Reaction of a Zirconocene(butadiene)borate-Betaine Single-Component Ziegler Catalyst with Trimethylphosphane

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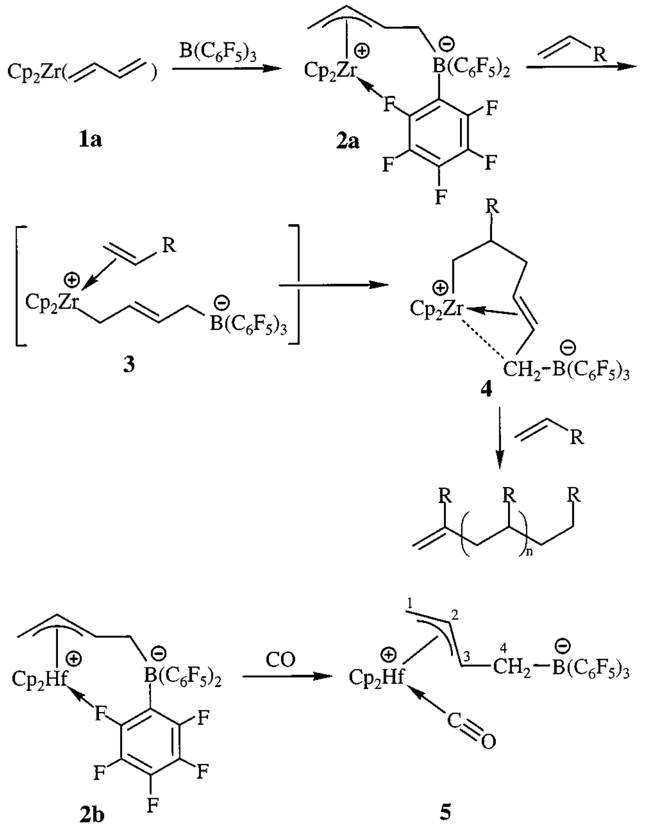
Trimethylphosphane adds to the zirconocene–[$C_4H_6B(C_6F_5)_3$] betaine complex **2a** regioselectively by an overall inversion pathway, with opening of the internal ZrF–C_{Ar} bond and formation of the $Cp_2Zr(PMe_3)[C_4H_6B(C_6F_5)_3]$ adduct **6**. Complex **6** was characterized by X-ray diffraction. The betaine complex **6** contains a $–CH_2B(C_6F_5)_3$-substituted π-allyl ligand with characteristic bonding parameters of C1–C2: 1.402(8) Å, C2–C3: 1.373(7) Å, Zr–C1: 2.443(5) Å, Zr–C2: 2.526(4) Å, and Zr–C3: 2.681(4) Å.

Introduction

Tris(pentafluorophenyl)borane adds to (butadiene)zirconocene (**1**) to yield the $Cp_2Zr[C_4H_6B(C_6F_5)_3]$ betaine **2a** (Scheme 1). Complex **2** and its substituted Group-4 metallocene analogues are active single-component homogeneous Ziegler catalysts.[1] In addition, complex **2** and its congeners insert one equivalent of an α-olefin under selected reaction conditions to selectively form the primary product **4** of the initiative sequence leading into the catalytic cycle of the olefin polymerization process.[2,3] From a detailed kinetic study it is known that a reactive (η^2-alkene)(σ-allyl)metallocene-type intermediate (**3**) is formed in a preceding equilibrium step, followed by rate-determining alkene insertion into the Zr−C σ-bond.[4] The intermediate **3** cannot be observed directly because of its rapid subsequent CC-coupling reaction.[5] Therefore, we tried to model the structural chemistry of this first step by the addition of a suitable non-olefin two-electron donor ligand. THF added to **2a** with opening of the ZrF coordination, but we could not obtain crystals of the addition product that were suited for an X-ray crystal structure analysis.[1b,6,7] A carbon monoxide addition product to the hafnium homolog **2b** was characterized by X-ray diffraction, but turned out to be the wrong regioisomer (**5**) in comparison with the pathway probably followed in the alkene insertion reaction.[1a,8] We have now prepared and structurally characterized the PMe_3 adduct to the $Cp_2Zr[C_4H_6B(C_6F_5)_3]$ betaine, and found that its coordination characteristics may potentially resemble a structural situation expected at an early stage of the alkene addition reaction.



