

Formation of stable organometallic planar-tetracoordinate carbon compounds containing a cationic $(\mu\text{-R}^1\text{CCR}^2)[\mu\text{-chloro}(\text{ZrCp}_2)_2]$ framework

Dirk Röttger, Gerhard Erker^{*}, Roland Fröhlich

Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität Münster, Corrensstr. 40, D-48149 Münster, Germany

Received 22 December 1995

Abstract

The methylzirconocene cation $[\text{Cp}_2\text{ZrCH}_3(\text{THF})^+\text{BPh}_4^-]$ reacts with $\text{Cp}_2\text{Zr}(\text{Cl})(\text{C}\equiv\text{C}-\text{R})$ reagents (**5a–c**, $\text{R} = -\text{CH}_2\text{Ph}$, $-\text{CH}_2\text{CH}_2\text{CH}_3$, $-\text{CH}_3$) to yield the dinuclear metallocene cations $[(\text{Cp}_2\text{Zr})_2(\mu\text{-Cl})(\mu\text{-}\eta^1:\eta^2\text{-RCCCH}_3)]^+$ (**6a–c**) (with BPh_4^- anion) that contain a planar-tetracoordinate carbon atom. Complex **6b** was characterized by X-ray diffraction. The activation energy of the degenerate rearrangement of **6c** was determined by temperature dependent dynamic ^1H NMR spectroscopy ($\Delta G^\ddagger(240\text{ K}) = 11.3 \pm 0.5\text{ kcal mol}^{-1}$).

Keywords: Planar-tetracoordinate carbon; Group 4 metallocene cations; Dynamic metallocene complexes; Zirconocene; Van't Hoff/Le Bel compound

1. Introduction

Stable organometallic planar-tetracoordinate carbon compounds (**1**) are formally derived from the combination of $(\eta^2\text{-alkyne})\text{Group 4 metallocene complexes}$ with electrophilic $\text{X}-[\text{M}]$ systems. We and others have prepared a large variety of such dimetallic systems containing metal combinations such as $\text{Cp}_2\text{M}/\text{M}^1\text{R}_2$ ($\text{M} = \text{Zr}, \text{Hf}$; $\text{M}^1 = \text{B}, \text{Al}, \text{Ga}$) and also $\text{Cp}_2\text{M}^1/\text{M}^2\text{Cp}_2^+$ ($\text{M}^1, \text{M}^2 = \text{Zr}, \text{Hf}$) [1–4]. Examples of the latter class of compounds are usually synthesized by treating “Jordan’s cation” $\text{Cp}_2\text{ZrCH}_3(\text{THF})^+$ (**4**) (with BPh_4^- anion) with bis(alkynyl)metallocene complexes (**3**). A variety of cationic $\mu\text{-(}\eta^1\text{-C}:\eta^2\text{-C,C-alkyne)}$ bis(zirconocene) complexes (**2**) have been prepared by this route, that all necessarily contain a $\mu\text{-alkynyl}$ group as the second stabilizing ligand bridging between the two Group 4 metal centers [3,5].

One may ask to what extent this additional bridging ligand determines the properties of these dimetallic cation systems. Therefore, it was necessary to develop a new synthetic entry to analogous systems that bear bridging ligands other than the $\mu\text{-C}\equiv\text{C}-\text{R}$ group. A

comparison of structural properties, dynamic features, and regiochemical preferences at the equilibrium situation would then allow for a qualitative evaluation of the role of the additional bridging ligand. We have now, for the first time, prepared such dimetallic planar-tetracoordinate carbon complexes $[(\text{Cp}_2\text{Zr})_2(\mu\text{-R}^1\text{CCR}^2)(\mu\text{-X})]^+$ containing a chloride ligand bridging between the two Group 4 metallocene moieties, and compared their characteristic properties with those of the well studied $[(\text{Cp}_2\text{Zr})_2(\mu\text{-R}^1\text{CCR}^2)(\mu\text{-C}\equiv\text{C}-\text{R})]^+$ systems.

