# Stabilization of a Planar-Tetracoordinate Carbon Center in an Organometallic Complex Containing both a Zirconocene and a Hafnocene Moiety

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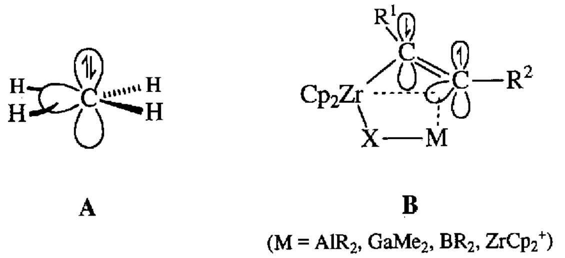
Received October 17, 1995

**Key Words:** Planar-tetracoordinate carbon atoms / Metallocene cations, methyl / Metallocene complexes, alkynyl group-4

The methylhafnocene cation **2a** reacts with bispropynylzirconocene to give a single regioisomeric planar-tetracoordinate carbon compound (**4a**) that contains the hafnium atom singly-bonded and the zirconium center $\eta^2$-coordinated to the bridging $\mu$-($\eta^1$-C:$\eta^2$-C,C-2-butyne) ligand. However, the reaction between the methylzirconocene cation **2b** with bis(phenylacetylide)hafnocene (**3b**) gives the pure regioisomer **4b** with an opposite relative arrangement of the two group 4 transition metals (the methyl is at the planar-tetracoordinate carbon atom C2). Complex **4a** was characterized by an X-ray crystal structure analysis.

Planar-tetracoordinate carbon is $sp^2$ hybridized; it contains an electron-deficient $\sigma$ system (six electrons making a total of four bonds) and an occupied *p* orbital oriented normal to the $\sigma$-plane (**A**)[1]. A closely related situation is found in the dimetallic complexes **B** where a planar-tetracoordinate carbon atom is part of a double bond and features two "normal" two-center-two-electron bonds to the neighbouring carbon atoms in addition to a three-center-two-electron bonding situation connecting it to two adjacent metal centers[2].

Scheme 1

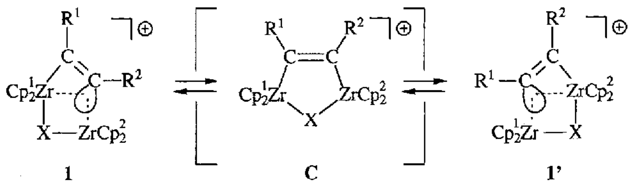


**A** **B**

(M = $AlR_2$, $GaMe_2$, $BR_2$, $ZrCp_2^+$)

The cationic dizirconium complexes **1** exhibit a dynamic behaviour that leads to an exchange of the zirconocene units[3]. This intramolecular rearrangement is rapid on the NMR time scale and is probably proceeding through a $C_{2v}$ symmetric transition state geometry (**C**). Two important consequences arise from this situation: a) the activation barrier of the $\mathbf{1} \rightleftharpoons \mathbf{1'}$ rearrangement may serve as a measure of the stabilization energy of planar-tetracoordinate (as opposed to planar-tricoordinate) carbon in this specific environment, and b) equilibrium mixtures of complexes **1** and **1'** are usually obtained synthetically, since the rather low rearrangement barrier (e.g. $\Delta G^{\neq}$ (250 K) $\approx$ 12 kcal mol$^{-1}$, $R^1 = R^2 = CH_3$, X = $C{\equiv}CCH_3$) forces the system into a regime of thermodynamic control[4].

Scheme 2



**1** **C** **1'**

The equilibrium situation is remarkably sensitive to steric and electronic effects of the alkenyl substituents $R^1$ and $R^2$ and of the substituents at the Cp rings of the metallocene systems[4]. To achieve an even more complete picture of this interesting equilibrium situation of planar-tetracoordinate carbon complexes it was desirable to learn about the influence of the involved metals themselves. Therefore, we have substituted one of the zirconium centers by hafnium and determined the favoured equilibrium situation for two representative situations.