Scheme 1

Results and Discussion

The betaine complex $Cp_2Zr[C_4H_6B(C_6F_5)_3]$ (**2a**) was generated in situ by treatment of (butadiene)zirconocene (**1**)[9] with the organometallic Lewis acid tris(pentafluorophenyl)borane[10,11] in toluene. If care is taken to ensure that the two components are employed in a 1:1 ratio, then the formation of **2a** is close to quantitative, and it is not necessary to isolate the resulting metallocene−borate betaine complex, and the toluene solution of **2a** can be used directly to carry out subsequent reactions.

The addition of a four-fold excess of trimethylphosphane resulted in an instantaneous formation of the 1:1 addition product **6**, of the phosphane to the zirconium complex

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[+] X-ray crystal-structure analysis.

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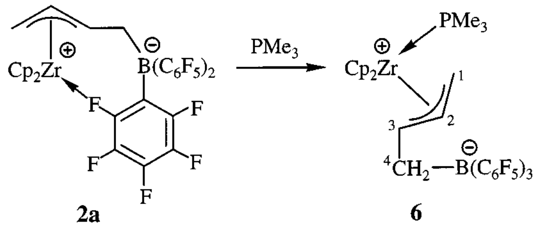

2a **6**

Scheme 2

(Scheme 2). The $Cp_2Zr(PMe_3)[C_4H_6B(C_6F_5)_3]$ complex (**6**) crystallized in pure form from the reaction mixture at −20 °C, and was isolated in > 90% yield as a pale yellow crystalline material. Since the product was poorly soluble once it was precipitated, solutions of **6**, generated in situ in a deuterated solvent, were used for some of the NMR spectroscopic characterization.

The ^1H-NMR spectrum reveals that the PMe_3 addition complex **6** is chiral. It shows the signals of a pair of diastereotopic Cp-ligands at $\delta = 4.88$ and 4.64. Each signal is split into a doublet by coupling with the phosphorus nucleus of the coordinated PMe_3 ligand ($J_{PH} = 2$ Hz).[12] Consequently, a ^{31}P-NMR resonance is observed for **6** at $\delta = 1.25$, which is markedly shifted to a higher δ value relative to free trimethylphosphane ($\delta = -62.1$). Coordination of the PMe_3 donor ligand to zirconium has opened the ZrF interaction that was characteristic of the starting material **2a** (^{19}F NMR: $\delta = -213$ for the $ZrF-C_6H_4[B]$ unit).[1a] In **6**, only a set of three ^{19}F-NMR resonances is observed in the typical $RB(C_6F_5)_3^-$ range. A distorted (π-allyl)Zr moiety is retained in complex **6** as judged from the characteristic ^1H- and ^{13}C-NMR chemical shifts (see Table 1). The regiochemical preference of the PMe_3 addition, leading to a "$-CH_2B-$ inside" (as found in **5**) or "$-CH_2B-$ outside" structure[8a] (as formulated for **6** in Scheme 2) cannot be deduced from the NMR data of the obtained product. We were able to answer this question by an X-ray crystal structure analysis of **6**.

The single crystals obtained from the preparation of **6** (see above) were suitable for an X-ray crystal-structure analysis. The betaine complex exhibits a pseudo-tetrahedral coordination environment around the central zirconium atom. In the front sector of the bent metallocene wedge one finds the $C_4H_6[B]$ moiety, coordinated to the metal center through its carbon atoms C1−C3, and the PMe_3 ligand. The substituted allyl unit is coordinated in a η^3-fashion, but it is distorted toward a σ,π-type coordination geometry, as it is often observed for (allyl)zirconocene complexes.[13] However, this distortion in **6** is much less pronounced than it was, for instance, in the metallacyclic betaine complex **2a** (see Table 2). In **6** the $d(Zr-C2) - d(Zr-C3)$ bond lengths difference [Δ(ZrC2/3)] amounts to only 0.155 Å, whereas Δ(ZrC2/3) = 0.216 Å was observed for complex **2a**.

