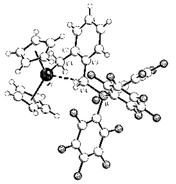


Using bent metallocenes for stabilizing unusual coordination geometries at carbon

Gerhard Erker

Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, D-48149 Münster, Germany. E-mail: erker@uni-muenster.de. Fax: +49 251 8336503

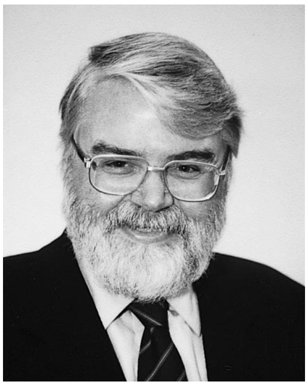
Received 11th January 1999

Novel unusually structured organic compounds can be made available with the aid of organometallic chemistry. A variety of typical examples are presented in this account where the unique stereoelectronic features of the bent metallocene bis(cyclopentadienyl)zirconium are used to stabilize uncommon coordination geometries of the element carbon. This includes internal ion pair phenomena and the electronic stabilization of planar-tetracoordinate carbon, examples of distorted C_{2v}-methane derivatives and of unprecedented geometries of pentacoordinated carbon compounds. For many such systems their specific energetic stabilization was estimated from suitable experiments.

1 Introduction

It is so accepted that most typical organic compounds contain carbon in close to four-coordinate tetrahedral, three-coordinate trigonal planar, or two-coordinate linear coordination geometries that arrangements distinctly different from these archetypes are considered to be unusual. But such uncommon coordination behavior of the element carbon occurs frequently in 'non-natural' ligand environments. Typical examples include the 'hypercarbon-chemistry' of penta- and higher-valent carbocations or interstitial carbon compounds.[1] Organometallic environments very often lead to the observation of unusual carbon coordination geometries of extraordinary stability. The special stereoelectronic features of a number of organometallic substituents can be utilized to induce and stabilize novel coordination polyhedra at carbon, that would be regarded as uncommon from a classical organic chemist's perspective, but are very stable and often kinetically quite persistent.

Gerhard Erker studied chemistry at the Universität Köln. He obtained his doctoral degree from the Ruhr-Universität Bochum in 1973 (with Professor Wolfgang R. Roth). He was a DFG-postdoctoral fellow at Princeton University with Professor Maitland Jones, Jr., in 1974–1975 and did his habilitation at Bochum in 1981. He was a Heisenberg fellow at the Max-Planck-Institut für Kohlenforschung in Mülheim a. d. Ruhr in 1984–1985 before he joined the Institut für Organische Chemie at the Universität Würzburg as a C3-Professor. Since 1990 he has been a C4-Professor at Münster. His major current research interests are in the areas of organic reaction mechanisms, organometallic chemistry and catalysis.

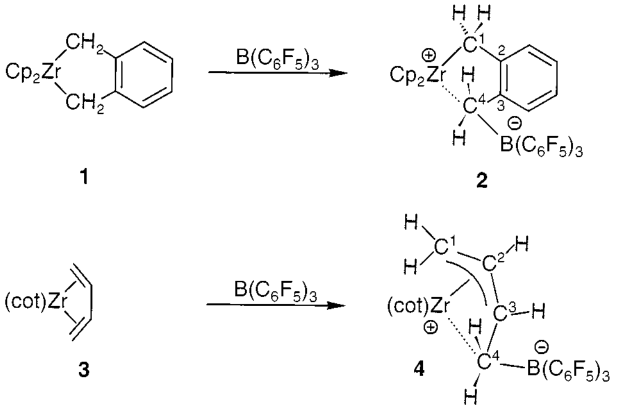


The Group 4 metal based bent metallocenes, *i.e.* titanocene, zirconocene, and hafnocene, and a few related organometallic frameworks, have been especially useful in designing and preparing unusually structured carbon compounds of high thermodynamic stability. The Cp_2M-units may serve as strong σ-donors and σ- or π-acceptors. Moreover, they exhibit a unique valence orbital arrangement that confines most of the chemistry to their central major symmetry plane.[2] It was found that the bent metallocenes assist the formation of uncommon coordination geometries at carbon in two different ways, namely by internal ion pairing and, more importantly, by forming stereoelectronically well defined three-center-two-electron bonds. The application of these features is illustrated and discussed in this account using selected typical examples.

