Coordination Chemistry of $\{[Zr]-Cl-[Zr]\}^+$ Complexes[‡]

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Treatment of the tris(cyclopentadienyl) cation (1^+) with zirconocene dichloride **2** gave, in almost quantitative yield, the 1:1 adduct 7^+, which was isolated with $[(CH_3)B(C_6F_5)_3]^-$ as the counterion. Reaction of 1^+ with the organometallic ligand Cp_3ZrCl afforded the 1:1 adduct 8^+, again isolated with $[(CH_3)B(C_6F_5)_3]^-$. The X-ray analysis revealed that 7^+ displays a strongly bent Zr–Cl–Zr coordination mode, in contrast to 8^+, which has a tendency to linear coordination. A theoretical analysis suggests that a subtle balance between steric and electronic factors determines the geometries in such organometallic adducts.

Introduction

We have recently investigated the coordination chemistry of the tris(cyclopentadienyl) zirconium cation $[Cp_3Zr]^+$ (1^+) and determined the crystal structures of several $[Cp_3Zr-L]^+$ adducts.[1] The transition metal cation 1^+ displays Lewis acid behavior and forms adducts with a variety of donor ligands, such as nitriles, isonitriles, or carbon monoxide. Further, it is known that catalytically important $[Cp_2ZrR]^+$ cations show a marked tendency to bind to their neutral $[Cp_2ZrR_2]$ precursors and related $[Cp_2ZrX_2]$ systems, yielding less active resting stages or dormant derivatives of their active metallocene catalyst systems.[2] It was tempting to find out whether the $[Cp_3Zr]^+$ cation (1^+) would react in a similar fashion as $[Cp_2ZrR]^+$ species and bind the neutral metallocene derivatives $[Cp_2ZrCl_2]$ (**2**) or $[Cp_3ZrCl]$ (**3**) despite its higher coordinative saturation.

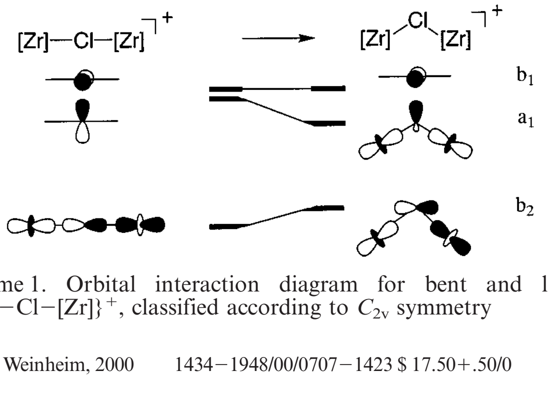
During the course of this investigation the question of the coordination geometry around the bridging Cl^- became of special interest. We were able to determine the structures of two similar $\{[Zr]-Cl-[Zr]\}^+$ cations, which in the solid state show very different bridging geometries. Only a few systems with unsupported $(Cp)_nZr-Cl-M$ bridges have been described in the literature. Two adducts between Cp_2ZrCl_2 and the Lewis acids AlR_3 [R = Cl, $C(CH_3)_3$] have been structurally characterized.[3] In these systems the bridging chloride and the two metal centers form $Zr-Cl-M$ bond angles τ of 126° and 149°, respectively.

Independent of our experimental work, we initiated a theoretical study on $\{[Zr]-Cl-[Zr]\}^+$ cations, based on density functional theory,[4] in which we examined various coordination geometries not only around the μ-Cl bridge, but also around the Zr center. We begin the discussion with our computational work before giving an account of our experimental results and comparing theory and experiment.

Results and Discussion

Theoretical Studies

Molecular Orbital Considerations: From a molecular orbital point of view, the question of the coordination geometry of $[R_3Zr-(\mu\text{-}Cl)-ZrR_3]^+$ complexes is related to the problem of the geometries of AH_2 molecules.[5] We can analyze the bonding angle τ by considering the interaction of two cationic metal fragments $[Zr]^+$ with a Cl^- ion. The LUMO of the metal fragment is in any case a Zr-based d_{z^2}-orbital and is independent of the coordination around the transition metal center, which might be planar or trigonal pyramidal. When interacting with the p-orbitals of the chloride ion, these orbitals have the same nodal characteristics as the 1s orbital of H, and we might consider $HClH^+$ as an isolobal analog of $\{[Zr]-Cl-[Zr]\}^+$. The three highest occupied orbitals of such a C_{2v} symmetric moiety are shown in Scheme 1, and the bent geometry would be stabilized due to the energetic lowering of the orbital a_1.



