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Models for Solvation of Zirconocene Cations: Synthesis, Reactivity, and Computational Studies of Cationic Zirconocene Benzyl Compounds

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The reactions of the zirconocene compounds $[(\eta^5\text{-}C_5H_5)_2\text{-}Zr(CH_2C_6H_4R)_2]$ (R = F (**1**), CMe_3 (**2**), Me (**3**)) with either $B(C_6F_5)_3$ or the trityl salt $[Ph_3C]^+[B(C_6F_5)_4]^-$ in CD_2Cl_2 were monitored by NMR spectroscopy. In all cases, the cationic compound $[(\eta^5\text{-}C_5H_5)_2\text{-}Zr(\eta^2\text{-}CH_2C_6H_4R)]^+$ was obtained, irrespective of the activator used ($B(C_6F_5)_3$ or the trityl salt). Whereas NMR studies suggest a η^2-coordination of the benzyl ligand to the cationic zirconium metal, detailed DFT studies revealed that in CD_2Cl_2 this is only the case if one solvent molecule is coordinated via the lone pair of one chlorine to the metal. Without this coordination, a η^3-coordination is more likely to occur. Computed NMR shifts at the B3LYP/IGLO II level corroborate this observation, which is in concert with a detailed NBO analysis of the cationic zirconocene compounds.

Introduction

Group 4 metallocene compounds play an important role as catalyst precursors for the hydrogenation,[1] hydrosilylation, and polymerization of olefins.[2−11] In particular for alkene polymerization, these precursors need to be activated by a *cationic generating compound* (CGA) to form what is believed to be the active species $[\eta^5\text{-}Cp_2MR]^+$ (Cp = (substituted) cyclopentadienyl, M = Ti, Zr, Hf). Obviously, this rather "naked" ion does not exist by itself in solution; rather it is paired with a weakly coordinating ligand $[\eta^5\text{-}Cp_2MR^+\cdots D]$ (D = X^- (anion), monomer, solvent). Whereas much effort has gone into elucidating the role of the anion and the coordination of the monomer,[2,3,5,8,10,12−16] the role of the solvent acting as a ligand has, to the best of our knowledge, been less actively pursued, probably due to a lack of suitable model systems. We have recently developed such models for the polymerization of monomers such as ethene and propene.[17−19] We have noted a strong propensity of the attached arene ligand to coordinate to the cationic metal center. As metallocene-based catalysts are also known to polymerize styrene to syndiotactic polystyrene,[20] we wanted to extend our investigations of solvent adducts to cationic zirconocene compounds in this direction. Recent investigations in the mechanism of styrene polymerization suggest that secondary insertion into the metal−polymer bond is favored over primary insertion.[21] Concequently, we decided to use cationic zirconocene benzyl compounds, first reported by Jordan et al.,[22,23] as a model compound. To investigate any possible electronic effects, we introduced various substituents (F, Me, and CMe_3) in the *para*-position of the benzyl ligand. These prepared compounds were subjected to detailed low-temperature NMR studies and DFT investigations. A complete overview of the discussed zirconocene compounds and their synthesis is given in Scheme 1.

The paper is organized as follows: in part I of the Results and Discussion, the synthesis and the low-temperature multinuclear NMR studies of the zirconocene compounds $[(\eta^5\text{-}C_5H_5)_2\text{-}Zr(CH_2C_6H_4R)_2]$ (R = F (**1**), CMe_3 (**2**), Me (**3**)) with either $B(C_6F_5)_3$ or the trityl salt $[Ph_3C]^+[B(C_6F_5)_4]^-$ in CD_2Cl_2 are discussed. Part II reports the DFT investigations of the cationic compounds $[(\eta^5\text{-}C_5H_5)_2\text{-}Zr(CH_2C_6H_4R)]^+$ (R = F (**1c**), CMe_3 (**2c**), Me (**3c**)) and their corresponding dichloromethane adducts $[(\eta^5\text{-}C_5H_5)_2\text{-}Zr(CH_2C_6H_4R)ClCH_2Cl]^+$ (R = F (**1c-sol**), CMe_3 (**2c-sol**), Me (**3c-sol**)).

Results and Discussions

I. Experimental Investigations: (a) Preparation of the Metallocenes 1−3.

The zirconocene benzyl compounds **1−3**

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[1] Qian, Y.; Li, G.; Huang, Y. *J. Mol. Catal.* **1989**, *54*, L 19.

[2] Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270.

[3] Bochmann, M. *Top. Catal.* **1999**, *7*, 9−22.

[4] Bochmann, M.; Pindado, G. J.; Lancaster, S. J. *J. Mol. Catal. A: Chem.* **1999**, *146*, 179−190.

[5] Bochmann, M. *J. Organomet. Chem.* **2004**, *689*, 3982−3998.

[6] Brintzinger, H.-H.; Fischer, D.; Mühlhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem.* **1995**, *107*, 1255−1383.

[7] Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447.