The bis-zirconocene complexes **1** (with X = $C{\equiv}C{-}R$) were prepared by reacting the methylzirconocene cation (employed as the THF adduct[5], $BPh_4^-$ counterion) with the $Cp_2Zr(-C{\equiv}C{-}R)_2$ reagents[6]. Consequently, we have now treated bis(propynyl)zirconocene (**3a**) with $[Cp_2HfCH_3(THF)^+BPh_4^-]$ (**2a**). The reaction takes place readily at ambient temperature in bromobenzene, and we obtained a single reaction product (**4a**) that was isolated in >70% yield.

Complex **4a** exhibits a single set of NMR resonances at high as well as low temperature. Thus we conclude that only one regioisomer is present at equilibrium conditions. In the $^1$H-NMR spectrum, **4a** exhibits two Cp singlets, each rep-

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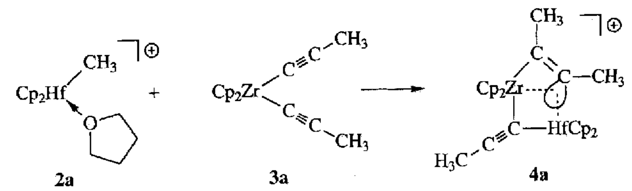
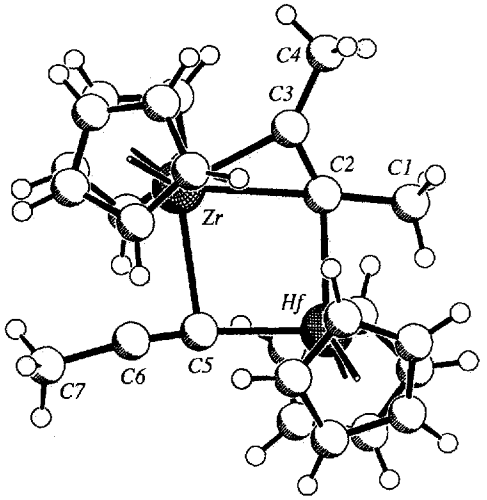
Scheme 3



resenting 10 hydrogen atoms, at $\delta = 5.88$ and 5.78 (in $CD_2Cl_2$ at 300 K), and there are three methyl resonances ($\delta = 2.51$, 2.34, and 0.00). Similarly, one observes two Cp resonances in the $^{13}C$-NMR spectrum at $\delta = 109.7$, 109.3, and there are three methyl resonances at $\delta = 29.1$ ($^1J_{CH} = 137$ Hz), 10.2 ($^1J_{CH} = 132$ Hz), and $-21.4$ ppm ($^1J_{CH} = 130$ Hz). The latter chemical shift is typical of a $CH_3$ group in the sterically rather confined arrangement at the planar-tetracoordinate carbon atom. The quaternary carbon resonances appear at $\delta = 217.1$ (C3, numbering scheme used as in Figure 1), 129.5, 122.6, and 114.7.

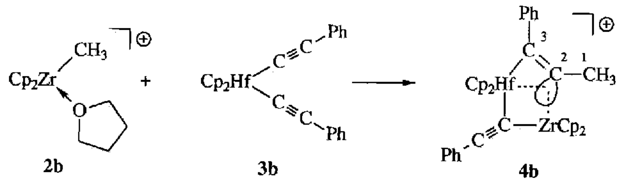
These NMR data reveal that there is only a single isomer present in solution. Which of the two possibilities (Hf $\eta^1$-bonded to C2 or $\eta^2$-coordinated to C2/C3) is favoured, unfortunately cannot be decided from these data. We have obtained single crystals of complex **4a** and found that the regioisomer featuring the hafnium atom in the "south-east position" is the favoured isomer present in the solid state. The X-ray crystal structure analysis also shows that the carbon atom C2 is indeed planar-tetracoordinate, exhibiting short contacts to its neighbours C1, C3, Zr and Hf in a singular plane. The central framework of complex **4a** is very similar to that found for the related [$\mu$-($\eta^1$:$\eta^2$-2-butyne)($\mu$-propynyl)$(ZrCp_2)_2^+$ $BPh_4^-$] complex that we have recently described in the literature[4]. In **4a** the "semibridging" $\mu$-propynyl ligand[7] is $\eta^1$-coordinated to the hafnocene unit, and it is also leaning toward the adjacent $Cp_2Zr$ moiety. Further details of the structure of complex **4a** shall not be discussed due to the rather large R value (>8%) of the X-ray crystal structure analysis.