Scheme 1. Orbital interaction diagram for bent and linear $\{[Zr]-Cl-[Zr]\}^+$, classified according to C_{2v} symmetry

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[‡] Experimental work was carried out at the University of Münster, theoretical work at the University of Zürich.

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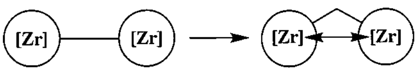
Thus, if the geometry of $\{[Zr]-Cl-[Zr]\}^+$ systems is determined by orbital interactions of the bridging fragments, we would predict a bent geometry for such molecules. The analysis is complicated, however, by the fact that the orbitals introduced above are normally not amongst the frontier orbitals of such systems. The highest occupied orbitals are usually based on ligands of the transition metal fragments. Bending also leads to an increase in steric repulsion, which then counteracts the electronic stabilization.[6]



In order to explore possible coordination geometries of $\{[Zr]-Cl-[Zr]\}^+$ systems, we choose $[ZrCl_3]^+$ ($\mathbf{4}^+$) and $ZrCl_4$ (**5**) as models for the adduct-forming reaction $R_3ZrCl + [ZrR_3]^+ \rightarrow \{[Zr]-Cl-[Zr]\}^+$. From these fragments, a variety of $[Zr_2Cl_7]^+$ ($\mathbf{6}^+$) complexes containing a single bridging μ-Cl$^-$ can be constructed. Our preliminary excursion led to the conclusion that a variety of coordination modes might be realized by $\{[Zr]-Cl-[Zr]\}^+$ systems, which coexists as local minimum structures.[7a] The predictions arising from the qualitative molecular orbital arguments are met,[7b] the energetic differences between linear and bent coordination, however, are fairly small. Keeping these results in mind, we now proceed with the analysis of complexes involving the $[Cp_3Zr]^+$ cation ($\mathbf{1}^+$).

Interaction of $\mathbf{1}^+$ with Organometallic Zirconium Chlorides: We begin with a brief introduction of the Zr fragments considered (Figure 1).

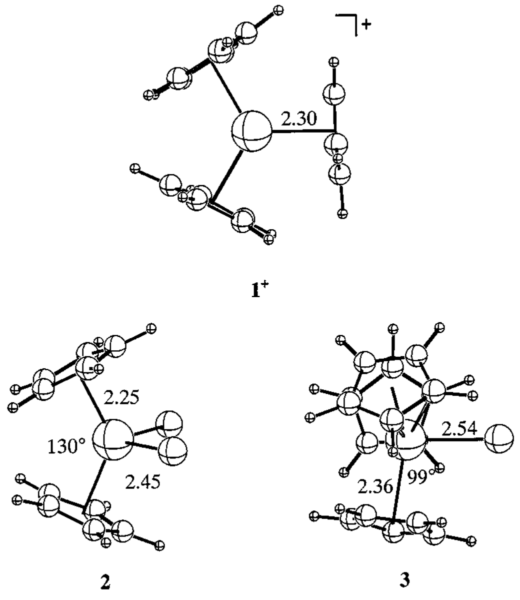
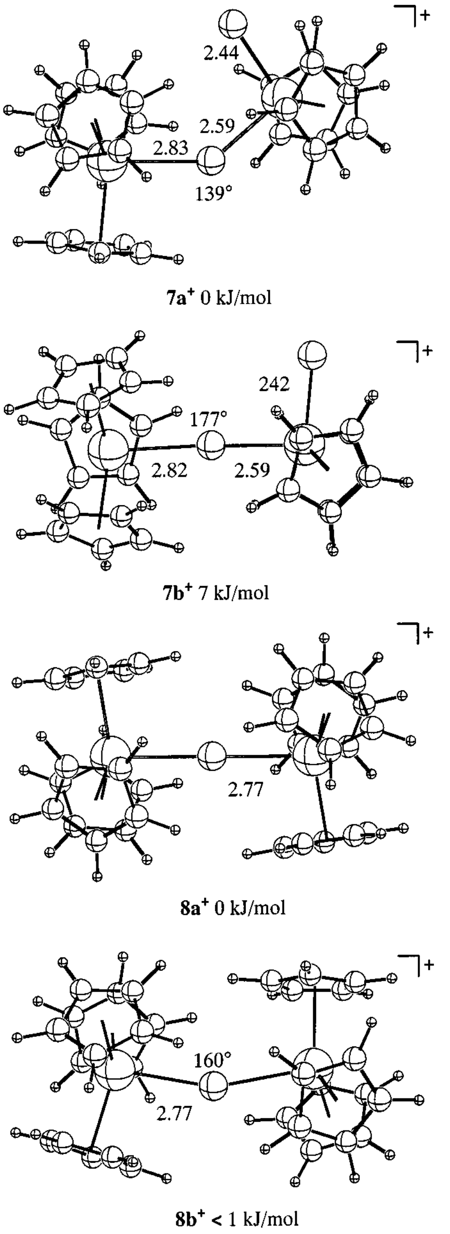