2 Internal ion pairing

Non-covalent interactions between carbon atoms and metal centers are gaining in importance in organometallic chemistry. Within this growing field belong the ion pair interactions of metallocene based cations with some of their complex counter-anions, *e.g.* in reactive Group 4 metallocene Ziegler catalyst systems.[3] However, internal ion pairing, although it is in its essential bonding characteristics dominated by electrostatic effects and thus mostly undirected, is becoming more important as a structural tool in the construction of organometallic frameworks. Two typical examples will be presented here.

We have treated the 2-metallaindane system **1** with one molar equivalent of the strong organometallic Lewis acid tris(pentafluorophenyl)borane (Scheme 1). Selective addition to one of the CH_2-groups takes place to yield **2** (70% isolated). The X-ray crystal structure analysis of **2** has revealed the formation of a



Scheme 1

new ring system, in which the metallacyclic structure contains a strong internal ion pair interaction.[4] In **2** the newly formed $H_2C4–B$ bond is strong (1.682(3) Å). Carbon atom C4 exhibits an ion pair interaction with the zirconium center (C4–Zr: 2.595(3) Å, angles C3–C4–B: 119.1(3)°, Zr···C4–B: 155.3(2)°, Zr···C4–C3: 85.4(2)°) (Fig. 1). These characteristic bonding features are to be compared with the internal ordinary $Cp_2Zr–C1H_2$- σ-bond (Zr–C1 bond length: 2.264(3) Å, angle Zr–C1–C2: 93.5(2)°).

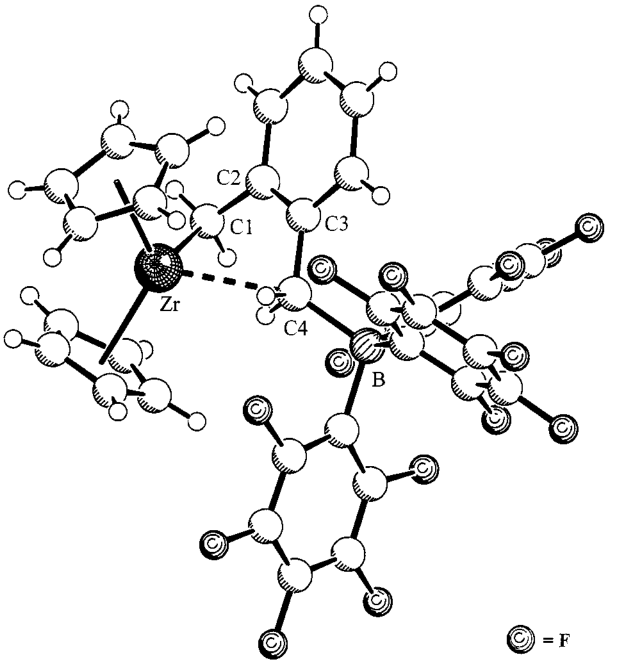


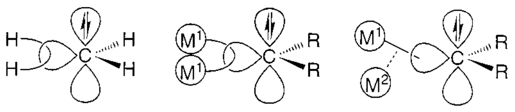
Fig. 1 A view of the molecular structure of the metallocene borate–betaine complex **2**.