[8] Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434.

[9] Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1995**, *127*, 144−187.

[10] Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345−354.

[11] Rempel, G. L.; Huang, J. *Prog. Polym. Sci.* **1995**, *20*, 459−526.

[12] Silanes, I.; Ugalde, J. M. *Organometallics* **2005**, *24*, 3233−3246.

[13] Vanka, K.; Ziegler, T. *Organometallics* **2001**, *20*, 905−913.

[14] Maccioni, A. *Chem. Rev.* **2005**, *105*, 2039−2073.

[15] Song, F.; Lancaster, S. J.; Cannon, R. D.; Schormann, M.; Humphrey, S. M.; Zuccacia, C.; Macchioni, A.; Bochmann, M. *Organometallics* **2005**, *24*, 1315−1328.

[16] Zuccaccia, C.; Stahl, N. G.; Macchioni, A.; Chen, M.-C.; Roberts, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 1448−1464.

[17] Sassmannshausen, J.; Green, J. C.; Stelzer, F.; Baumgartner, J. *Organometallics* 2006.

[18] Doerrer, L. H.; Green, M. L. H.; Häussinger, D.; Sassmannshausen, J. *J. Chem. Soc., Dalton Trans.* **1999**, 2111−2118.

[19] Bühl, M.; Sassmannshausen, J. *J. Chem. Soc., Dalton Trans.* **2001**, 79−84.

[20] Ishihara, N.; Seimiya, T.; Kuramono, M.; Uoi, M. *Polym. Prepr. Jpn.* **1986**, *35*, 240.

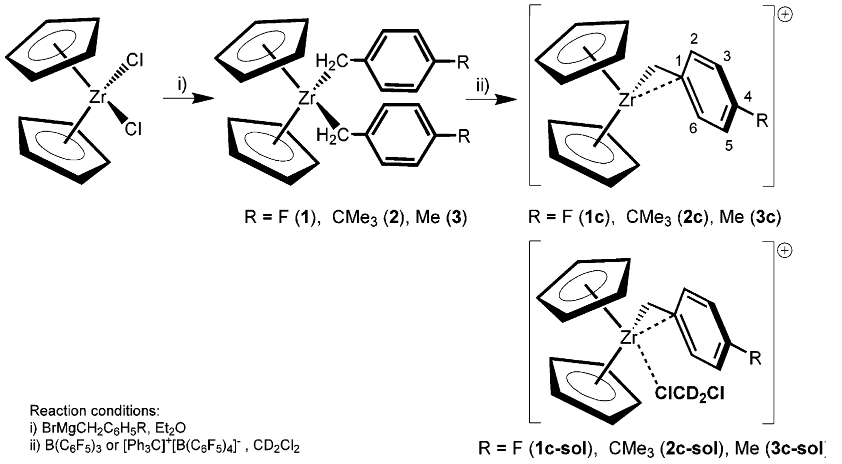
[21] Yang, J. H.; Huh, J.; Jo, W. H. *Organometallics* **2006**, *25*, 1144−1150.

[22] Jordan, R. F.; LaPointe, R. E.; Baenzinger, N. C.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539−1545.

[23] Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willet, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111−4113.

10.1021/om060538z CCC: \$33.50

Scheme 1

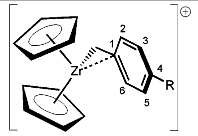
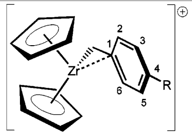


were synthesized according to a modified literature procedure.[24] Thus, zirconocene dichloride, purchased form Aldrich and used as received, was treated in diethyl ether with a large excess of a freshly prepared Grignard reagent, $(RC_6H_4CH_2)MgBr$ (R = F, CMe_3, Me). The large excess was required, as during the preparation of the Grignard the coupling product $(RC_6H_4CH_2)_2$ was obtained in various yields as a side-product. As the zirconocene benzyl compounds are known to be light sensitive, the benzylation was performed under exclusion of light. The compounds obtained are light organge to yellow microcrystalline compounds that are soluble in pentane and can be stored for a prolonged period of time under an inert atmosphere of nitrogen at −30 °C. Elemental analysis was also performed on the halides Cl and Br to check for remaining Grignard reagent or zirconocene dichloride.

The $^1J_{HC}$ coupling constant of 120 Hz for the CH_2 group, together with a characteristic low-field shift of the *ipso*-carbon of 148 ppm, suggests a η^1-bonded benzyl group.