Figure 1. Optimized structures for the Zr-based building blocks $\mathbf{1}^+$, **2**, and **3**

The cation $\mathbf{1}^+$ has already been extensively studied.[1] An important feature is the planar coordination around the transition metal center. Whereas the structure of $[Cp_2ZrCl_2]$ (**2**) is well-known,[8] the geometry of complex $[Cp_3ZrCl]$ (**3**) has not yet been described. The system with ansa-cyclopentadienyl rings $[(CpCMe_2Cp)CpZrCl]$ that was reported by Green and co-workers[9] is similar to compound **3**. The calculated Zr−Cl bond in **3** is elongated by 0.09 Å compared to **2**, and it agrees very well with the experimental value of $d(Zr-Cl) = 2.536$ Å for Green's complex. The coordination of the Cp rings deviates only slightly from a planar arrangement, resulting in $\sigma_P = 352°$, with $\sigma_P = \Sigma <$ [Cp(centroid)−Zr−Cp(centroid)].

Two coordination geometries have been calculated for the complex $[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_2Cl]^+$ ($\mathbf{7}^+$) (Figure 2).



7a$^+$ 0 kJ/mol

7b$^+$ 7 kJ/mol

8a$^+$ 0 kJ/mol

8b$^+$ < 1 kJ/mol

Figure 2. Optimized linear and bent geometries for the cations $[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_2Cl]^+$ ($\mathbf{7}^+$), and $[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_3]^+$ ($\mathbf{8}^+$)

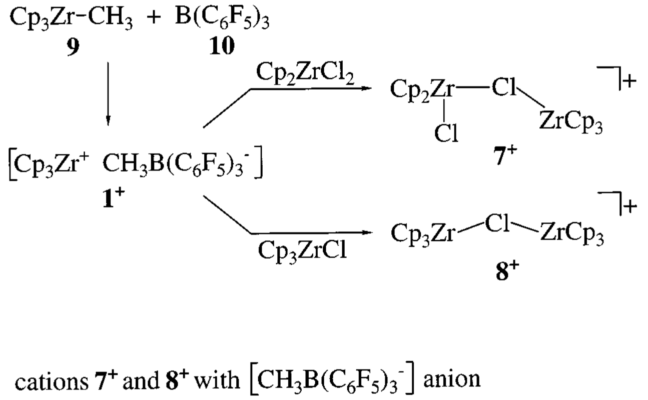
The geometric features of **7a$^+$** and **7b$^+$** are similar but again the bent complex **7a$^+$**, with $\tau = 139°$, is energetically more stable. The bending angle τ is larger than those found for the complexes **8** but the stabilization energy for bent coordination is of the same order of magnitude and is again rather small. Two different Zr−(μ-Cl) bond lengths are obtained, again with a longer bonding contact for the metal center coordinated in a planar fashion. The σ_P values in both cases are 354°, indicating that the coordination around the {Cp_3Zr} fragment is essentially planar.