Figure 1. A view of the molecular structure of complex **4a** (cation only) with atom numbering scheme. Selected bond lengths (Å) and angles (°): C2−Hf 2.32(2), C2−C1 1.52(3), C2−C3 1.29(3), C2−Zr 2.49(2), Zr−C3 2.17(2), Zr−C5 2.49(2), Zr−C6 2.75(2), Hf−C5 2.20(2), C5−C6 1.18(2), C6−C7 1.52(3), Zr−C2−Hf 94.8(7), Zr−C2−C3 60.6(12), C3−C2−C1 122(2), C1−C2−Hf 82.7(12), Hf−C5−Zr 97.7(7), Hf−C5−C6 172(2), C5−C6−C7 171(2), Zr−C5−C6 90(2), Zr−C3−C2 88.2(14), C2−Zr−C5 78.7(6), C2−Hf−C5 88.8(7)



In order to estimate how pronounced the thermodynamic-directing regiochemical effect of the introduced hafnium center might be, we carried out an additional experiment. From work on the corresponding dizirconium cation series, we had learned that there is a pronounced regiochemical substituent effect at the $\mu$-($\eta^1$:$\eta^2$-alkyne) ligand. Phenyl groups want to be at C3 and the small methyl substituents prefer to be placed at the planar-tetracoordinate carbon atom C2 (numbering scheme used as in Figure 1). In a suitably designed experiment we countered the regiochemical preference of a phenyl substituent with the aptitude of hafnium to end up in the "south-east position" of the dinuclear $\mu$-hydrocarbyl metallocene cation framework. For this purpose we have treated bis(phenylacetylide)hafnocene **3b** with the methylzirconocene cation, employed as the $[Cp_2ZrCH_3(THF)^+$ $BPh_4^-]$ reagent (**2b**). This reaction gave a single organometallic product (**4b**) that was isolated in close to 80% yield. Complex **4b** is characterized by $^1H$-NMR Cp resonances at $\delta = 6.06$ and 5.88 and a methyl singlet at $\delta = 0.33$. The corresponding $^{13}C$-NMR methyl resonance appears at $\delta = -11.6$. This is a typical feature of a methyl substituent at the planar-tetracoordinate carbon center in this general complex framework. In addition, it is well-established that there is a highly pronounced memory effect operative in the formation of the dimetallic cation complexes of type **4**, leading exclusively to product formation where the alkynyl groups and metallocene units introduced by any specific reagent tend to stay as closely together as possible[4]. Therefore, the product obtained contains the zirconium atom placed adjacent to the $CH_3$ substituent at the planar-tetracoordinate carbon center C2, that is, in the "south-east position"; whereas, in this case, the hafnium atom must be $\eta^2$-C2,C3-coordinated to the bridging $PhCCCH_3$ ligand.

Scheme 4



We thus conclude that the regiochemical substituent effect at the $\mu$-alkyne ligand is strong enough to override the directing metal effect that has led to the selective positioning of the hafnium atom into the "south-east position" of the metallacyclic framework of complex **4a** under equilibrium conditions. Therefore, it seems that the influence of a variation of the group 4 metal centers, as introduced here, leads to effects that may, in specifically selected cases, be pronounced (e.g. as has become evident in the selective formation of **4a**). But in a more general comparison this must be regarded as a rather small influence, that is, less pronounced than the "disturbance" introduced by the choice of organic substituents at the dimetallabicyclic framework.

Financial support from the *Fonds der Chemischen Industrie*, the *Volkswagen-Stiftung* and the *Alfried Krupp von Bohlen und Halbach-Stiftung* is gratefully acknowledged. S. K. thanks the *Academy of Finland* for a postdoctoral fellowship.