Table 1. A comparison of selected NMR data of the complexes **2a** and **6**

^1H NMR[a]						
	1-H	1-H′	2-H	3-H	4-H	4-H′
2a	1.85	1.47	5.88	5.23	2.56	2.25
6	1.43	0.49	3.79	4.00	3.29	2.06
^{13}C NMR[a]						
	C-1		C-2	C-3		C-4
2a	52.7		131.3	123.8		28.5
6	44.1 (J_{PC}=12 Hz)		109.6	117.1 (J_{PC}=7 Hz)		32.5

[a] In $[D_8]$toluene at 303 K (**2a**) or 298 K (**6**).

Table 2. A comparison of selected bond lengths (in Å) between the complexes **2a**, **6**, and **5**

Compound (M)	**2a** (Zr)[a]	**6** (Zr)	**5** (Hf)[a]
C1−C2	1.414(9)	1.402(8)	1.399(8)
C2−C3	1.342(8)	1.373(7)	1.369(8)
C3−C4	1.521(8)	1.499(7)	1.497(7)
C4−B	1.633(9)	1.665(6)	1.675(8)
M−C1	2.339(5)	2.443(5)	2.396(5)
M−C2	2.494(6)	2.526(4)	2.514(5)
M−C3	2.710(5)	2.681(4)	2.742(5)
M−X	2.423(3)[b]	2.705(1)[c]	2.246(7)[d]

[a] From ref.[1a]. − [b] Zr···F. − [c] Zr−P. − [d] Hf−CO.

The addition of the phosphane ligand has resulted in a cleavage of the ZrF−C interaction that was typical for the betaine system **2a**,[14] and has led to a conformational change of the $C_4H_6B(C_6F_5)_3$ chain. In **6**, rotation around the C3−C4 vector has oriented the $C4-B(C_6F_5)_3$ unit away from the metallocene moiety [θC2−C3−C4−B = −95.4(5)°] to minimize steric interaction between these two bulky groups.

The PMe_3 ligand was added to the bent metallocene from a position oriented as far away as possible from the bulky $-CH_2-B(C_6F_5)_3$ end of the 1-3η-$C_4H_6-B(C_6F_5)_3$ ligand (see Figure 1). It is found attached at the front side of the bent metallocene wedge in a position close to the CH_2-terminus of the $-CH_2$-borane-substituted π-allyl ligand.[15] The Zr−P bond length is 2.705(1) Å. The $Me_3P-ZrCp_2L$ unit attains a staggered-like conformational arrangement of groups along the P−Zr vector. In **6**, the bond angles at phosphorus show a systematic deviation from an ideal tetrahedron: the three H_3C-P angles are markedly smaller [101.6(3)°, 101.9(4)°, 102.6(3)°] than the adjacent C−P−Zr angles [115.7(2)°, 116.1(2)°, 116.7(2)°]. This is probably due to steric interactions, and indicates the importance of steric factors governing the regiochemistry of the adduct formation in complexes of types **6** (Figure 1) and **5** (see Scheme 1).[16]

Conclusions

The ZrF bond in the metallocene betaine complex **2a** is rather weak, estimated at ca. 8 kcal mol^{-1} bond dissociation energy from dynamic ^{19}F-NMR spectroscopy.[1b] Therefore, it is not surprising, that the zirconium−fluorine linkage in **2a** is rapidly cleaved by the addition of typical 2-electron donor ligands such as carbon monoxide or trimethylphosphane. The small CO ligand can apparently be added from the sterically less favorable side to yield the