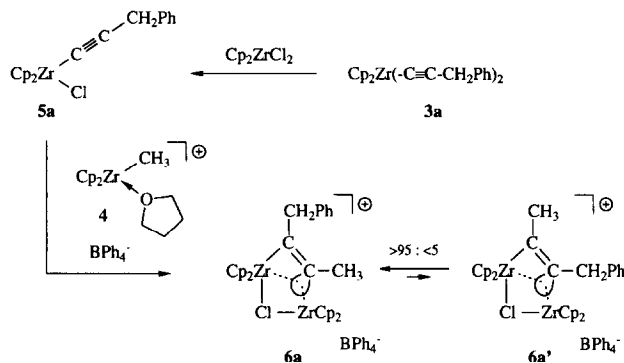
2. Results and discussion

The chloride ligand was introduced through the zirconocene–acetylide reagent. Chloro(acetylide)zirconocenes can be prepared by means of metathetical exchange between bis(acetylide)zirconocene complexes and zirconocene dichloride [6]. Typically, the $(\text{RC}\equiv\text{C})_2\text{ZrCp}_2/\text{Cp}_2\text{ZrCl}_2$ reaction mixture is stirred for several days at ambient temperature in toluene solution. The remaining bis(acetylide)zirconocene is then removed by extraction with pentane and the resulting $\text{Cp}_2\text{Zr}(\text{Cl})\text{C}\equiv\text{CR}$ reagent, that still contains Cp_2ZrCl_2 (some 20–40%) and a few unidentified minor components, employed as a starting material in this study without further purification.

^{*} Corresponding author.

Thus prepared, (benzylethynyl)chlorozirconocene (**5a**) was treated with $[\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{THF})]^+[\text{BPh}_4]^-$ (**4**) [7] in a ca. equimolar ratio in bromobenzene solution at room temperature (20 h). A single dinuclear organometallic compound was isolated (80% yield) to which we have assigned the structure of the planar-tetracoordinate carbon complex **6a**. The dimetallic cation **6a** exhibits a single set of NMR signals that is very typical of a dimetallabicyclic system that contains a distorted “square-planar” carbon center at a bridgehead position. There are $^1\text{H}/^{13}\text{C}$ NMR resonances (in CD_2Cl_2 at 223 K) of two non-equivalent Cp_2Zr moieties at δ 5.94, 5.61/113.1, 108.8, and the signals of a benzyl group [δ 4.00/25.3 ($^1J_{\text{CH}} = 133$ Hz)] that is attached to the carbon atom C3. Very typical $^1\text{H}/^{13}\text{C}$ NMR features indicate that the methyl substituent is bonded to the planar-tetracoordinate carbon atom C2 (CH_3 : δ 0.34/−16.1, $^1J_{\text{CH}} = 129$ Hz). The ^{13}C NMR resonance of the planar-tetracoordinate carbon center C2 is at δ 125.5; the signal of its neighbor C3 is located at a characteristically high δ value of 220.0.

Complex **6a** shows some dynamic NMR behavior. On lowering the monitoring temperature from ambient to ca. 250 K, the ^1H NMR resonances of the 2- CH_3 , 3- CH_2Ph and Cp-hydrogens all get broad, but become sharp again upon lowering the temperature further. Although only a single regioisomer of complex **6a** is observed at 223 K by ^1H and ^{13}C NMR spectroscopy, this behavior probably indicates that there is a second minor regioisomer present and slightly populated in this system, whose relative amount increases with increasing temperature. However, the increasing isomerization rate does not allow us to directly observe this minor isomer at high temperature on the NMR time scale. This equilibrium of regioisomers is very characteristic of the planar-tetracoordinate carbon compounds of the (μ -hydrocarbyl)bis(zirconocene) cation type [3,5]. Similar observations were made in the series of the related μ -acetylide bridged systems **2**. From the dynamic ^1H NMR behavior of **6a** it can be assumed that the equilibrium amount of the minor isomer **6a'** is certainly below 5% in the temperature range covered in this study.

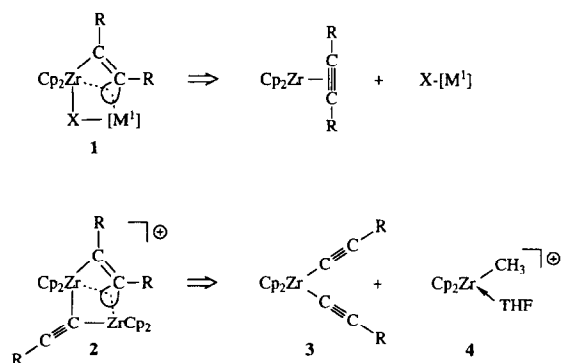


Chloro(1-pentynyl)zirconocene (**5b**) was generated in a slightly different way, namely by treatment of Cp_2ZrCl_2 with one molar equivalent of 1-pentynyl lithium in toluene (3 h, 20°C). After washing with pentane this starting material was employed as a 60:40 mixture with zirconocene dichloride. Treatment of a suspension of this mixture with “Jordan’s cation” [7] in bromobenzene furnished **6b** in 97% yield with ca. 95% purity as judged by ^1H NMR spectroscopy.