## Experimental

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. The starting materials **2a, b** and **3a, b** were prepared according to literature procedures[5,6]. For additional general information including a listing of equipment used for physical characterization of compounds see ref.[4].

*Preparation of* **4a**: The methylhafnocene cation reagent **2a** (1.50 g, 2.10 mmol) was stirred together with 700 mg (2.34 mmol) of bispropynylzirconocene **3a** at room temperature in a solvent mixture containing 50 ml of bromobenzene and 10 ml of dichloromethane. The solution was then concentrated in vacuo to a volume of 40 ml. The precipitated product was collected by filtration, washed with 30 ml of toluene and dried in vacuo to give 1.43 g (72%) of **4a**, m.p. 139 °C (dec., DSC). $^1$H NMR (200 MHz, 300 K, $CD_2Cl_2$): $\delta$ = 5.88 (s, 10H, Cp), 5.78 (s, 10H, Cp), 2.51 (s, 3H, $CH_3$), 2.34 (s, 3H, $CH_3$), 0.00 (s, 3H, $CH_3$), 7.40–7.30 (m, 8H), 7.10–7.00 (m, 8H), 7.00–6.84 (m, 4H, $BPh_4^-$). $^{13}$C NMR (50 MHz, 300 K, $CD_2Cl_2$): $\delta$ = 217.1 (C3), 129.5, 122.6, 114.7 (q. C), 109.7, 109.3 (Cp), 29.1 ($^1J_{CH}$ = 137 Hz, $CH_3$), 10.2 ($^1J_{CH}$ = 132 Hz, $CH_3$), −21.4 ($^1J_{CH}$ = 130 Hz, $CH_3$), 163.4 ($^1J_{BC}$ = 50 Hz), 136.4 ($^1J_{CH}$ = 153 Hz), 126.0 ($^1J_{CH}$ = 154 Hz), 122.2 ($^1J_{CH}$ = 157 Hz, $BPh_4^-$). IR (KBr): $\tilde{\nu}$ = 3094, 3053, 2981, 2067 (C≡C), 1578, 1570, 1476, 1441, 1426, 1067, 1016, 815, 791, 743, 733, 705, 607 cm$^{-1}$. – $C_{51}H_{49}BHfZr$ (942.47): C 65.00, H 5.24; found C 64.05, H 5.07.

*X-ray Crystal Structure Analysis of* **4a**: single crystals were obtained by letting toluene slowly diffuse into a solution of **4a** in dichloromethane. $C_{51}H_{49}BZrHf \cdot 1.5\ CH_2Cl_2$ (1069.81), crystal size 0.60 × 0.30 × 0.05 mm, $T$ = 223(2) K, $\lambda$ = 0.71073 Å, monoclinic, space group *C2/c* (No. 15), cell parameters $a$ = 34.547(5) Å, $b$ = 13.535(3) Å, $c$ = 23.332(4) Å, $\beta$ = 124.23(1)°, $V$ = 9020(3) Å$^3$, $Z$ = 8, $\rho_{calcd.}$ = 1.576 gcm$^{-3}$, $\mu$ = 2.74 mm$^{-1}$, 6008 collected reflections, 5892 independent and 2943 observed reflections, full matrix least squares refinement on $F^2$, $R$ = 0.082, $wR^2$ = 0.190, programs used: SHELX86, SHELX93, SCHAKAL. Further information about the X-ray structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404412, the names of the authors, and the journal citation.