The increase in steric bulk in $[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_3]^+$ (**8^+**) further lowers the energy difference between a bent and a linear coordination. The two calculated geometries **$8a^+$** and **$8b^+$** (Figure 2) are virtually identical in energy, with a marginal preference for the linear coordination.

The potential energy hypersurface around the Zr−Cl−Zr bending mode is very shallow, and one can expect that effects due to the nature of the counterion and crystal packing will influence the molecular arrangement of **8** in the solid state. All calculations indicate that τ can take on values that vary over a larger range and are influenced by the steric bulk of the interacting fragments. The crystal structure of the $Cp_2ZrCl_2-AlR_3$ adducts further support this observation. The Zr−(μ-Cl) separation is about 0.07 Å larger than the average obtained for both Zr−Cl distances calculated for **7^+**. Again, the σ_P values for all $ZrCp_3$ systems amount to 353°, and are close to the ideal value of 360° for a perfectly planar coordinated Zr.

Experimental Studies

The tris(cyclopentadienyl)zirconium cation (**1^+**) was generated in situ by treatment of $[Cp_3ZrCH_3]$ (**9**) with the strong organometallic Lewis acid tris(pentafluorophenyl)borane (**10**) and trapped by added zirconocene dichloride (**2**). The 1:1 adduct **7** was formed almost quantitatively (Scheme 2).



Scheme 2. Preparation of adducts **7** and **8** from the cation $[Cp_3Zr^+]$ (1^+)

Compound **7** is characterized by the occurrence of a pair of ^1H-/^{13}C-NMR Cp-resonances (2:3 intensity) at δ = 6.67, 6.24/118.2, 117.0 in addition to the signals of the separated $[CH_3B(C_6F_5)_3]^-$ anion. Single crystals of **7** suitable for X-ray crystal analysis were obtained from a saturated solution in dichloromethane at −30 °C. In the crystal the $[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_2Cl]^+$ cation (**7^+**) is well separated from the $[CH_3B(C_6F_5)_3]^-$ anion (shortest B−Zr distance: 7.142 Å). The cation **7^+** (Figure 3) features a Cp_3Zr subunit that is close to trigonal planar.

