, 6.17, 6.19, 6.26, 6.30, 6.31, 6.34, 6.36, 6.45, 6.59, 6.66, 6.70, 6.76, 6.77 (m, each 2 H, C_5H_4) ppm. ^{13}C{^{1}H} NMR (150.8 MHz, CD_2Cl_2, 213 K): δ = 13.5, 13.6, 14.2, 14.4 (CHCH$_3$), 42.3, 44.9, 49.1 (NMe_2), 59.6, 59.8, 59.9, 60.0 (CHCH$_3$), 101.1, 101.2, 101.2, 104.8, 106.6, 106.7,108.2, 108.5, 108.5, 111.3, 114.8, 115.8, 120.6, 121.3, 121.3, 122.2, 122.5, 122.5, 125.7, 128.0 (C_5H_4) ppm. $[B(C_6F_5)_4]^-$ anion: ^{13}C{^{1}H} NMR (150.8 MHz, CD_2Cl_2, 213 K): δ = 135.8 (dm, $J_{C,F}$ = 251 Hz, m-C_6F_5), 137.6 (dm, $^1J_{C,F}$ = 251 Hz, p-C_6F_5), 147.4 (dm, $J_{C,F}$ = 239 Hz, o-C_6F_5) ppm, (*ipso*-C, C_6F_5) not observed. ^{11}B{^{1}H} NMR (64.2 MHz, CD_2Cl_2, 300 K): δ = −16.5 (s, $w_{1/2}$ = 38 Hz) ppm. ESI-MS: *m*/*z* (%) = 397 (100) [$C_{18}H_{28}ClN_2Zr$]. $C_{42}H_{28}BClF_{20}N_2Zr$ (1078.15): calcd. C 46.78, H 2.62, N 2.60; found C 46.99, H 2.92, N 2.50.

Supporting Information: Additional NMR spectroscopic data of complexes **5**, **11** and **12**, and the dynamic ^{1}H NMR spectra of the cation complexes **11** and **12a** in CD_2Cl_2 and $C_2D_2Cl_4$ (see footnote on the first page of this article).

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[1] Reviews: [1a] T. J. Marks, *Acc. Chem. Res.* **1992**, *25*, 57−65. [1b] M. Aulbach, F. Küber, *Chem. Unserer Zeit* **1994**, *28*, 197−208. [1c] H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.* **1995**, *107*, 1255−1283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143−1170. [1d] M. Bochmann, *J. Chem. Soc.; Dalton Trans.* **1996**, 255−270. [1e] W. Kaminsky, *J. Chem. Soc., Dalton Trans.* **1998**, 1413−1418.

[2] Reviews. [2a] R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325−387. [2b] E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391−1434.

[3] M. Bochmann, A. J. Jaggar, J. C. Nicholls, *Angew. Chem.* **1990**, *102*, 830−832; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 780−782.

[4] M. Bochmann, S. J. Lancaster, *J. Organomet. Chem.* **1992**, *434*, C1−C5.

[5] J. C. W. Chien, W.-M. Tsai, M. D. Rausch, *J. Am. Chem. Soc.* **1991**, *113*, 8570−8571.

[6] C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031.

[7] S. Beck, S. Lieber, F. Schaper, A. Geyer, H.-H. Brintzinger, *J. Am. Chem. Soc.* **2001**, *123*, 1483−1489.

[8] Z. Liu, E. Somsook, C. B. White, K. A. Rosaaen, C. R. Landis, *J. Am. Chem. Soc.* **2001**, *123*, 11193−11207.

[9] X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1991**, *113*, 3623−3625.

[10] [10a] A. G. Massey, A. J. Park, F. G. A. Stone, *Proc. Chem. Soc. London* **1963**, 212. [10b] A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245−250. [10c] A. G. Massey, A. J. Park in *Organometallics Syntheses* (Eds.: R. B. King, J. J. Eisch), Elsevier, New York, **1986**, vol. 3, p. 461−462.

[11] B. E. Bosch, G. Erker, R. Fröhlich, O. Meyer, *Organometallics* **1997**, *16*, 5449−5456.

[12] B. E. Bosch, G. Erker, R. Fröhlich, *Inorg. Chim. Acta* **1998**, *270*, 446−458, and references cited therein.

[13] Reviews: [13a] P. Jutzi, J. Dahlhaus, *Coord. Chem. Rev.* **1994**, *137*, 179−199. [13b] J. Okuda, *Commments Inorg. Chem.* **1994**, *16*, 185−205. [13c] P. Jutzi, U. Siemeling, *J. Organomet. Chem.* **1995**, *500*, 175−185. [13d] H. Butenschön, *Chem. Rev.* **2000**, *100*, 1527−1564.