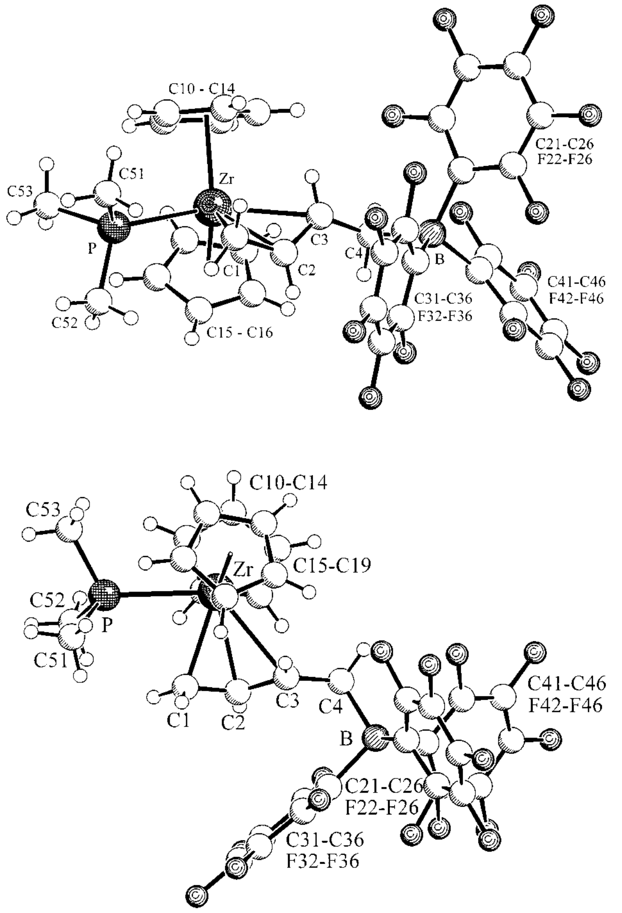

Figure 1. Two projections of the molecular structure of complex **6**; selected bond lengths [Å] and angles [°]: Zr−C1 2.443(5), Zr−C2 2.526(4), Zr−C3 2.681(4), Zr−C4 3.768(5), Zr-P 2.705(1), C1−C2 1.402(8), C2−C3 1.373(7), C3−C4 1.499(7), C4−B 1.665(6), B−C21 1.649(7), B−C31 1.665(6), B−C41 1.650(7), P−C51 1.832(6), P−C52 1.821(7), P−C53 1.829(6); Zr−C1−C2 76.9(3), Zr−C2−C1 70.4(3), Zr−C2−C3 81.1(3), Zr−C3−C2 68.6(2), Zr−C3−C4 126.4(3), C1−Zr−C2 32.7(2), C1−Zr−C3 57.3(2), C2−Zr−C3 30.4(2), C1−C2−C3 125.2(5), C2−C3−C4 123.2(4), C3−C4−B 114.9(4), C4−B−C21 115.8(4), C4−B−C31 104.1(4), C4−B−C41 107.6(4), C21−B−C31 110.3(4), C21−B−C41 104.9(4), C31−B−C41 114.4(4), C1−Zr−P 70.5(1), Zr−P−C51 116.7(2), Zr−P−C52 115.7(2), Zr−P−C53 116.1(2), C51−P−C52 101.9(4), C51−P−C53 102.6(3), C52−P−C53 101.6(3)

"$-CH_2-B(C_6F_5)_3-$ inside" regioisomer **5**,[1a] but the addition of the sterically more demanding PMe_3 ligand already leads to the exclusive observation of a typical stereochemical inversion pathway. Addition of the phosphane takes place *trans* to the ZrF bond in the σ-ligand plane at the front sector of the bent metallocene wedge, leading to the selective formation of the observed regioisomer **6**, however, it is unclear whether this product formation is thermodynamically or kinetically controlled.