(b) Low-Temperature NMR Spectroscopy Reaction Studies. All spectroscopic data for these studies are summarized in Table 1. The reaction of **1**−**3** with either $B(C_6F_5)_3$ or the trityl salt $[Ph_3C]^+[B(C_6F_5)_4]^-$ in CD_2Cl_2 at −60 °C was monitored by NMR spectroscopy. CD_2Cl_2 is the solvent of choice in these experiments, as it provides high solubility of the highly polar cationic products. Recently, the use of halogenated benzene has been reported as well. However, to compare our results with previously published data, we continued to use CD_2Cl_2, particularly as we have shown recently that aromatic solvents can coordinate to cationic zirconocene compounds.[17−19] In all cases the expected cation $[(\eta^5\text{-}C_5H_5)_2\text{-}Zr(\eta^2\text{-}CH_2C_6H_4R)]^+$ was observed. We did not observe any interaction of either anion ($[RC_6H_4CH_2B(C_6F_5)_3]^-$ or $[B(C_6F_5)_4]^-$) with the cation. The chemical shifts of the benzylic CH_2 group of around δ (^1H) 3.08 ppm and δ (^{13}C) 47 ppm, together with the observed shift of δ (^{13}C) 128 ppm for the *ipso*-carbon and the large $^1J_{CH}$ coupling constant of 147 Hz, fit very well with previous observations[23−25] and indicate a η^2-bonding mode of the phenyl group to the cationic zirconium center. The observered cationic compounds possess a mirror plane in the zirconium, CH_2, and *ipso*-carbon of the phenyl group, thus rendering the "top" and the "bottom" of the molecule identical. Therefore only one signal for the cyclopentadienyl ring and one signal for the *ortho*- and *meta*-carbon atoms were observed. We did not observe any influence of the *para* substituent in terms of reactivity.

Table 1. Observed Chemical Shifts for Cations 1c−3c

Cation 1c[a]	 R = F $[FC_6H_4CH_2B(C_6F_5)_3]^-$		 R = F $[B(C_6F_5)_4]^-$	
	^1H[b] δ(ppm)	^{13}C[c] δ(ppm)	^1H δ(ppm)	^{13}C δ(ppm)
Cp	6.24	112.5	6.24	110.8
CH_2	3.08	47.6	3.08	47.3
				($^1J_{CH}$ = 148.5 Hz)
Ph^1		128.5		128.5
$Ph^{2,6}$	7.00	137.1	6.80	137.2
$Ph^{3,5}$	7.10	118.5	7.20	118.5
Ph^4		165.2		165.4
Cation 2c[a]	R = CMe_3 $[Me_3CC_6H_4CH_2B(C_6F_5)_3]^-$		R = CMe_3 $[B(C_6F_5)_4]^-$	
Cp	6.18	110.5	6.20	110.4
CH_2	3.07	47.5	3.07	47.5
				($^1J_{CH}$ = 146.5 Hz)
Ph^1		128.9		128.7
$Ph^{2,6}$	7.14	128.3	7.14	130.9
$Ph^{3,5}$	7.37	124.1	7.32	125.7
Ph^4		156.8		156.8
CMe_3		34.5		34.5
C*Me*$_3$	1.17	31.4	1.20	31.3
Cation 3c[a]	R = Me $[MeC_6H_4CH_2B(C_6F_5)_3]^-$		R = Me $[B(C_6F_5)_4]^-$	
Cp	6.17	110.5	6.19	110.5
CH_2	3.03	47.8	3.03	47.8
				($^1J_{CH}$ = 147.0 Hz)
Ph^1		128.6		128.6
$Ph^{2,6}$	6.92	129.5	6.93	129.5
$Ph^{3,5}$	7.27	128.0	7.32	128.7
Ph^4		143.2		
Me	2.48	21.8	2.47	21.6

[a] In CD_2Cl_2 at −60 °C. [b] 270 MHz. [c] 67.8 MHz. Ph^n ($n = 1-6$) denotes hydrogens and carbons on the phenyl ring.

II. DFT Calculations. (a) Structural and NMR Shift Calculations. Having established the formation of the expected cationic benzyl compounds $[(\eta^5\text{-}C_5H_5)_2\text{-}Zr(\eta^2\text{-}CH_2C_6H_4R)]^+$, we performed detailed DFT calculations on the observed cations **1**−**3** to gain a deeper insight into the coordination nature of the η^2-bonding mode of the benzyl group. To validate our computational model, we used Jordan's solid-state structure of the cationic acetonitrile compound $[(\eta^5\text{-}C_5H_5)_2\text{-}Zr(\eta^2\text{-}CH_2C_6H_5)\text{-}NCCH_3]^+$ (**4**).[23] With the employed level of theory and basis set, we found a good agreement between the calculated and observed characteristic bond distances and angles (see Figure 1). An initial optimization of the unsubstituted zirconocene benzyl cation **5** yielded a structure with a η^3-coordinated benzyl

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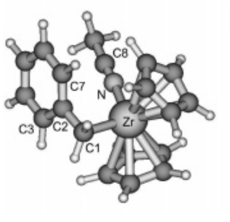
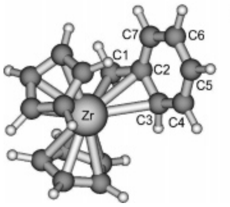
(24) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Maik, K. M. A. *Organometallics* **1994**, *13*, 2235−2243.