[14] A. Bertuleit, C. Fritze, G. Erker, R. Fröhlich, *Organometallics* **1997**, *16*, 2891−2899.

[15] J. Pflug, A. Bertuleit, G. Kehr, R. Fröhlich, G. Erker, *Organometallics* **1999**, *18*, 3818−3826.

[16] J. Pflug, G. Erker, G. Kehr, R. Fröhlich, *Eur. J. Inorg. Chem.* **2000**, 1795−1801.

[17] [17a] M. Bochmann, L. M. Wilson, *J. Chem. Soc., Chem. Commun.* **1986**, 1610−1611. [17b] M. Bochmann, L. M. Wilson, M. B. Hursthouse, R. L. Short, *Organometallics* **1987**, *6*, 2556−2563.

[18] [18a] S. Döring, G. Erker, R. Fröhlich, *J. Organomet. Chem.* **2000**, *643−644*, 61−68. [18b] R. E. LaPointe, G. R. Roof, K. A. Abboud, J. Klosin, *J. Am. Chem. Soc.* **2000**, *122*, 9560−9561. [18c] D. Vagedes, G. Erker, R. Fröhlich, *J. Organomet. Chem.* **2002**, *641*, 148−155. [18d] H. S. Strauss, *Chem. Rev.* **1993**, *93*, 927−942.

[19] J. W. Lauher, R. Hoffmann, *J. Am. Chem. Soc.* **1976**, *98*, 1729−1742.

[20] D. A. Kleier, G. Binsch, *D NMR3*, Indiana University, **1970**: D. A. Kleier, G. Binsch, *J. Magn. Reson.* **1970**, *3*, 146−160. K. Marat, *XSIM*, University of Manitoba, **1997**.

[21] M. L. H. Green, L.-L. Wong, A. Sella, *Organometallics* **1992**, *11*, 2660−2668, and references cited therein.

[22] [22a] K. Ziegler, W. Schäfer, *Justus Liebigs Ann. Chem.* **1934**, *511*, 101−109. [22b] K. Ziegler, H.-G. Gellert, H. Martin, K. Nagel, J. Schneider, *Justus Liebigs Ann. Chem.* **1954**, *589*, 91−121. [22c] M. F. Sullivan, W. F. Little, *J. Organomet. Chem.* **1967**, *8*, 277−285. [22d] P. Renaut, G. Tainturier, B. Gautheron, *J. Organomet. Chem.* **1978**, *148*, 43−51. [22e] M. D. Brickhouse, R. R. Squires, *J. Am. Chem. Soc.* **1988**, *110*, 2706−2714. [22f] J. Okuda, *Chem. Ber.* **1989**, *122*, 1075−1077. [22g] R. R. Squires, *Acc. Chem. Res.* **1992**, *25*, 461−467. [22h] T. J. Clark, C. M. Killian, S. Luthra, T. A. Nile, *J. Organomet. Chem.* **1993**, *462*, 247−257.

[23] [23a] K. Hafner, G. Schultz, K. Wagner, *Justus Liebigs Ann. Chem.* **1964**, *678*, 39−53. [23b] K. H. Vöpel, G. Ploss, C. König, *Org. Synth.* **1967**, *47*, 52−54, and references cited therein.

[24] K. Kunz, J. Pflug, A. Bertuleit, R. Fröhlich, E. Wegelius, G. Erker, E.-U. Würthwein, *Organometallics* **2000**, *19*, 4208−4216.

[25] K. J. Stone, R. D. Little, *J. Org. Chem.* **1984**, *49*, 1849−1853.

[26] L. E. Manzer, *Inorg. Synthesis* **1982**, *21*, 135−136.

[27] G. Erker, K. Berg, L. Treschanke, K. Engel, *Inorg. Chem.* **1982**, *21*, 1277−1278.

[28] For other examples of ^{15}N NMR studies of group-4 organometallic systems, see, e.g.: H. G. Alt, K. Föttinger, W. Milius, *J. Organomet. Chem.* **1999**, *572*, 21−30.

[29] S. Braun, H.-O. Kalinowski, S. Berger, *150 and More Basic NMR Experiments*, Wiley-VCH, Weinheim, **1998**, and references cited therein.

[30] B. E. Bosch, doctoral thesis, Univ. Münster, **1997**.

[31] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326.

[32] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33−37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421−426.

[33] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

[34] G. M. Sheldrick, Universität Göttingen, **1997**.

[35] E. Keller, Universität Freiburg, **1997**.

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