The involvement of a (σ-allyl)(π-olefin)metallocene betaine-type intermediate, such as **3** (see Scheme 1) in the course of the alkene insertion/polymerization sequence starting from **2**, has been indirectly demonstrated by kinetic measurements. These have shown that the typical metallocene−allyl-inversion process of **2a**, followed by dynamic NMR spectroscopy, is markedly slower in pure toluene ($\Delta G^{\ddagger}_{inv}$ = 19.8 kcal mol^{-1}) than in the presence of added propene ($\Delta G^{\ddagger}_{inv}$ = 16.5 kcal mol^{-1}).[4] The allyl inversion process must proceed through a (σ-allyl)-metallocene-type intermediate,[17] in the presence of the alkene this means by involvement of **3**. The observed allyl inversion barrier ($\Delta G^{\ddagger}_{inv}$) is lowered because the essential reactive intermediate is stabilized by π-alkene coordination, and so is the preceding transition state, according to the Hammond postulate.[18] Since the addition reactions to **2** respond very sensitively to steric interferences, it may be that an alkene adds to **2a** in a manner very similar to PMe_3, namely from the less hindered side adjacent to the unsubstituted allyl side. This potentially leads to a stereochemical inversion at the metal center upon replacing the weak F−C(Ar) coordination to zirconium. The resulting PMe_3 adduct **6**, that we obtained and structurally characterized, may therefore, potentially resemble the structural situation during the alkene addition reaction to the metallocene betaine system at an early stage on the reaction coordinate.

Experimental Section

Reactions were carried out under argon using Schlenk-type glassware or in a glove-box. Solvents were dried and distilled under argon prior to use. For additional general information, including a list of spectrometers and instruments used for physical characterization, see ref.[1b] (Butadiene)zirconocene[9] and $B(C_6F_5)_3$[10] were prepared according to literature procedures. For this study, the betaine complex **2a** (see below) was generated in situ and spectroscopically shown to be identical to the previously isolated material.

Reaction of 2a with Trimethylphosphane. − Preparation of 6. − a) NMR Experiment: For its spectroscopic characterization, complex **6** was generated in situ in [D$_8$]toluene. A solution of 8 mg (29.0 μmol) of (butadiene)zirconocene (**1**) in 0.4 mL of [D$_8$]toluene was added dropwise to a solution of 15 mg (29.3 μmol) of $B(C_6F_5)_3$ in 0.2 mL of [D$_8$]toluene at ambient temperature in a vial inside the glove-box. The reaction mixture was kept for 30 min at ambient temperature; during this time a small fraction of the betaine **2a** precipitated. The clear supernatant solution was transferred to an NMR tube and sealed with a septum. Trimethylphosphane (0.02 mL) was syringed into the solution. After mixing, a pale yellow solution of **6** was obtained that was used for some of the spectroscopic characterization.

b) Formation of 6 on a Preparative Scale: A solution of 54 mg (105 μmol) of $B(C_6F_5)_3$ in 3 mL of toluene was added dropwise at ambient temperature to a solution of 29 mg (105 μmol) of (butadiene)-zirconocene in 6 mL of toluene. After 30 min trimethylphosphane (0.13 mL, 420 μmol) was added and the mixture stirred for 20 min at room temperature. The pale yellow solution was kept for 1 d at −20 °C. The product crystallized as yellow needles, which were collected by filtration, washed with toluene (4 mL), and dried in vacuo to yield 85 mg (93%) of **6**, m.p. 234 °C (decomp.). The isolated product shows a low solubility in toluene. Single crystals from this preparation were used for the X-ray crystal structure analysis of **6**: formula $C_{35}H_{25}BF_{15}PZr \times 2\ C_7H_8$, M = 1047.82, light yellow crystal 0.30 × 0.20 × 0.10 mm, a = 32.936(1), b = 15.360(1), c = 21.055(1) Å, β = 113.93(1)°, V = 9736.1(8) Å^3, $\rho_{calcd.}$ = 1.430 g cm^{-3}, μ = 3.49 cm^{-1}, empirical absorption correction via SORTAV (0.903 ≤ T ≤ 0.966), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 0.71073 Å, T = 198 K, ω and φ scans, 28280 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.62 $Å^{-1}$, 9810 independent (R_{int} = 0.041) and 7840 observed reflections [$I \geq 2\ \sigma(I)$], 607 refined parameters, R = 0.076, wR^2 = 0.234, max. residual electron density 3.55 (−0.56) e $Å^{-3}$, beside the localized toluene molecules there is probably a further solvent molecule around 0,y,1/4. Even with strong geometrical constraints a chemical meaningful description is not possible and therefore this electron density is not taken into account in the final refinement, hydrogens calculated and refined as riding atoms.