(25) Mintz, E. A.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4692.



	x-ray	calculated
d (Zr – C_1)	2.34 Å	2.34 Å
d (Zr – C_2)	2.65 Å	2.71 Å
d (Zr – C_3)	3.25 Å	3.37 Å
d (Zr – C_7)	3.24 Å	3.33 Å
d (Zr – N)	2.30 Å	2.31 Å
∠ (Zr – C_1 – C_2)	84.9°	87.3°
∠ (N – Zr – C_1)	115.1°	114.4°
∠ (C_1 – Zr – C_2)	33.3°	33.0°
∠ (C_8 – N – Zr)	173.5°	175.7°

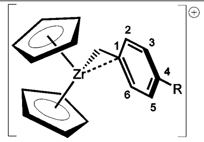
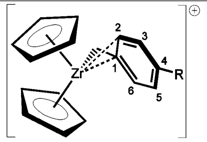
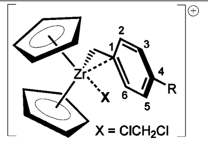
Figure 1. Comparison between calculated and solid-state structure of **4**.



	calculated	ref. 26
d (Zr – C_1)	2.34 Å	2.34 Å
d (Zr – C_2)	2.63 Å	2.70 Å
d (Zr – C_3)	2.65 Å	2.75 Å
d (C_1 – C_2)	1.47 Å	1.44 Å
d (C_2 – C_3)	1.43 Å	1.40 Å
d (C_2 – C_7)	1.42 Å	1.43 Å
∠ (H_3 – C_3 – C_6)	13.5°	9.6°
∠ (Zr – C_1 – C_2)	83.8°	87.6°
∠ /C_1 – C_2 – C_5)	170.4°	174.3°

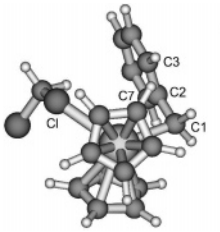
Figure 2. Calculates structure **5** and data taken from ref 26.

Table 2. Measured and Calculated ^{1}H and ^{13}C NMR Data of 5, 1c, and 1c-sol

						
Measured Shifts[a]			Calculated Shifts		Calculated Shifts	
	^{1}H δ (ppm)[b]	^{13}C δ (ppm)[c]	^{1}H δ(ppm)	^{13}C δ(ppm)	^{1}H δ(ppm)	^{13}C δ(ppm)
5	R = H[d]		R = H		R = H	
Cp	6.18	110.26	6.27	118.1	6.17	112.3
CH_2	3.97	47.49	3.76	64.8	3.41	53.5
Ph^1		121.17		145.7		126.4
Ph^2	6.99	128.26	7.17	98.2	7.43	142.1
Ph^3	7.42	130.62	7.06	139.8	7.57	130.4
Ph^4	7.52	130.71	7.61	131.9	7.47	132.5
Ph^5	7.42	130.62	8.01	138.3	7.47	131.7
Ph^6	6.99	128.26	7.84	141.2	7.02	137.6
1c	R = F		R = F		**1c-sol** R = F	
Cp	6.24	112.5	6.29	118.0	6.14	111.8
CH_2	3.08	47.6	3.73	64.5	3.25	50.9
Ph^1		128.5		140.2		120.2
Ph^2	7.00	137.1	7.11	100.2	7.17	140.9
Ph^3	7.10	118.5	6.70	123.6	7.05	117.0
Ph^4		165.2		169.3		169.6
Ph^5	7.10	118.5	7.70	127.1	7.15	119.3
Ph^6	7.00	137.1	7.81	144.2	7.04	141.5

[a] In CD_2Cl_2 at −60 °C, activated with $B(C_6F_5)_3$. [b] 270 MHz. [c] 67.8 MHz. [d] Values taken from ref 24. Ph^n ($n = 1-6$) denotes hydrogens and carbons on the phenyl ring.

group (Figure 2). This kind of "edge-on" coordination mode of the benzyl ligand has been observed before by Pellecchia for the cationic compound $[(\eta^5\text{-}C_5Me_5)Zr(\eta^3\text{-}CH_2C_6H_5)(\eta^7\text{-}CH_2C_6H_5)$ (**6**).[26] The structural features of **5** and **6** are very similar; relevant distances and angles are listed in Figure 2. Like **6**, **5** shows the characteristic bond length alteration of the asymmetric arene ring. The η^3-coordination of **5** is rather weak; only 3.07 kcal/mol is necessary for bond breaking and inversion of the configuration. As expected, the calculated chemical shifts of **5** do not fit well with the observed chemical shifts (Table 2). In particular, the calculated chemical shift for the CH_2 group of 64.8 ppm is in strong contrast to the observed chemical shift of 47.5 ppm.[24] Similar observations can be made for the *para*-substituted zirconocene benzyl compounds. For example, the calculated shift of the CH_2 group of **1c** of 64.5 ppm is in strong contrast to the observed shift of 47.6 ppm. Furthermore, as the calculated structures suggest a η^3-coordinated benzyl group whereas the observed NMR spectrum suggests a η^2-coordinated benzyl group in solution, we can draw the conclusion that these calculated structures do not represent the observed structure in solution. As all our low-temperature NMR studies were conducted in dichloromethane, we looked into the possibility of the coordination of one solvent molecule to the cationic metal center. Indeed, placing one molecule of dichloromethane in close proximity to the metal leads to a η^2-coordinated benzyl group with a dative chlorine−zirconium bond. The structural features of **5-sol** are in good agreement with those of **4** (Figure 3).