A very similar situation is found when (s-*cis*-η^4-butadiene)(η^8-cyclooctatetraene)zirconium (**3**) is treated with $B(C_6F_5)_3$ to yield the *anti*-configurated mono-substituted (π-allyl)(cot)-zirconium betaine system **4**. The *Z*-configurated allyl moiety brings the -H_2C4-borate end of the dipole into such close proximity to the Cp_2Zr cation unit that an internal ion pair interaction results to form a uniquely structured metallacyclic betaine system. The bond length of the additional Zr–C4 interaction is 2.614(4) Å,[4] which is very typical for this type of electrostatic interaction (angles C3–C4–B: 114.7(3)°, Zr···C4–B: 148.8(3)°). The -CH_2-[B] moiety in the internally ion paired structure of **4** shows $^1H/^{13}C$ NMR features at δ 0.07, −1.00 (^1H) / δ 14.1 ppm (^{13}C).

3 Planar-tetracoordinate carbon

There have been numerous attempts to force tetracoordinate carbon into a planar geometry by steric methods.[5] This approach cannot be regarded as general because of the involvement of very large strain energies. The orbital analysis of square planar methane, as carried out by Hoffmann *et al.*[6] and later extended by Schleyer *et al.*,[7] points to a general possibility of utilizing the specific features of organometallic substituents to stabilize this ‘unnatural’ coordination geometry and to actually design viable synthetic routes to stable planar-tetracoordinate carbon compounds.

Square planar methane can formally be constructed by letting sp^2-hybridized carbon interact with four hydrogen atoms in a plane. This leads to an electron-deficient σ-system with six electrons making four C–H bonds and leaves an electron pair in the remaining p-orbital perpendicular to the σ-plane (see Scheme 2). This energetically very unfavorable situation becomes electronically stabilized by exchanging hydrogen atoms for *e.g.* metal based σ-donor/π-acceptor substituents. Thus, the hypothetical monomeric 1,1-dilithiocyclopropane molecule was calculated to just favor planar- over tetrahedral-tetracoordinate geometry.[7] We have also shown experimentally that an unsymmetrical three-center-two-electron bonding situation involving a combination of two electronically different metal substituents is even more effective in stabilizing the electron-deficient σ-system. In combination with additional structural means that take care of the π-electron situation this leads to synthetically readily available, stable planar-tetracoordinate carbon compounds (see Scheme 2).[8]



Scheme 2

Here is a typical example. The reactive $Cp_2Zr–C\equiv C–CH_3^+$ cation **6**, generated *in situ* by treatment of bis(propynyl)zirconocene (**5a**) with trityl tetraphenylborate in dichloromethane, reacts instantaneously with one equivalent of the neutral starting material **5a**. CC-coupling between two of the propynyl ligands yields the dimetallic product **7** (Scheme 3). The X-ray crystal structure analysis shows that the cation **7** contains a planar dimetallabicyclic framework that has in its center a planar-tetracoordinate carbon atom (C36) (Fig. 2).[9] This carbon atom is part of a C=C double bond (C37–C36: 1.317(8) Å). In addition, C36 is connected to the acetylene carbon atom C35 by a C(sp)–C(sp^2) σ-bond (C36–C35: 1.401(8) Å), and it exhibits two close bonding contacts to the adjacent zirconium atoms. This situation represents an example of an unsymmetrical three-center-two-electron interaction (C36–Zr1: 2.435(6); C36–Zr2: 2.530(5) Å). The central core of atoms around C36 is coplanar. The sum of the bonding angles of the distorted square-planar carbon atom C36 is 360°.