In this case a ca. 90:10 mixture of the two regioisomers is obtained. These are in a rapid equilibrium at ambient temperature on the NMR time scale, but below an approximate coalescence temperature of ca. 250 K the very characteristic ^1H NMR Cp signals of the minor isomer can be observed separately. The major component is clearly the regioisomer **6b** having the methyl substituent bonded to the planar-tetracoordinate carbon atom C2. The $^1\text{H}/^{13}\text{C}$ NMR methyl resonances at low temperature (in CD_2Cl_2) of **6b** are found at δ −0.09/−16.1 ($^1J_{\text{CH}} = 128$ Hz), and complex **6b** exhibits two Cp singlets each in the ^1H (δ 5.91, 5.81) and ^{13}C NMR spectrum (δ 113.3, 109.1).

The minor isomer exhibits four ^1H NMR Cp singlets (in CD_2Cl_2 at 193 K at 600 MHz) at δ 6.10, 5.95, ca. 5.8 and 5.77. Although the alkyl resonances could not be observed, the very characteristic Cp signal pattern indicates that the regioisomer **6b'** is populated to ca. 10% at equilibrium conditions. We recently showed that such compounds are chiral due to an agostic $\text{Zr} \cdots \text{H}-\text{C}$ interaction that becomes “frozen” on the NMR time scale at sufficiently low temperature and leads to the observation of pairwise diastereotopic Cp-ligands of the two bent metallocene units [4,8].

From a dichloromethane/pentane solution single crystals of the major isomer **6b** were obtained that were suited for an X-ray crystal structure determination. The structure of the cation (see Fig. 1) is characterized by the presence of a planar dimetallabicyclic framework with Zr1 and C2 representing the bridgehead positions. The two zirconium centers are connected by means of a μ -chloride and a μ -($\eta^1\text{-C2}:\eta^2\text{-C2,C3-2-hexyne}$) bridge. Carbon atom C2 is planar-tetracoordinate. The distorted



“square-planar” carbon bears the methyl substituent, whereas the n-propyl substituent is bonded to C3. Typically, the C2–C3 distance is in the C=C double bond range and Zr–C3 is very short (see Fig. 1). Details of the X-ray crystal structure will not be discussed because of its rather large *R* value (ca. 8%).

Chloro(propynyl)zirconocene (**5c**), obtained by σ -ligand disproportionation as described above and contaminated with some residual zirconocene dichloride, was also treated with the $\text{Cp}_2\text{ZrCH}_3(\text{THF})^+$ cation. After 4 h reaction time in bromobenzene a solid product material was isolated in close to quantitative yield that consisted of two organometallic components in a 60:40 ratio. The major component was identified as the planar-tetracoordinate carbon complex **6c**, owing to its very typical NMR spectra and characteristic dynamic NMR behavior (see below). The minor component was tentatively assigned the structure of the dimetallic μ -alkenylidene complex **7**. It shows temperature invariant ^1H NMR signals at δ 5.97 (Cp) and 2.63 (CH_3), and its formation by means of a competing carbometallation reaction of the (alkynyl)zirconocene chloride starting material is in accord with the general reaction schemes observed in such systems [4,9].