*Preparation of* **4b**: The methylzirconocene cation reagent **2b** (800 mg, 1.24 mmol) was stirred with 760 mg (1.49 mmol) of **3b** in 50 ml of bromobenzene for 18 h at ambient temperature. The precipitate formed was collected by filtration, washed with 30 ml of toluene, then 10 ml of pentane and dried in vacuo to give 1.06 g (78%) of **4b**, m.p. 149 °C (dec., DSC). $^1$H NMR (360 MHz, 300 K, $CD_2Cl_2$): $\delta$ = 7.90–7.20 (m, 10H, Ph), 6.06 (s, 10H, Cp), 5.88 (s, 10H, Cp), 0.33 (s, 3H, $CH_3$). $^{13}$C NMR (90 MHz, 300 K, $CD_2Cl_2$): $\delta$ = 218.1 (C3), 151.0, 149.9 (q. C, aromatic), 134.5, 133.8, 131.2, 130.5, 129.5, 126.9, 125.5 (Ph), 122.8, 120.0 (q. C), 112.0, 108.9 (Cp), −11.6 ($^1J_{CH}$ = 130 Hz, $CH_3$), 164.5 ($^1J_{CB}$ = 50 Hz), 136.4 ($^1J_{CH}$ = 153 Hz), 126.0 ($^1J_{CH}$ = 154 Hz), 122.2 ($^1J_{CH}$ = 157 Hz, $BPh_4^-$). – IR (KBr): $\tilde{\nu}$ = 3089, 3054, 3043, 3029, 3000, 2981, 2062, 1579, 1481, 1440, 1428, 1019, 813, 736, 614 cm$^{-1}$. $C_{62}H_{53}BHfZr$ (1066.61): C 68.69, H 5.01; found C 67.01, H 4.88.

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[1] R. Hoffmann, R. W. Alder, C. F. Wilcox, Jr., *J. Am. Chem. Soc.* **1970**, *92*, 4992; R. Hoffmann, *Pure Appl. Chem.* **1971**, *28*, 181. See also: J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, J. A. Pople, *J. Am. Chem. Soc.* **1976**, *98*, 5419.

[2] G. Erker, R. Zwettler, C. Krüger, R. Noe, S. Werner, *J. Am. Chem. Soc.* **1990**, *112*, 9620. G. Erker, M. Albrecht, C. Krüger, S. Werner, *Organometallics* **1991**, *10*, 3791. M. Albrecht, G. Erker, M. Nolte, C. Krüger, *J. Organomet. Chem.* **1992**, *427*, C21. G. Erker, M. Albrecht, S. Werner, M. Nolte, C. Krüger, *Chem. Ber.* **1992**, *125*, 1953. G. Erker, M. Albrecht, C. Krüger, S. Werner, P. Binger, F. Langhauser, *Organometallics* **1992**, *11*, 3517. G. Erker, M. Albrecht, C. Krüger, S. Werner, *J. Am. Chem. Soc.* **1992**, *114*, 8531. P. Binger, F. Sandmeyer, C. Krüger, G. Erker, *Tetrahedron* **1995**, *51*, 4277. Theoretical study: R. Gleiter, I. Hyla-Kryspin, S. Niu, G. Erker, *Organometallics* **1993**, *12*, 3828. R. Gleiter, I. Hyla-Kryspin, S. Niu, G. Erker, *Angew. Chem.* **1993**, *105*, 753; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 754. Reviews: G. Erker, *Comments Inorg. Chem.* **1992**, *13*, 111. G. Erker, *Nachr. Chem. Techn. Lab.* **1992**, *40*, 1099. M. Albrecht, G. Erker, C. Krüger, *Synlett* **1993**, 441.

[3] G. Erker, D. Röttger, *Angew. Chem.* **1993**, *105*, 1691; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1623. See also: A. D. Horton, A. G. Orpen, *Angew. Chem.* **1992**, *104*, 912; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 876.

[4] D. Röttger, G. Erker, R. Fröhlich, M. Grehl, S. J. Silverio, I. Hyla-Kryspin, R. Gleiter, *J. Am. Chem. Soc.* **1995**, *117*, 10503.

[5] R. J. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325, and references cited therein.

[6] G. Erker, W. Frömberg, R. Benn, R. Mynott, K. Angermund, C. Krüger, *Organometallics* **1989**, *8*, 911.

[7] G. Erker, W. Frömberg, R. Mynott, B. Gabor, C. Krüger, *Angew. Chem.* **1986**, *98*, 456. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 463. P. N. V. P. Kumar, E. D. Jemmis, *J. Am. Chem. Soc.* **1988**, *110*, 125. G. Erker, M. Albrecht, C. Krüger, M. Nolte, S. Werner, *Organometallics* **1993**, *12*, 4979, and references cited therein.

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