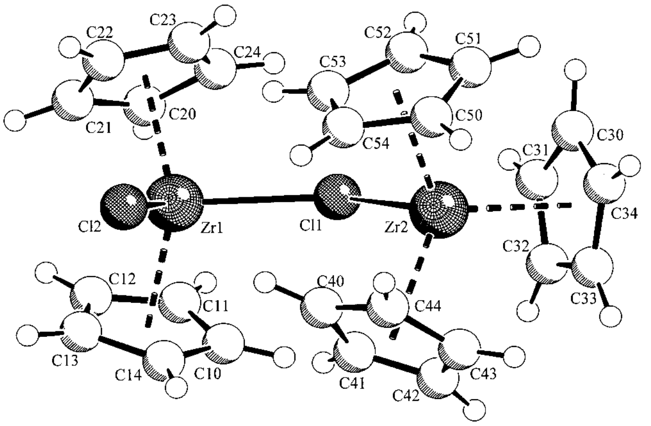


Figure 3. A view of the molecular geometry of the cation $[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_2Cl]^+$ (7^+), as obtained from X−ray crystal structure analysis. Selected bond lengths [Å] and angles [°]: Zr1−Cl1 2.544(1), Zr1−Cl2 2.405(1), Zr1−C(Cp1) 2.490, Zr1−Cp1 2.187, Zr1−C(Cp2) 2.480, Zr1−Cp2 2.190, Zr2−Cl1 2.722(1), Zr2−C(Cp3) 2.596, Zr2−Cp3 2.311, Zr2−C(Cp4) 2.576, Zr2−Cp4 2.290, Zr2−C(Cp5) 2.570, Zr2−Cp5 2.281; Cl1−Zr1−Cl2 95.80(4), Cl1−Zr1−Cp1 107.4, Cl1−Zr1−Cp2 104.0, Cl2−Zr1−Cp1 107.6, Cl2−Zr1−Cp2 106.6, Cp1−Zr1−Cp2 130.2, Zr1−Cl1−Zr2 137.15(5), Cl1−Zr2−Cp3 95.2, Cl1−Zr2−Cp4 99.8, Cl1−Zr2−Cp5 100.0, Cp3−Zr2−Cp4 117.7, Cp3−Zr2−Cp5 117.7, Cp4−Zr2−Cp5 118.3. Zr−C(Cp) is the average Zr−C distance between Zr and the C atoms of the Cp ring, Zr−Cp is the distance between the calculated centroid of the Cp ring zirconium

The sum of the corresponding Cp(centroid)−Zr−Cp(centroid) angles σ_P amounts to 353.7° (Cp3−Zr2−Cp4: 117.7°, Cp4−Zr2−Cp5: 118.3°, Cp3−Zr2−Cp5: 117.7°). The zirconium atom (Zr2) is located 0.333 Å above the plane of the Cp3 to Cp5 centroids. The $[Cp_2ZrCl_2]$ donor is coordinated to the $[Cp_3Zr^+]$ cation through one of its chloride ligands (Cl1). The Zr2−Cl1 vector is oriented normal to the Cp3 to Cp5 plane. The Zr2−Cl1 bond is rather long at 2.722(1) Å, which is markedly longer than the adjacent terminal Zr1−Cl2 linkage [2.405 (1) Å] of the bent metallocene unit. The remaining bonding features at the coordinated Cp_2ZrCl_2 unit are not exceptional [angle Cl2−Zr−Cl1: 95.80(4)°]. The adduct is strongly bent at the bridging μ-chloride ligand [angle Zr1−Cl1−Zr2: 137.15(5)°], and the substituents Cl2 and Zr(2)Cp_3 are found in a *syn*-periplanar orientation at the Zr1−Cl1 bond [dihedral angles Zr2−Cl1−Zr1−Cl2 7.50(8)°].

We also synthesized the $[Cp_3Zr-Cl]$ adduct of the $[Cp_3Zr]^+$ cation. In this case the salt $[Cp_3Zr^+ CH_3B(C_6F_5)_3^-]$ (**1**) was prepared and the organometallic ligand Cp_3Zr-Cl was added to it in CH_2Cl_2 at −60 °C (Scheme 2). Workup at ambient temperature furnished the adduct complex $\{[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_3]^+[CH_3B(C_6F_5)_3]^-\}$ (**8**). Complex **8** features a single ^1H-/^{13}C-NMR resonance at δ = 6.25 (30 H)/116.6 along with the anion methyl resonance at δ = 0.51 (3 H, broad)/10.5. Single crystals of **8** were again obtained from a saturated solution in dichloromethane at −30 °C.

The $[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_3]^+$ cation (**8^+**) contains two Cp_3Zr units that each feature an almost trigonal pyramidal arrangement of the three η^5 Cp ligands and the single bridging chloride around zirconium (Figure 4).