Data set was collected with Nonius Kappa CCD diffractometer, equipped with a rotating anode generator, Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307−326), absorption correction SORTAV (R. H. Blessing, *Acta Cryst.* **1995**, *A51*, 33−37; R. H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421−426), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138789. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223)336−033, E-mail: deposit@ccdc.cam.ac.uk].

^{1}H NMR (599.9 MHz, [D$_8$]toluene, 298 K): δ = 4.88, 4.64 (each d, J_{PH} = 2.0 Hz, each 5 H, C_5H_5), 4.00 (m, 1 H, 3-H), 3.79 (ddd, 2× ^3J = 14.5 Hz, ^3J = 8.5 Hz, 1 H, 2-H), 3.29 (br d, J = 11.3 Hz, 1 H, 4-H), 2.06 (partially under solvent signal, 1 H, 4-H′), 1.43 (m, 1 H, 1-H), 0.49 (ddd, ^2J = 5.0 Hz, ^3J = 14.5 Hz, ^3J = 5.0 Hz, 1 H, 1-H′), 0.40 [d, $^2J_{PH}$ = 7.2 Hz, 9 H, P(CH$_3$)$_3$]. − ^{13}C NMR (150.8 MHz, [D$_8$]toluene, 298 K): δ = 149.1 [d, $^1J_{CF}$ = 240 Hz, *o*-B(C$_6$F$_5$)$_3$], 138.6 [d, $^1J_{CF}$ = 250 Hz, *p*-B(C$_6$F$_5$)$_3$], 137.4 [d, $^1J_{CF}$ = 250 Hz, *m*-B(C$_6$F$_5$)$_3$], 117.1 (d, J_{PC} = 7 Hz, CH, C-3), 109.6 (CH, C-2), 105.2, 104.5 (each CH, C_5H_5), 44.1 (d, J_{PC} = 12 Hz, CH$_2$, C-1), 32.5 (CH$_2$, C-4), 15.8 [d, $^1J_{PC}$ = 23 Hz, CH$_3$, P(CH$_3$)$_3$], *ipso*-C of B(C$_6$F$_5$)$_3$ not detected. − GHSQC[19] (599.9 MHz, [D$_8$]toluene, 298 K): δ = 4.88/105.2; 4.64/104.5 (each C_5H_5/C_5H$_5$), 4.00/117.1 (3-H/C-3), 3.79/109.6 (2-H/C-2), 3.29/32.5 (4-H/C-4), 2.06/32.5 (4-H′/C-4), 1.43/44.1 (1-H/C-1), 0.49/44.1 (1-H′/C-1), 0.40/15.8 (P(CH_3)$_3$/P(CH$_3$)$_3$). − ^{19}F NMR (564.3 MHz, [D$_8$]toluene, 298 K): δ = −167.1 (t, 2× $^3J_{FF}$ = 21 Hz, 6F, *m*-F), −163.7 (t, $^3J_{FF}$ = 21 Hz, 3F, *p*-F), −132.6 (d, $^3J_{FF}$ = 21 Hz, 6F, *o*-F). − ^{31}P NMR (202.6 MHz, [D$_8$]toluene, 298 K): δ = 1.25. − IR (KBr): $\tilde{\nu}$ = 3137 (w), 2964 (w), 2918 (w), 1641 (m), 1512 (vs), 1459 (vs), 1294 (m), 1271 (m), 1147 (m), 1080 (s), 977 (s), 959 (s), 819 (s), 808 (s), 801 (s), 758 (m), 682 (m) cm^{-1}. − $C_{35}H_{25}BF_{15}PZr$ (863.6): calcd. C 48.68, H 2.92; found C 48.97, H 3.19.