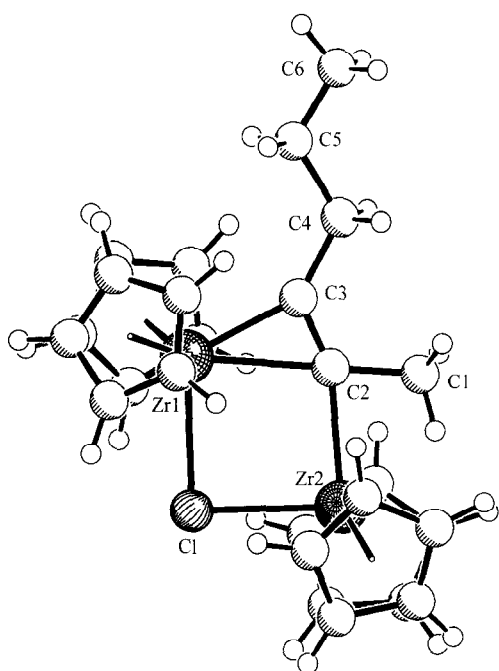
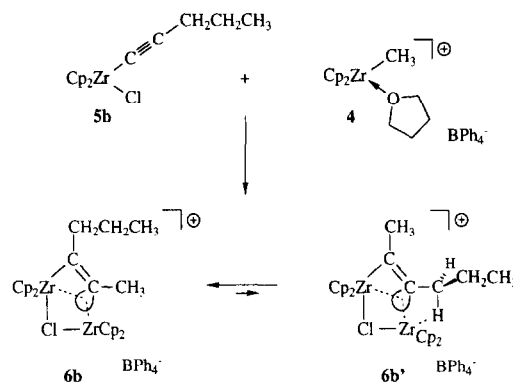
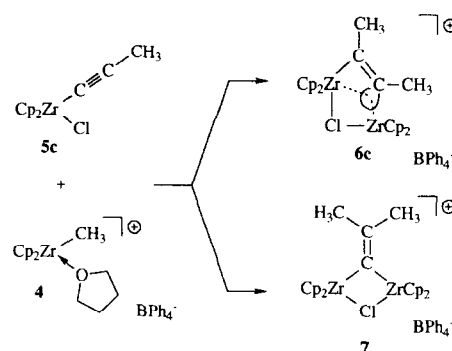
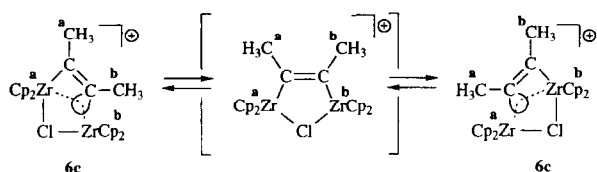


Fig. 1. A view of the molecular structure of complex **6b** (cation only) with atom numbering scheme. Selected bond lengths (Å) and angles (°): Zr1–C2 2.445(9), Zr1–C3 2.136(11), Zr2–C2 2.331(10), C2–C3 1.295(13), Zr1–Cl1 2.573(3), Zr2–Cl1 2.535(3), Zr1–C2–C3 60.8(6), Zr1–C2–Zr2 98.8(4), Zr2–C2–Cl1 81.3(6), C3–C2–Cl1 119.1(10), Zr1–Cl1–Zr2 90.5(1). Further information about the X-ray crystal structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-404628, the names of the authors, and the journal citation.



Complex **6c** exhibits dynamic NMR spectra. Upon cooling, the ^1H NMR Cp singlet rapidly broadens and below 240 K splits into two resonances of equal intensity that are observed at δ 5.99 and 5.81 in CD_2Cl_2 at 233 K. Analogously, the methyl resonance separates into two respective signals below the coalescence point at δ –0.01 (2- CH_3) and δ 2.47 (3- CH_3). This automerization behavior leading to a mutual exchange of the zirconocene units at the bridging RCCR ligand is very typical for symmetrically substituted planar-tetracoordinate carbon compounds of this organometallic type. A combination of experimental and theoretical studies [3,5] at the analogous μ -alkynyl bridged systems **2** has revealed that this intramolecular exchange process is likely to proceed via a C_{2v} -symmetric “di-metalla-olefin-type” transition state and, therefore, that the activation barrier of this automerization reaction is a good qualitative measure of the extra-stabilization energy introduced to the system by forming the planar-tetracoordinate carbon geometry [10]. In the case of the automerization reaction of **6c** we have determined the Gibbs activation energy [11] of the degenerate rearrangement at the coalescence point of the ^1H NMR Cp resonances to be $\Delta G^\ddagger(240\text{ K}) = 11.3 \pm 0.5\text{ kcal mol}^{-1}$. This is nearly identical to the previously determined values in the analogous μ -propynyl bridged $[(\text{Cp}_2\text{Zr})_2(\mu\text{-C}\equiv\text{C}-\text{CH}_3)(\mu\text{-CH}_3\text{CCCH}_3)]^+$ cation complex [$\Delta G^\ddagger(250\text{ K}) = 11.8 \pm 0.5\text{ kcal mol}^{-1}$]. This result





convincingly demonstrates that the essential features of the planar-tetracoordinate carbon center in this type of complex is only marginally dependent on the chemical identity of the second bridging ligand (here μ -chloro- vs. μ -alkynyl). Knowing this will probably help to increase the number of viable synthetic entries to this class of compounds and related systems, and thus serve to rapidly expand and develop this new area of the chemistry of planar-tetracoordinate carbon compounds [12].