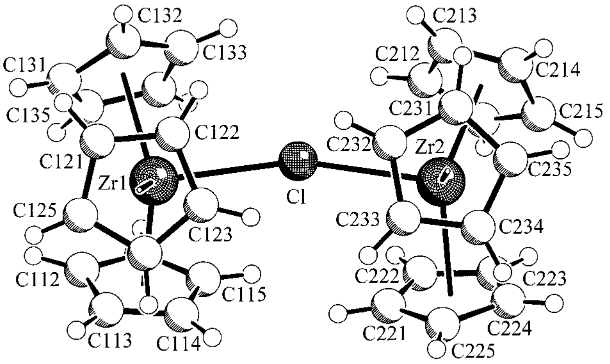


Figure 4. Molecular structure of 8^+ in the crystal. Selected bond lengths [Å] and angles [°]: Zr1−Cl 2.6918(6), Zr1−C(Cp11) 2.586, Zr−Cp11 2.296, Zr1−C(Cp12) 2.576, Zr1−Cp12 2.286, Zr1−C(Cp13) 2.586, Zr1−Cp13 2.297, Zr2−Cl 2.6893(6), Zr2−C(Cp21) 2.589, Zr2−Cp21 2.298, Zr2−C(Cp22) 2.582, Zr2−Cp22 2.291, Zr2−C(Cp23) 2.577, Zr2−Cp23 2.286; Cl−Zr1−Cp11 99.7, Cl−Zr1−Cp12 100.2, Cl−Zr1−Cp13 96.4, Cp11−Zr1−Cp12 117.5, Cp11−Zr1−Cp13 117.7, Cp12−Zr1−Cp13 117.9 Zr1−Cl−Zr2 160.88(2), Cl−Zr2−Cp21 97.9, Cl−Zr2−Cp22 99.1, Cl−Zr2−Cp23 99.8, Cp21−Zr2−Cp22 117.9, Cp21−Zr2−Cp23 117.4, Cp22−Zr2−Cp23 117.6. Nomenclature as described for Figure 3

The angle σ_P, as defined above, is 353.1° at Zr1 and 352.9° at Zr2. Again, the Zr−Cl vector is arranged almost normal to the respective Cp planes [Cp(centroid)−Zr−Cl angles at Zr1: 99.7°/100.2°/96.4°; at Zr2: 97.9°/99.1°/99.8°]. The Zr1−Cl bond length in **8** is 2.692(1) Å, which is almost identical to Zr2−Cl [2.689(1) Å], but both are slightly shorter that the $Cp_3Zr-(\mu\text{-}Cl)$ bond in **7** (see above). The Zr1−Cl−Zr2 angle in **8** is 160.88(2)°. This represents the most pronounced difference between the structures of the adducts **7** and **8**. The marked tendency of $[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_3]^+$ ($\mathbf{8}^+$) towards a linear Zr−Cl−Zr structure, in contrast to the strongly bent $[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_2Cl]^+$ ($\mathbf{7}^+$) framework, is in accord with the theoretical analysis and probably reflects the subtle balance of steric and electronic factors that eventually determines the structural features of such organometallic adducts of the C_{3v}-symmetrical Cp_3Zr^+ cation systems.

Comparison between Calculated Geometries and Experimental Structures

Both the X-ray crystal structure analyses, as well as the density functional calculations, result in the same molecular shape for $\mathbf{7}^+$ and $\mathbf{8}^+$. Measured and optimized bond angles are in good agreement for both cations. It is striking, however, that the calculated Zr−Cl distances are significantly overestimated by up to 0.09 Å in the calculation, as shown for $\mathbf{7}^+$ in Figure 5.

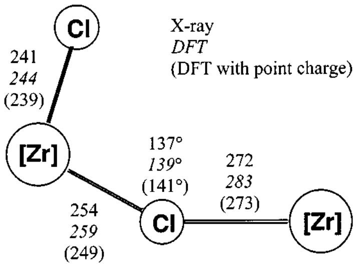


Figure 5. A comparison of the molecular framework of $\mathbf{7}^+$ obtained from crystal structure analysis and theoretical calculations

We performed additional calculations for this complex, including a negative point charge, which was located in space in close proximity to the position where the boron atom of the counterion would be found in the crystal. The Zr−Cl bonds shorten under the influence of the point charge, and are now in closer agreement to the value obtained from the X-ray structural analysis (Figure 5). The molecular environment has a significant influence on the molecular geometry of the cations for $\mathbf{7}^+$ and $\mathbf{8}^+$, especially concerning geometric parameters that are associated with the shallow potentials on the energy hypersurface.

Conclusion

In this work we have demonstrated that the tris(cyclopentadienyl)zirconium cation ($\mathbf{1}^+$) displays a similar coordination chemistry to the well studied $[Cp_2ZrR]^+$ species and is able to bind the neutral metallocene derivatives $[Cp_2ZrCl_2]$ (**2**) or $[Cp_3ZrCl]$ (**3**) as ligands. The X-ray crystal structure analyses revealed that the Zr−Cl−Zr bridging angle τ can take on values representing both a strongly bent and an almost linear coordination geometry. Our theoretical analysis suggests that a subtle balance between steric and electronic factors determines the geometries in such organometallic adducts.