	calculated
d (Zr – C_1)	2.32 Å
d (Zr – C_2)	2.72 Å
d (Zr – C_3)	3.35 Å
d (Zr – C_7)	3.43 Å
d (Zr – Cl)	2.89 Å
∠ (Zr – C_1 – C_2)	88.5°
∠ (Cl – Zr – C_1)	120.2°
∠ (C_1 – Zr – C_2)	33.0°

Figure 3. Calculated structure of **5-sol**.

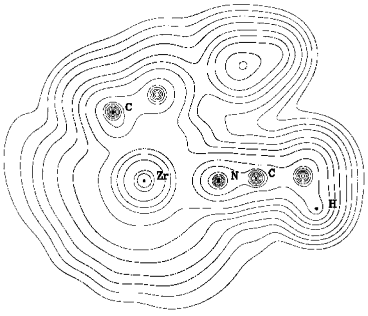


Figure 4. Density plot of **4**.

Now the calculated NMR shifts are in much better agreement with the observed values. For example, in the case of **1c**, the observed values for the CH_2 group are δ (^{1}H) 3.08 ppm and δ (^{13}C) 47.6 ppm, and the calculated values for **1c-sol** are 3.25 and 50.9 ppm, respectively (Table 2). We can conclude that in dichloromethane one solvent molecule is coordinated. A close inspection of the *ortho*- and *meta*-carbons of the aromatic ring reveal, however, some differences in the calculated values, indicating a different electronic environment of the corresponding atoms. We therefore investigated the electronic structure of the cations **1c**−**3c** and **1c-solv**−**3c-solv**.

(b) Electronic Investigations. To gain a detailed insight in the electronic structures of the cations **4**, **5**, and **5-solv**, we performed a Bader analysis on these compounds using the recommended Hay−Wadt basis set.[27] In particular, we wanted to investigate the nature of the coordinating ligand acetonitrile and dichloromethane. In the case of **4**, the total electron density plot through the Zr−N−C_{ipso} plane clearly indicates the coordination of the *ipso*-carbon to the cationic zirconium (Figure 4). As expected, in the case of **5** the η^3-coordination is clearly visible (Figure 5a). Most remarkable, the plots for **5-sol** and **4** are very similar, indicating not only that the coordination of the chlorine from the solvent to the cationic zirconium is similar to the coordination of acetonitrile, but also the benzyl group is coordinated in a similar fashion (Figure 5b). Bader analysis confirms the observed bonding modes and indicates that this bonding takes place not because of electrostatic interactions but due to Lewis-type bonds.

As Bader analysis does not tell us the orbitals involved in the bonding, we performed a more detailed NBO (natural bond

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[26] Pellecchia, C.; Immirzi, A.; Pappalardo, D.; Peluso, A. *Organometallics* **1994**, *13*, 3773−3775.

[27] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

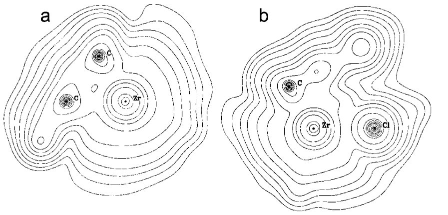

Figure 5. (a) Density plot of **5**. (b) Density plot of **5-solv**.

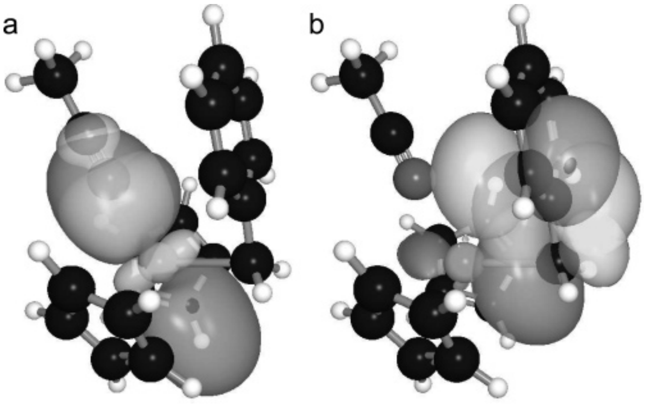

Figure 6. (a) Dative bond between lone pair of N and empty d orbital of Zr. (b) Back-bonding between Zr$-$C$_1$ bond and C$_2-$C$_3$ antibonding orbital.

orbital) analysis.[28] In **4**, we found that the lone pair of the nitrogen donates electron density into an empty orbital of the zirconium and forms a dative acetonitrile$-$zirconium bond. The second-order pertubation energy theory of the donor$-$acceptor energy was estimate to be 43.7 kcal/mol, indicating a rather strong bond. The Zr$-$C$_{ipso}$ bond back-bonds into the antibonding orbital between C$_{ipso}-$C$_{ortho}$. The engery was estimate to be 17.5 kcal/mol, much weaker than the dative bond of the acetonitrile bond (Figure 6, see Supporting Information for more detailed, colored plots).