Acknowledgments

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[1] [1a] B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich, S. Kotila, *Angew. Chem.* **1995**, *107*, 1867−1869; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1755−1757. − [1b] J. Karl, G. Erker, R. Fröhlich, *J. Am. Chem. Soc.* **1997**, *119*, 11165−11173. − [1c] See also: G. Kehr, R. Fröhlich, B. Wibbeling, G. Erker, *Chem. Eur. J.* **2000**, *6*, 258−266.

[2] B. Temme, J. Karl, G. Erker, *Chem. Eur. J.* **1996**, *2*, 919−924. J. Karl, G. Erker, *Chem. Ber./Recueil* **1997**, *130*, 1261−1267. J. Karl, G. Erker, *J. Mol. Catal.* **1998**, *128*, 85−102.

[3] For related systems see e.g.: R. F. Jordan, D. F. Taylor, *J. Am. Chem. Soc.* **1989**, *111*, 778−779. R. F. Jordan, R. E. LaPointe, P. K. Bradley, N. Baenziger, *Organometallics* **1989**, *8*, 2892−2903. R. F. Jordan, D. F. Taylor, N. C. Baenziger, *Organometallics* **1990**, *9*, 1546−1557. A. S. Guram, R. F. Jordan, D. F. Taylor, *J. Am. Chem. Soc.* **1991**, *113*, 1833−1835. A. S. Guram, R. F. Jordan, *Organometallics* **1991**, *10*, 3470−3479. Z. Guo, D. C. Swenson, R. F. Jordan, *Organometallics* **1994**, *13*, 1424−1432. Y. W. Alelyunas, N. C. Baenziger, P. K. Bradley, R. F. Jordan, *Organometallics* **1994**, *13*, 148−156. C. Pellecchia, A. Grassi, A. Zambelli, *J. Chem. Soc., Chem. Commun.* **1993**, 947−949. C. Pellecchia, A. Grassi, A. Immirzi, *J. Am. Chem. Soc.* **1993**, *115*, 1160−1162. C. Pellecchia, A. Immirzi, A. Zambelli, *J. Organomet. Chem.* **1994**, *479*, C9−C11. C. Pellecchia, A. Immirzi, D. Pappalardo, A. Peluso, *Organometallics* **1994**, *13*, 3773−3775. C. Pellecchia, A. Grassi, A. Zambelli, *Organometallics* **1994**, *13*, 298−302.

[4] J. Karl, M. Dahlmann, G. Erker, K. Bergander, *J. Am. Chem. Soc.* **1998**, *120*, 5643−5652.

[5] For related d^0-metallocene π-alkene complexes see e.g.: Z. Wu, R. Jordan, *J. Am. Chem. Soc.* **1995**, *117*, 5867−5868. C. P. Casey, S. L. Hallenbeck, D. W. Pollock, C. R. Landis, *J. Am. Chem. Soc.* **1995**, *117*, 9770−9771. M. V. Galakhov, G. Heinz, P. Royo, *J. Chem. Soc., Chem. Commun.* **1998**, 17−18. C. P. Casey, D. W. Carpenetti II, H. Sakurai, *J. Am. Chem. Soc.* **1999**, *121*, 9483−9484.

[6] M. Dahlmann, Dissertation, Universität Münster, **1999**.

[7] For related metallocene-betaine-THF adducts see: M. Dahlmann, G. Erker, M. Nissinen, R. Fröhlich, *J. Am. Chem. Soc.* **1999**, *121*, 2820−2828.

[8] [8a] K. Tatsumi, A. Nakamura, P. Hofmann, P. Stauffert, R. Hoffmann, *J. Am. Chem. Soc.* **1985**, *107*, 4440−4451 and references cited therein. − [8b] G. Fachinetti, G. Fochi, C. Floriani, *J. Chem. Soc., Dalton Trans.* **1977**, 1946−1950. F. Fachinetti, C. Floriani, H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.* **1977**, 2297−2302. G. Erker, F. Rosenfeldt, *J. Organomet. Chem.* **1980**, *188*, C1−C4.