Experimental Section

General Remarks: All reactions were carried out under argon using Schlenk-type glassware or in a glove-box. All solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under argon prior to use. Tris(pentafluorophenyl)borane (**10**),[10] $[Cp_3ZrCH_3]$ (**9**),[1] $[Cp_3ZrCl]$ (**3**),[11] and $[Cp_2ZrCl_2]$ (**2**)[12] were prepared as described in the literature. − M.p. DSC 2010 (TA Instruments). − IR spectra: Nicolet-5-DXC-FT IR spectrometer; $\tilde{\nu}$ in cm^{-1}. − NMR spectra: Bruker AC-200P (^{1}H 200 MHz, ^{13}C 50 MHz) and Bruker AM 360 (^{1}H 360 MHz, ^{13}C 75 MHz) spectrometer; δ in ppm. − Elemental analyses: Foss Heraeus CHNO Rapid.

$[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_2Cl]^+[CH_3B(C_6F_5)_3]^-$ (7): To a mixture of tris(η^5-cyclopentadienyl)methylzirconium (**9**) (80.0 mg, 0.27 mmol), tris(pentafluorophenyl)borane (**10**) (136 mg, 0.27 mmol) and zirconocene dichloride (**5**) (78.0 mg, 0.27 mmol) was added 15 mL of dichloromethane by means of vacuum distillation. The resulting yellow solution was allowed to warm up to room temperature with stirring. After stirring for an additional 10 min at room temperature the solvent was removed in vacuo to yield 285 mg (97%) of the orange-yellow salt **7**. Single crystals of **7** were obtained from a saturated dichloromethane solution at −30 °C, m.p. 171 °C (DSC, decomp.). − $C_{44}H_{28}BCl_2F_{15}Zr_2$ (1106): calcd. C 47.49, H 2.55; found C 46.68, H 2.72. − IR (KBr): $\tilde{\nu}$ = 3124 cm^{-1}, 2949, 1642, 1511, 1458, 1381, 1366, 1266, 1088, 1017, 978, 966, 952, 818, 740. − ^1H NMR (200.13 MHz, [D$_2$]dichloromethane, 300 K): δ = 6.67 (s, 10 H, Cp-*H*), 6.24 (s, 15 H, Cp-*H*), 0.51 (br s, 3 H, B−C*H*$_3$). − ^{13}C NMR (75.47 MHz, [D$_2$]dichloromethane, 300 K): δ = 148.8 (d, $^1J_{CF}$ = 238 Hz), 137.9 (d, $^1J_{CF}$ = 243 Hz), 136.9 (d, $^1J_{CF}$ = 251 Hz) and 129.8 [br, *o*-, *p*-, *m*- and *ipso*-B(C_6F_5)$_3$], 118.8 and 117.0 (each Cp), 10.5 (s, B−CH$_3$).

$[Cp_3Zr-(\mu\text{-}Cl)-ZrCp_3]^+[CH_3B(C_6F_5)_3]^-$ (8): A Schlenk flask was charged with tris (η^5-cyclopentadienyl)methylzirconium (**9**) (80.0 mg, 0.27 mmol) and tris(pentafluorophenyl)borane (**10**) (136 mg, 0.27 mmol). Dichloromethane (15 mL) was added and the resulting solution was cooled to −60 °C. At that temperature a cold solution of tris(η^5-cyclopentadienyl)chlorozirconium (**6**) (86.0 mg, 0.27 mmol) in dichloromethane (10 mL) was added. The reaction mixture was stirred for 10 min at −60 °C and then allowed to warm up to room temperature. The solvent was removed from the resulting pale yellow solution to yield 287 mg (95%) of **8**. Single crystals were obtained from a saturated dichloromethane solution at −30 °C, m.p. 159 °C (DSC, decomp.). − $C_{49}H_{33}BClF_{15}Zr_2$ (1135): calcd. C 51.83, H 2.93; found C 49.94, H 2.61. − IR (KBr): $\tilde{\nu}$ = 3125 cm^{-1}, 2959, 1642, 1510, 1458, 1366, 1267, 1087, 1010, 980, 963, 952, 845, 813, 737. − ^1H NMR (200.13 MHz, [D$_2$]dichloromethane, 300 K): δ = 6.25 (s, 30 H, Cp-*H*), 0.51 (br s, 3 H, B−C*H*$_3$). − ^{13}C NMR (75.47 MHz, [D$_2$]dichloromethane, 300 K): δ = 148.8 (d, $^1J_{CF}$ = 238 Hz), 137.9 (d, $^1J_{CF}$ = 243 Hz), 136.8 (d, $^1J_{CF}$ = 240 Hz) and 129.8 [br, *o*-, *p*-, *m*-, and *ipso*-B(C_6F_5)$_3$], 116.6 (Cp), 10.5 (s, B−CH$_3$).