3. Experimental section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a drybox. Solvents were dried and distilled under argon prior to use. The following instruments were used for product characterization: Bruker AC 200 P NMR spectrometer (^1H , 200 MHz; ^{13}C , 50 MHz), Varian unityplus NMR spectrometer (^1H , 600 MHz; ^{13}C , 151 MHz), Nicolet 5 DXC FT-IR spectrometer; DuPont 2910 DSC, STA Instruments (melting points). The $^1\text{H}/^{13}\text{C}$ NMR resonances (in CD_2Cl_2) of the BPh_4^- anion were observed at δ 7.36–7.28 (m, 8 H), 6.95–6.90 (m, 8 H), 6.81–6.76 (m, 4 H) and 164.3 (q, B–C, $^1J_{\text{BC}} = 50$ Hz), 136.4, 126.0, 122.2 (CH, Ph) ppm.

3.1. Synthesis of 6a

A suspension of zirconocene dichloride (2.50 g, 8.55 mmol) and benzylethynyllithium (2.09 g, 17.1 mmol) in 200 ml ether was stirred for 12 h at room temperature. Then the solvent was removed in vacuo, toluene was added, followed by separation of the insoluble lithium chloride. After addition of additional zirconocene dichloride (1.80 g, 6.16 mmol) the brown solution was stirred for 24 h, then the solvent was again removed in vacuo. The resulting brown solid was washed with pentane yielding a 75:25 mixture of **5a** and zirconocene dichloride. **5a** ^1H NMR (300 K, benzene- d_6): δ 7.40 (m, 2 H, Ph), 7.30–7.00 (m, 3 H, Ph), 5.97 (s, 10 H, Cp), 3.63 (s, 2 H, CH_2); ^{13}C NMR (300 K, benzene- d_6): δ 129.8, 123.7 ($\text{C}\equiv\text{C}$), 138.4, 128.7, 128.3, and 126.5 (Ph), 113.1 (Cp), 27.7 (CH_2). A mixture of this crude product (1.70 g) and “Jordan’s cation” **4** (1.92 g, 3.06 mmol) was then stirred for 12 h in 70 ml of bromobenzene. The resulting light-green

precipitate of **6a** was collected by filtration, washed with 10 ml of toluene and dried in vacuo (2.28 g, 80%, m.p. 77°C, dec. (DSC)). ^1H NMR (223 K, CD_2Cl_2): δ 7.65–7.20 (m, 5 H, Ph), 5.94 (s, 10 H, Cp), 5.61 (s, 10 H, Cp), 4.00 (s, 2 H, CH_2 -Ph), 0.34 (s, 3 H, CH_3); ^{13}C NMR (223 K, CD_2Cl_2): δ 220.0 (C3), 139.7 (*ipso*-C, Ph), 125.5 (C_{planar}), 128.9, 128.7, 126.4 (Ph), 113.1 (Cp), 108.8 (Cp), 25.3 ($^1J_{\text{CH}} = 133$ Hz, CH_2 -Ph), –16.1 ($^1J_{\text{CH}} = 129$ Hz, CH_3); IR (KBr): $\tilde{\nu} = 3102$, 3052, 2989, 1589, 1482, 1431, 1240, 1128, 1069, 1018, 812, 739, 703, 610 cm^{-1} . Anal. Found: C, 68.63; H, 5.38. $\text{C}_{54}\text{H}_{50}\text{BClZr}_2$ (927.70) Calc.: C, 69.91; H, 5.43%.