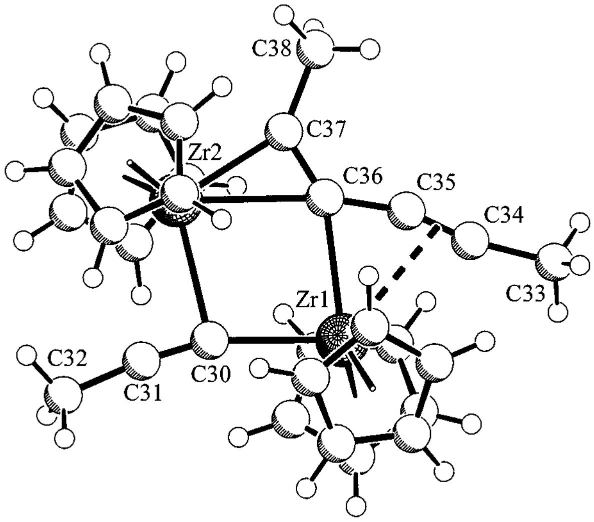


Fig. 2 A view of the *anti*-van’t Hoff–Le Bel compound **7** (cation only). The central carbon atom C36 is planar-tetracoordinate.

The extended coplanar arrangement of the central framework is supported by the bridging propynyl ligand (Zr1–C30: 2.259(6), Zr2–C30: 2.446(5) Å) and the ‘π-agostic’ interaction[10] of the pendant propynyl substituent at the planar-tetracoordinate carbon center (Zr1–C35: 2.453(5), Zr1–C34: 2.763(6) Å).

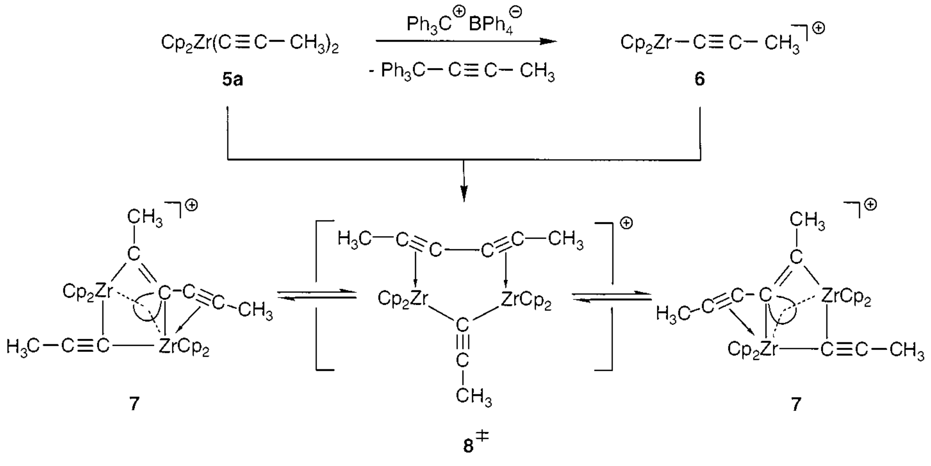
The overall bonding situation at the planar-tetracoordinate carbon atom C36 corresponds to the general bonding scheme expected for a distorted planar methane derivative,[6] except that the excess p-electron density has been made part of an ordinary

C=C double bond. The necessary additional stabilization of the σ-system in **7** has been brought about by forming an unsymmetrical three-center-two-electron situation, quite similar to that depicted schematically in Scheme 2 (see above). In **7** the Zr1–C36 bond represents the dominant M^1–C σ-interaction. The complex is markedly stabilized by a strong in-plane interaction of the electron-rich Zr1–C36 σ-bond with the strong Cp_2Zr2 electron acceptor.[11]