In the case of **5** this bonding mode contributes 25.1 kcal/mol, which is significantly stronger than in the case of **4**. Additional bonding contribution is gained by two dative bonds between of the C$_{ipso}-$C$_{ortho}$ into an empty d orbital of the zirconium (14.2 and 5.1 kcal/mol) (Figure 7).

In **5-sol** the bonding situation is similar to **4**: a dative bond between a lone pair of the chlorine and an empty orbital of the zirconium of 39.4 kcal/mol and a back-bonding between the Zr$-$C$_{ipso}$ bond and the C$_{ipso}-$C$_{ortho}$ antibond (14.7 kcal/mol) (see Supporting Information). These values are similar to those computed for **4** and indicate that the solvent dichloromethane is bonded quite strongly to the cationic zirconium.

This back-bonding is particularly strong in the case of **5**, where no solvent molcule is donating electron density into empty d orbitals of the zirconium and consequently turning the phenyl ring in such a position to enable η^3-bonding rather than the expected η^2-bonding mode of the benzyl ligand.

Similar observations are made for the cationic compounds **1c**$-$**3c** and **1c-solv**$-$**3c-solv**. We did not observe any significant influence of the *para* substituent on the energies of these bonding modes.

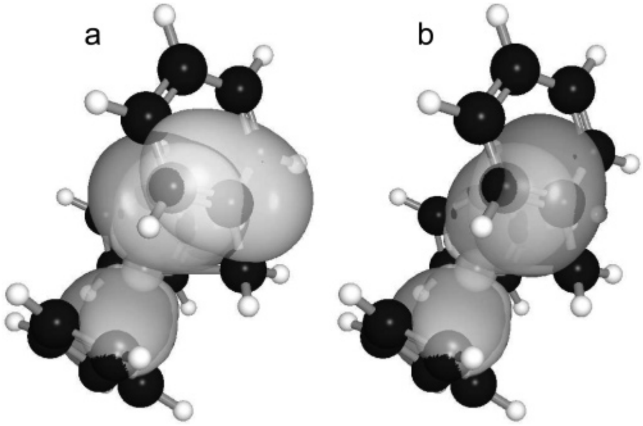

Figure 7. (a) Dative bonding between C$_2-$C$_3$ and empty d orbital of Zr. (b) Dative bonding between C$_2-$C$_3$ and empty d orbital of Zr.

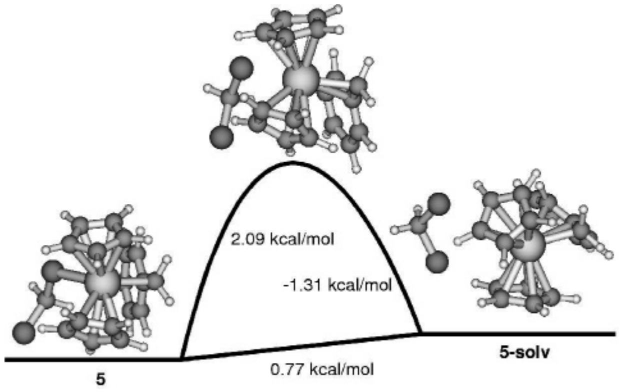

Figure 8. Reaction profile between **5** and **5-solv**.

(c) Computational Kinetic Investigations. Although the low-temperature NMR investigations suggest a η^2-coordination of the benzyl ligand and our computational studies suggest that this can only be achieved with one solvent molecule coordinating to the cationic zirconium, we did not find any evidence in the spectra for a coordinated solvent molecule. Therefore we can safely assume that even at low temperature this coordinated solvent molecule is rather labile, leading to rapid exchange between coordinated and noncoordinated solvent molecules. Indeed, kinetic studies on **5** support this. The small activation barrier of 2.09 kcal/mol and the very small energy difference between **5** and **5-solv** of 0.77 kcal/mol indicate facile exchange between both species (Figure 8). Given that in solution the solvent is in large excess, we can safely assume that **5** only exists in minute amounts in the NMR tube.

We investigated the possible reaction path between **5-solv** and **5** by moving the solvent in steps of 0.3 Å away from the zirconium. We located a transition state at a zirconium$-$chlorine distance of 3.64 Å. This transition state was confirmed by an intrinsic reaction coordinate (IRC) calculation.