3.2. Synthesis of 6b

The reaction mixture of zirconocene dichloride (4.00 g, 13.7 mmol) and pentynyllithium (1.00 g, 13.5 mmol) was stirred in 150 ml of toluene. After 3 h the resulting lithium chloride precipitate was filtered off and the solvent removed in vacuo. A 60:40 mixture of **5b** and zirconocene dichloride was obtained after washing with pentane. **5b** ^1H NMR (300 K, benzene- d_6): δ 6.00 (s, 10 H, Cp), 2.23 (t, 2 H, $\equiv\text{C}-\text{CH}_2$ -, $^3J_{\text{HH}} = 6.8$ Hz), 1.48 (tq, 2 H, $-\text{CH}_2-\text{CH}_3$, $^3J_{\text{HH}} = 6.8$ Hz, $^3J_{\text{HH}} = 7.6$ Hz), 0.98 (t, 3 H, CH_3 , $^3J_{\text{HH}} = 7.6$ Hz); ^{13}C NMR (300 K, benzene- d_6): δ 128.6, 126.7 ($\text{C}\equiv\text{C}$), 113.0 (Cp), 23.4 (CH_2), 23.1 (CH_2), 13.8 (CH_3). 900 mg of this mixture was added to a suspension of **4** (850 mg, 1.35 mmol) in 30 ml of bromobenzene. After 6 h the product **6b** had formed as an insoluble yellow solid, which was collected, washed with toluene and pentane and dried in vacuo (1.15 g, 97%, m.p. 101°C, dec. (DSC)). Single crystals suitable for an X ray crystal structure analysis were obtained from pentane/dichloromethane. ^1H NMR (**6b**, 193 K, 600 MHz, CD_2Cl_2): δ 5.91 (s, 10 H, Cp), 5.81 (s, 10 H, Cp), 2.51 (t, 2 H, 4-*H*, $^3J_{\text{HH}} = 8.0$ Hz), 1.75 (tq, 2 H, 5-*H*, $^3J_{\text{HH}} = 7.2$ Hz, $^3J_{\text{HH}} = 8.0$ Hz), 1.10 (t, 3 H, 6-*H*, $^3J_{\text{HH}} = 7.2$ Hz), –0.09 (s, 3 H, 1-*H*); the Cp resonances of the minor isomer **6b'** are observed at 6.10, 5.95, ca. 5.8 and 5.77 ppm; ^{13}C NMR (230 K, CD_2Cl_2): δ 224.9 (C3), 125.3 (C2), 113.3 (Cp), 109.1 (Cp), 45.9 ($^1J_{\text{CH}} = 128$ Hz, C4), 22.4 ($^1J_{\text{CH}} = 125$ Hz, C5), 14.8 ($^1J_{\text{CH}} = 125$ Hz, C6), –16.1 ($^1J_{\text{CH}} = 128$ Hz, C1); numbering scheme as used in the X-ray structure (see Fig. 1). Based on ^1H NMR Cp shift differences and the coalescence temperature the barrier of the **6b/6b'** rearrangement was estimated at $\Delta G^\ddagger$ (254 K) $\approx 12.5 \pm 1$ kcal mol^{-1} [11]. IR (KBr): $\tilde{\nu} = 3058$, 3030, 2983, 1579, 1531, 1428, 1266, 1014, 815, 709, 607 cm^{-1} .

3.2.1. X-ray crystal structure analysis of 6b

$\text{C}_{50}\text{H}_{50}\text{BClZr}_2$ (879.60), crystal size $0.5 \times 0.35 \times 0.25$ mm³, cell parameters $a = 14.949(2)$, $b = 13.935(2)$, $c = 19.867(4)$ Å, $\beta = 97.18(1)^\circ$, $V = 4106.1(12)$ Å³, $\rho_{\text{calc}} = 1.423$ g cm^{-3} , $\mu = 6.1$ cm^{-1} ,

empirical absorption correction, $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), Enraf-Nonius CAD-4 diffractometer, $\lambda = 0.71073 \text{ \AA}$, $\omega/2\theta$ scans, 7530 reflections measured ($+h, -k, \pm l$), $[(\sin \theta)/\lambda]_{\max} = 0.60 \text{ \AA}^{-1}$, 7235 independent and 3197 observed reflections, 488 refined parameters, $R = 0.081$, $wR^2 = 0.194$. Programs used: SHELX86, SHELX93, SCHAKAL92.