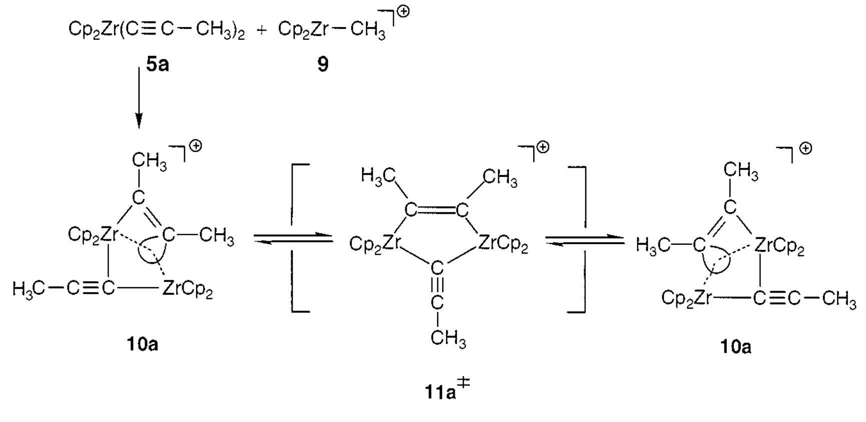
The dynamic features of complex **7** gave us an indication of the magnitude of the energetic stabilization of the planar-tetracoordinate carbon structure relative to a structural alternative containing the carbon atom in a close to ordinary trigonally planar coordination environment.[9] In solution a dynamic automerization process is observed at increased temperature on the NMR timescale that leads to a pairwise equilibration of the metallocene units and the propynyl-ends of the bridging Me–C_4–Me ligand. The bridging C≡C–CH_3 group remains unaffected by this process. It must be assumed that a symmetric structure (**8**, transition state or high lying intermediate, see Scheme 3) is passed through in the course of this degenerate rearrangement. Thus the observed activation barrier of $\Delta G^{\ddagger}_{\mathrm{rearr}}$ (190 K) $\approx 9.5 \pm 0.5$ kcal mol^{-1} probably represents a lower limit of the extra-stabilization energy of the unsymmetrical planar-tetracoordinate carbon structure in the organometallic *anti*-van't Hoff–LeBel compound **7**.

The formation of **7** is a specific example of a rather general synthetic scheme for the preparation of stable and isolable organometallic compounds that contain a planar-tetracoordinate carbon atom within their framework.[8,11*b*,12,13] We have found that a great variety of neutral (alkynyl) Group 4 metallocene complexes (**5**) of the general composition $Cp_2M^{IV}(X)(C{\equiv}CR)$ (M = Zr, Hf, X = N=CHR, C≡CR, CH_3, Cl) react readily with the $Cp_2ZrCH_3^+$ cation to give the respective *anti*-van't Hoff–LeBel compounds (**10**) in good yields (see Scheme 4). The mechanistic course of the reaction has been elucidated by using specifically isotopic or substituent-labelled precursors.[11*b*,14] The σ-ligand coupling takes place at the stage of a dimetallic addition product, and the rules for the regioselective preparation of a variety of derivatives of the compounds of this class were established. A number of examples of complexes of type **10** were characterized by X-ray diffraction. A typical example is complex **10a** that was prepared by treatment of bis(propynyl)zirconocene with the THF-stabilized methylzirconocene cation (**9**) ('Jordan's cation'[15] $[Cp_2Zr(THF)CH_3{}^+BPh_4{}^-]$).

The X-ray crystal structure analysis of **10a** (see Fig. 3) shows the typical planar dimetallabicyclic framework of the cation with the planar-tetracoordinate carbon atom C2 in the center. It is sp^2-hybridized and part of a C=C double bond (C1–C2: 1.305(6) Å; note that the adjacent C1–Zr distance is very short at 2.182(5) Å). This is a typical feature of most complexes of this general type. Carbon atom C2 has a methyl substituent attached to it (C2–C3: 1.543(6) Å) and it exhibits the typical unsymmetrical three-center-two-electron interaction with both zirconocenes (Zr2–C2: 2.324(5) Å, Zr1–C2: 2.508(4) Å). The bond angles around C2 add up to 360°. Both bent metallocene units are located such that their valence orbitals, located in the major plane and extending towards the front side of the bent metallocene wedge, are ideally oriented to form strong bonds with the carbon atoms of both bridging ligands in a single common plane. In this arrangement the Cp_2Zr^2 unit can to a first approximation be viewed as forming two strong σ-bonds, to the planar-tetracoordinate carbon atom C2 and the μ-σ^2-acetylide bridge, whereas the Cp_2Zr^1 moiety essentially serves as an electron-acceptor by interacting with the Zr2–C2 σ-bond. Zr2 is