Conclusion

Low-temperature NMR studies of *para*-substituted zirconocene benzyl compounds indicate the formation of cationic zirconocene benzyl compounds with the benyzl group bonded η^2 to the zirconium. We did not observe any coordination of the anion to the cation, as the same cation was obtained regardless of the activation with either (B(C$_6$F$_5$)$_3$ or the trityl salt [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$). From detailed DFT calculations, we obtained evidence that in solution one molecule of dichloromethane, the solvent, is coordinated to the cationic compound. This coordination is rather labile, and facial exchange between coordinated and free solvent molecules can be expected. The

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(28) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.G*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2001.

coordination is a dative bond from a lone pair of the chlorine to an empty orbital of the zirconium and is similar in engery to the corresponding acetonitrile compound **4**. Without the solvent, our calculations show that the benzyl group bonds η^3 to the zirconium, with strong dative bonds from the $C_{ispo}-C_{ortho}$ bonds into empty d orbitals of the zirconium. We can conclude that these solvent adducts may play an important role in the polymerization chemistry of styrene when dichloromethane is used as a solvent and the catalyst is a zirconocene compound.

Experimental Section

All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over sodium (toluene, low in sulfur), sodium/potassium alloy (diethyl ether, light petroleum, bp 40−60 °C, pentane), potassium (thf), and calcium hydride (dichloromethane). NMR solvents were dried over activated molecular sieves, freeze−thawed, and stored in Young's-Tap sealed ampules. All chemicals were purchased from Aldrich and used as received.

NMR spectra were recorded on a JEOL EX90FT or a JEOL EX270FT spectrometer and referenced to the residual proton solvent peak for ^{1}H. Chemical shifts are quoted in ppm relative to tetramethylsilane. ^{13}C NMR spectra were referenced with the solvent peak relative to TMS and were proton decoupled using a WALTZ sequence. CH-coupling constants were measured by a modified INEPT pulse sequence. Low-temperature NMR studies were conducted as previously reported.[17]

Computational Details. Density functional theory calculations were carried out using the GAUSSIAN03[29] program package, running on a Mandrake Linux Dual-Opteron or a Dual-Xeon system, respectively. Geometries have fully been optimized without symmetry constraints, involving the functional combinations according to Becke[30] (hybrid) and Lee, Yang, and Parr[31] (denoted B3LYP), with the corresponding valence basis set for Zr (Stuttgart−Dresden, keyword SDD in Gaussian) and standard 6-31G* basis set[32] for C, H, Cl, and F (denoted as ECP1). The stationary points and transition states were characterized as minima by analytical harmonic frequency (zero or one imaginary frequency, respectively), which were used without scaling for zero-point and thermal corrections.

Magnetic shieldings σ have been evaluated for the B3LYP/ECP1 geometries using a recent implementation of the GIAO (gauge-included atomic orbitals)-DFT method,[33] involving the same B3LYP level of theory, together with the recommended IGLO basis II[34] on C, H, and F. The former approach with this particular combination of functionals and basis sets has proven to be quite effective for chemical shift computations for transition metal complexes.[19] ^{1}H and ^{13}C chemical shifts have been calculated relative to benzene, with absolute shieldings for benzene $\sigma(^1H)$ 24.54 and $\sigma(^{13}C)$ 47.83 with the IGLO II basis set. The values for benzene were converted into the TMS scale using the experimental δ values of benzene (7.26 and 128.5 ppm, respectively). Tables of Cartesian coordinates of all calculated structures are available as electronic Supporting Information in *x*, *y*, *z* format. Bader analysis was performed using the Hay−Wadt all-electron basis set, and drawing of the electron charge density plots was performed using Xaim.[35] MOLDEN[36] was used for the chemical representation of the calculated compounds, and NBO-View for the representation of the orbitals.[28]

Preparation of the Grignard Reagent. Magnesium turnings (0.85 g, 35 mmol) were suspended in 70 mL of diethyl ether, and 30 mmol of the corresponding benzyl bromide was added under occasional ice-bath cooling. The reaction mixture was stirred for 2 h at room temperature and filtered.

This method was used in all preparations.