3.3. Synthesis of **6c**

Complex **5c** was prepared according to a literature procedure [6]; the crude reaction product contained 20% of zirconocene dichloride and was used without further purification. 1.20 g of this mixture and 700 mg (1.12 mmol) of **4** were stirred in 30 ml of bromobenzene for 4 h at room temperature. The resulting yellow–brown precipitate was collected by filtration, washed with pentane and dried in vacuo to give a 60:40 mixture of **6c** and **7** (920 mg, 97%). ^1H NMR (**6c**, 233 K, CD_2Cl_2): δ 5.99 (s, 10 H, Cp), 5.81 (s, 10 H, Cp), 2.47 (s, 3 H, 3- CH_3), -0.01 (s, 3 H, 2- CH_3); ^1H NMR (**7**, 233 K, CD_2Cl_2): δ 5.92 (s, 20 H, Cp), 2.60 (s, 6H, CH_3); ^{13}C NMR (233 K, CD_2Cl_2): δ 256.5 (s), 219.9 (s), 124.3 (s), 113.0 (**6c**, Cp), 110.8 (**7**, Cp), 108.9 (**6c**, Cp), 28.7 (CH_3), 20.3 (CH_3), -17.7 (**6c**, 2- CH_3); the resonance of one quaternary carbon was not observed; the Gibbs activation energy of the degenerate rearrangement of **6c** was calculated at the coalescence temperature of the ^1H NMR Cp signals: $\Delta G^\ddagger(240 \text{ K}) = 11.3 \pm 0.5 \text{ kcal mol}^{-1}$ [11].

Acknowledgements

Financial support from the Fonds der Chemischen Industrie and the Volkswagen-Stiftung is gratefully acknowledged.