Computational Details: Gradient-corrected density functional calculations were carried out with corrections for exchange and correlation according to Becke[13] and Perdew,[14] respectively (BP86). Geometries were optimized using the program system TURBOMOLE[15] within the framework of the RI-*J* approximation.[16] A triple ζ valence basis plus polarization (TZVP) was employed for all elements.[17]

X-ray Crystallographic Study: Data sets were collected with a Nonius Kappa CCD diffractometer, using a rotating anode generator FR591. Programs used: data collection: Collect;[18] data reduction: Denzo-SMN;[19] absorption correction: SORTAV;[20] structure solution: SHELXS-97;[21] structure refinement: SHELXL-97;[22] graphics: SCHAKAL.[23] X-ray crystal structure analysis of **7**: formula $C_{25}H_{25}Cl_2Zr_2 \cdot CH_3B(C_6F_5)_3 \cdot CH_2Cl_2$, M = 1190.74, 0.20 × 0.15 × 0.10 mm, a = 13.061(1), b = 13.431(1), c = 14.078(1) Å, α = 94.19(1), β = 109.85(1), γ = 104.51°, V = 2214.6(3) Å^3, $\rho_{calcd.}$ = 1.786 g cm^{-3}, μ = 8.10 cm^{-1}, empirical absorption correction ($0.855 \le T \le 0.923$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and phi scans, 23648 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.65 Å^{-1}, 10105 independent (R_{int} = 0.054) and 7131 observed reflections [$I \ge 2\,\sigma(I)$], 605 refined parameters, R = 0.057, wR^2 = 0.124, max. residual electron density 1.08 (−1.48) e Å^{-3}, hydrogens calculated and refined as riding atoms. X-ray crystal structure analysis of **8**: formula $C_{30}H_{30}ClZr_2 \cdot CH_3B(C_6F_5)_3$, M = 1135.45, 0.50 × 0.30 × 0.20 mm, a = 15.142(1), b = 12.601(1), c = 22.401(1) Å, β = 94.00(1)°, V = 4263.8(5) Å^3, $\rho_{calcd.}$ = 1.769 g cm^{-3}, μ = 6.55 cm^{-1}, empirical absorption correction ($0.735 \le T \le 0.880$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and phi scans, 33512 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.71 Å^{-1}, 12912 independent (R_{int} = 0.037) and 10797 observed reflections [$I \ge 2\,\sigma(I)$], 614 refined parameters, R = 0.035, wR^2 = 0.083, max. residual electron density 0.91 (−0.75) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Structural drawings of **7**$^+$ and **8**$^+$ displaying thermal ellipsoids are provided as supporting information.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137524 and 137525. 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 (0)1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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[7] [7a] Consult the supporting information for optimized geometries and relative energies of complexes **4**$^+$, **5**, and **6**$^+$.[7b] Besides the σ_{pd}-type orbital interaction as discussed in Scheme 1, we also considered additional π_{pd}-type interactions. An overlap population analysis for a bent and a linear system, however, indicated that these secondary interactions are not dominant in determining the angular dependence of the coordination geometry around the μ-Cl bridge.

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