Preparation of $Cp_2Zr(CH_2C_6H_4F)_2$ (1). Zirconocene dichloride (1.45 g, 5 mmol) was added to the solution of *para*-fluorobenzylmagnesium bromide. The reaction mixture was stirred overnight, and the color changed from light yellow to orange. The volatiles were removed under reduced pressure to yield an orange residue. The residue was extracted into a mixture of 30 mL of PE and 30 mL of toluene. The solvent was removed under reduced pressure and re-extracted into 12 mL of PE and 16 mL of toluene. The extract was stored at −20 °C for one week, yielding orange and some white crystals. The crystals were separated manually. Only the orange crystals were recrystallized from a mixture of 10 mL of PE and 14 mL of toluene, yielding the desired compound as orange crystals. Yield: 150 mg (6.8%) Anal. Found: C, 63.26; H, 4.98; F, 8.38. Calcd for $C_{24}H_{22}F_2Zr$: C, 63.57; H, 5.04; F, 8.64. No halides (Cl or Br) were detected in the sample. ^{1}H NMR (90 MHz, $CDCl_3$, 29 °C) δ (ppm): 1.77 (s, 4 H, C*H*$_2$-Ph′); 5.93 (s, 10 H, Cp), 6.66−6.71 (m, 8 H, Ph′). ^{13}C NMR (270 MHz, CD_2Cl_2, 22 °C) δ (ppm): 58.9 (*C*H$_2$-Ph′); 112.5 (Cp); 114.9 (d, *m-C*-Ph′, $^2J_{CF} = 21$ Hz); 126.7 (d, *o-C*-Ph′, $^3J_{CF} = 7$ Hz); 148.2 (*ipso-C*-Ph′); 158.5 (d, *p-C*-Ph′, $^1J_{CF} = 238$ Hz).

Preparation of $Cp_2Zr(CH_2C_6H_4CMe_3)_2$ (2). Zirconocene dichloride (1.45 g, 5 mmol) was added to the rapidly stirred solution of 4-*tert*-butylbenzylmagnesium bromide. The reaction mixture was stirred overnight, and the color changed from light yellow to light orange. The volatiles were removed under reduced pressure to yield a light orange residue, which was extracted into a mixture of 30 mL of toluene and 30 mL of PE. The extract was concentrated and stored at −30 °C. After 4 weeks crystals were obtained, which were recrystallized from 12 mL of petroleum ether. Yield: 100 mg (3.9%). Anal. Found: C, 74.83; H, 7.76. Calcd for $C_{32}H_{40}Zr$: C, 74.50; H, 7.82. No halides (Cl or Br) were detected in the sample. ^{1}H NMR (270 MHz, CD_2Cl_2, 21 °C) δ (ppm): 1.29 (s, 18 H, C*H*$_3$); 1.77 (s, 4 H, C*H*$_2$-Ph′); 5.91 (s, 10 H, Cp); 6.72 (d, 4 H, *o-H*-Ph′); 7.17 (d, 4 H, *m-H*-Ph′). ^{13}C NMR (62.9 MHz, CD_2Cl_2, 21 °C) δ (ppm): 31.5 (C-*C*H$_3$); 34.3 (*C*-CH$_3$); 48.2 (*C*H$_2$-Ph′); 112.3 (Cp); 125.2 (*m-C*-Ph′); 129.0 (*o-C*-Ph′); 143.8 (*ipso-C*-Ph′); 150.2 (*p*-C-Ph′).

Preparation of $Cp_2Zr(CH_2C_6H_4Me)_2$ (3). Zirconocene dichloride (1.45 g, 5 mmol) was added to the rapidly stirred solution of 4-methylbenzylmagnesium bromide. The reaction mixture was stirred at room temperature overnight. The color changed from light

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(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Jr., J. A. M.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *GAUSSIAN03*; Gaussian, Inc., Pittsburgh, PA, 2004.

(30) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5642.

(31) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(32) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261.

(33) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497−5509.

(34) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR Basic Principles and Progress*; Springer-Verlag: Berlin, 1990; Vol. 23, pp 165−262.

(35) Ortiz, J. C.; Bo, C. *XAIM*; Universitat Rovira i Virgil: Tarragona. Spain.

(36) Schaftenaar, G.; Noordik, J. H. Molden: a pre- and post-processing program for molecular and electronic structures. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123−134.

yellow to orange. The volatiles were removed under reduced pressure to yield an orange residue, which was extracted twice into 40 mL of petroleum ether. Fractional crystallization at −30 °C yielded the byproduct 1,2-(*para*-methylphenyl)ethane, the Grignard reagent, and the desired product as orange crystals. Yield: 200 mg (9.2%). Anal. Found: C, 72.22; H, 6.66. Calcd for $C_{26}H_{28}Zr$: C, 72.33; H, 6.53. No halides (Br or Cl) were detected in the sample. ^{1}H NMR (270 MHz, CD_2Cl_2, 23 °C) δ (ppm): 1.69 (s, 4 H, C*H*$_2$-Ph′); 2.19 (s, 6 H, Bz-C*H*$_3$); 5.83 (s, 10 H, Cp); 6.66 (d, 4 H, *o-H*-Ph′); 6.88 (d, 4 H, *m-H*-Ph′). ^{13}C NMR (62.9 MHz, CD_2Cl_2, 23 °C) δ (ppm): 19.6 (Bz-*C*H$_3$); 58.8 (*C*H$_2$-Ph′); 111.2 (Cp); 124.7 (*m-C*-Ph′); 127.9 (*o-C*-Ph′); 148.0 (*ipso-C*-Ph′); 148.0 (*p-C*-Ph′).

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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