References and notes

- [1] G. Erker, *Comments Inorg. Chem.*, **13** (1992) 111; G. Erker, *Nachr. Chem. Tech. Lab.*, **40** (1992) 1099; M. Albrecht, G. Erker and C. Krüger, *Synlett.*, (1993) 441; G. Erker, R. Zwetler, C. Krüger, R. Noe and S. Werner, *J. Am. Chem. Soc.*, **112** (1990) 9620; G. Erker, M. Albrecht, C. Krüger, S. Werner, P. Binger and F. Langhauser, *Organometallics*, **11** (1992) 3517; G. Erker, M. Albrecht, C. Krüger and S. Werner, *J. Am. Chem. Soc.*, **114** (1992) 8531; G. Erker, M. Albrecht, C. Krüger, M. Nolte and S. Werner, *Organometallics*, **12** (1993) 4979.
- [2] P. Binger, F. Sandmeyer and C. Krüger, *Organometallics*, **14** (1995) 2969; P. Binger, F. Sandmeyer, C. Krüger, J. Kuhnigk, R. Goddard and G. Erker, *Angew. Chem.*, **106** (1994) 213; *Angew. Chem. Int. Ed. Engl.*, **33** (1994) 197; P. Binger, F. Sandmeyer, C. Krüger and G. Erker, *Tetrahedron*, **51** (1995) 4277.
- [3] G. Erker and D. Röttger, *Angew. Chem.*, **105** (1993) 1691; *Angew. Chem., Int. Ed. Engl.*, **32** (1993) 1623; D. Röttger, G. Erker, R. Fröhlich and S. Kotila, *Chem. Ber.*, **129** (1996) 1.
- [4] A.D. Horton and A.G. Orpen, *Angew. Chem.*, **104** (1992) 912; *Angew. Chem., Int. Ed. Engl.*, **31** (1992) 876.
- [5] D. Röttger, G. Erker, R. Fröhlich, M. Grehl, S.J. Silverio, I. Hyla-Kryspin and R. Gleiter, *J. Am. Chem. Soc.*, **117** (1995) 10503.
- [6] G. Erker, W. Frömberg, R. Benn, R. Mynott, K. Angermund and C. Krüger, *Organometallics*, **8** (1989) 911; G. Erker, W. Frömberg, R. Mynott, B. Gabor and C. Krüger, *Angew. Chem.*, **98** (1986) 456; *Angew. Chem., Int. Ed. Engl.*, **25** (1986) 463.
- [7] R.F. Jordan, *Adv. Organomet. Chem.*, **32** (1991) 325 and references cited therein.
- [8] G. Erker and D. Röttger, unpublished results.
- [9] D. Röttger, G. Erker, R. Fröhlich and S. Kotila, *Chem. Ber.*, **129** (1996) 5.
- [10] For a discussion of general aspects of planar-tetracoordinate carbon stabilization see e.g.: R. Hoffmann, R.W. Alder and C.F. Wilcox, Jr., *J. Am. Chem. Soc.*, **92** (1970) 4992; R. Hoffmann, *Pure Appl. Chem.*, **28** (1971) 181; P.v.R. Schleyer and A.I. Boldyrev, *J. Chem. Soc., Chem. Commun.*, (1991) 1536; K. Krogh-Jespersen, D. Cremer, D. Poppinger, J.A. Pople, P.v.R. Schleyer and J. Chandrasekhar, *J. Am. Chem. Soc.*, **101** (1979) 4843; K. Sorger and P.v.R. Schleyer, *J. Mol. Struct. Theochem.*, **338** (1995) 317; R. Gleiter, I. Hyla-Kryspin, S. Niu and G. Erker, *Angew. Chem.*, **105** (1993) 753; *Angew. Chem., Int. Ed. Engl.*, **32** (1993) 754; R. Keese, A. Pfenninger and A. Roesle, *Helv. Chim. Acta*, **62** (1979) 326; R. Keese, *Nachr. Chem. Tech. Lab.*, **30** (1980) 844; J.E. Lyons, D.R. Rasmussen, M.P. McGrath, R.H. Nobes and L. Radom, *Angew. Chem.*, **106** (1994) 1722; *Angew. Chem., Int. Ed. Engl.*, **33** (1994) 1667.
- [11] H.S. Gutowsky and C.H. Holm, *J. Chem. Phys.*, **25** (1956) 1228; A. Allerhand, H.S. Gutowsky, J. Jonas and R.A. Meinzer, *J. Am. Chem. Soc.*, **88** (1966) 3185; M.L.H. Green, L.-L. Wong and A. Sella, *Organometallics*, **11** (1992) 2660.
- [12] For other recently disclosed examples of "anti-van't Hoff/Le-Bel compounds" see e.g.: R.H. Cayton, S.T. Chacon, M.H. Chisholm, M.J. Hampden-Smith, J.C. Huffman, K. Folting, P.D. Ellis and B.A. Huggins, *Angew. Chem.*, **101** (1989) 1547; *Angew. Chem., Int. Ed. Engl.*, **28** (1989) 1523; S.T. Chacon, M.H. Chisholm, K. Folting, J.C. Huffman and M.J. Hampden-Smith, *Organometallics*, **10** (1991) 3722; F.A. Cotton and E.S. Shamshoum, *J. Am. Chem. Soc.*, **107** (1985) 4662; F.A. Cotton and E.S. Shamshoum, *Polyhedron*, **4** (1985) 1727; F.A. Cotton, W. Schwotzer and E.S. Shamshoum, *Organometallics*, **4** (1985) 461; P. Leoni, M. Pasquali, G. Pieri, A. Albinati, P.S. Pregosin and H. Rüegger, *Organometallics*, **14** (1995) 3145; H. Dietrich, W. Mahdi and W. Störck, *J. Organomet. Chem.*, **349** (1988) 1; S. Harder, J. Boersma, L. Brandsma, A. van Heteren, J.A. Kanters, W. Bauer and P.v.R. Schleyer, *J. Am. Chem. Soc.*, **110** (1988) 7802; F.A. Cotton and M. Millar, *J. Am. Chem. Soc.*, **99** (1977) 7886; F.A. Cotton, G.E. Lewis, G.N. Graham and N. Mott, *Inorg. Chem.*, **22** (1983) 560; S.L. Buchwald, E.A. Lucas and W.M. Davis, *J. Am. Chem. Soc.*, **111** (1989) 397; W.J. Evans, T.P. Hanusa, J.H. Meadows, W.E. Hunter and J.L. Atwood, *Organometallics*, **6** (1987) 295; M. Menzel, D. Steiner, H.J. Winkler, D. Schwikart, S. Mehle, S. Fau, G. Frenking, W. Massa and A. Berndt, *Angew. Chem.*, **107** (1995) 368; *Angew. Chem., Int. Ed. Engl.*, **34** (1995) 327; A. Gunale, H. Pritzkow, W. Siebert, D. Steiner and A. Berndt, *Angew. Chem.*, **107** (1995) 1194; *Angew. Chem., Int. Ed. Engl.*, **34** (1995) 1111.