[9] [9a] H. Yasuda, Y. Kajihara, K. Mashima, K. Nagasuna, K. Lee, A. Nakamura, *Organometallics* **1982**, *1*, 388−396. G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich, C. Krüger, *J. Am. Chem. Soc.* **1980**, *102*, 6344−6346. G. Erker, J. Wicher, E. Engel, C. Krüger, *Chem. Ber.* **1982**, *115*, 3300−3310. − [9b] Reviews: G. Erker, C. Krüger, G. Müller, *Adv. Organomet. Chem.* **1985**, *24*, 1−39. H. Yasuda, K. Tatsumi, A. Nakamura, *Acc. Chem. Res.* **1985**, *18*, 120−126.

[10] A. G. Massey, A. J. Park, F. G. A. Stone, *Proc. Chem. Soc. London* **1963**, 212. A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245−250. A. G. Massey, A. J. Park, *Organometallic Syntheses*, R. B. King, J. J. Eisch, Eds., Elsevier, New York, **1986**, Vol. 3, p. 461−462.

[11] For related reactions see e.g.: X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031.

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

[13] D. J. Brauer, C. Krüger, *Organometallics* **1982**, *1*, 207−210. G. Erker, K. Engel, U. Dorf, J. L. Atwood, W. E. Hunter, *Angew. Chem.* **1982**, *94*, 915−916; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 914−915. G. Erker, K. Berg, C. Krüger, G. Müller, K. Angermund, R. Benn, G. Schroth, *Angew. Chem.* **1984**, *96*, 445−446; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 455−456. E. J. Larson, P. C. Van Dort, J. S. Dailey, J. R. Lakanen, L. M. Pederson, M. E. Silver, J. C. Huffman, S. O. Russo, *Organometallics* **1987**, *6*, 2141−2146. G. Erker, K. Berg, K. Angermund, C. Krüger, *Organometallics* **1987**, 6, 2620−2621. E. J. Larson, P. C. Van Dort, J. R. Lakanen, D. W. O′Neill, L. M. Pederson, J. J. McCandless, M. E. Silver, S. O. Russo, J. C. Huffman, *Organometallics* **1988**, *7*, 1183−1187. G. Erker, *Angew. Chem.* **1989**, *101*, 411−426; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 397−412.

[14] Steric hindrance, as present in $Cp_2^*Zr[C_4H_6B(C_6F_5)_3]$ leads to similar structural features: J. Karl, G. Erker, R. Fröhlich, *J. Organomet. Chem.* **1997**, *535*, 59−62.

[15] H. H. Brintzinger, L. S. Bartell, *J. Am. Chem. Soc.* **1970**, *92*, 1105−1107. W. Lauher, R. Hoffmann, *J. Am. Chem. Soc.* **1976**,

98, 1729−1742. J. C. Green, *Chem. Soc. Rev.* **1998**, *27*, 263−271.

[16] After submission of this paper, a very similar structure of the PMe_3 stabilized *ansa*-metallocene complex $[Zr\{Me_2C(\eta\text{-}C_5H_4)_2\}(\eta^3\text{-}C_4H_6B(C_6F_5)_3)PMe_3]$ with bond lengths Zr−C1 2.464(5) Å, Zr−C2 2.527(5) Å, Zr−C3 2.613(6) Å, C1−C2 1.410(8) Å, C2−C3 1.384(8) Å, and Zr−P 2.748(2) Å (atom numbering scheme analogous as in Figure 1) was reported in the literature: J. C. Green, M. L. H. Green, G. C. Taylor, J. Saunders, *J. Chem. Soc., Dalton Trans.* **2000**, 317−327.

[17] E. G. Hoffmann, R. Kallweit, G. Schroth, K. Seevogel, W. Stempfle, G. Wilke, *J. Organomet. Chem*. **1975**, *97*, 183−202.

[18] G. S. Hammond, *J. Am. Chem. Soc*. **1955**, *77*, 334−338. See also: D. Fàrcasiu, *J. Chem. Educ.* **1975**, *52*, 76−79.

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

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