Scheme 3



Scheme 4

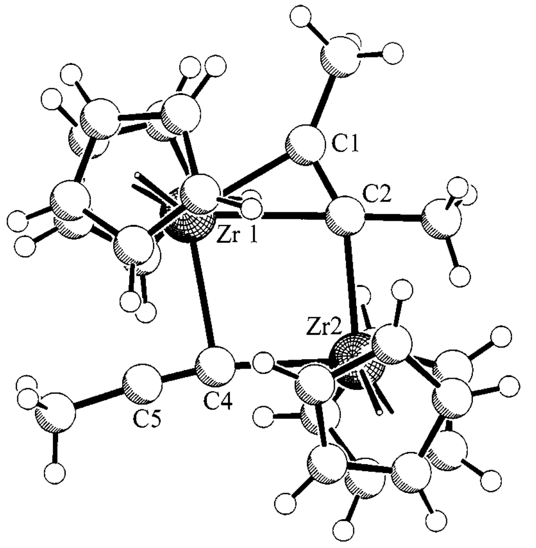


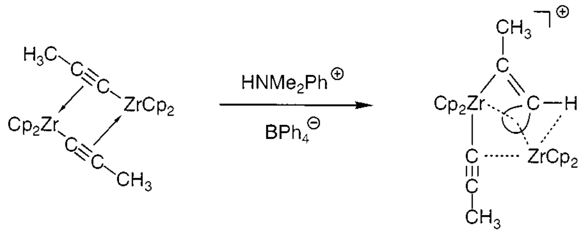
Fig. 3 Molecular structure of **10a** (cation only).

further stabilized by forming an agostic interaction[16] with a C–H bond of the methyl group at C2, but this is probably not a major stabilizing factor.

A detailed quantum chemical analysis[11] strongly supports the slightly different functions of the two metal centers in stabilizing the uncommon distorted square-planar coordination geometry of the central carbon atom C2 in complexes of this type. The calculation has located the alternative conventional monocyclic C_{2v}-symmetric structure, with ordinary planar-tricoordinate carbon in the bridge, at *ca.* 9 (RHF) to 14 (MP2//RHF) kcal mol^{-1} above the experimentally observed C_s-symmetric ground state.[11b] Moreover, the C_{2v}-structure was found to be probably a transition state (*i.e.* **11a**‡). In combination with the NMR behavior of **10a** in solution this has allowed for a reliable estimate of the stabilization energy of the planar-tetracoordinate carbon relative to planar-tricoordinate in this specific stabilizing organometallic environment. At 235 K complex **10a** shows a static low temperature limiting ^{1}H NMR spectrum at 200 MHz in CD_2Cl_2, exhibiting Cp-singlets at δ 5.87 and 5.72 and methyl singlets at δ 2.50 and -0.12 of the μ-Me_2C_2 ligand (the latter signal corresponds to the CH_3 group at the planar-tetracoordinate carbon center C2) in addition to the C≡C–CH_3 signal at δ 2.31. Whereas the latter signal is temperature invariant, the former two pairs of singlets undergo pairwise coalescence at increased temperature, resulting in a very simple three line ^{1}H NMR spectrum at high temperature. From the Cp and CH_3 coalescence a Gibbs activation energy for the degenerate rearrangement process depicted in Scheme 4 (*i.e.* of the **10a**$\rightleftharpoons$**11a**$\rightleftharpoons$**10a** transformation) was derived as $\Delta G^{\ddagger}_{\text{rearr}}$ (250 K) $\approx$ 11.8 ± 0.5 kcal mol^{-1}. In view of the results of the above mentioned theoretical analysis this value should serve as a good measure for the stabilization energy of the planar-tetracoordinate carbon in the complexes **10a**. Very similar $\Delta G^{\ddagger}_{\text{rearr}}$ values were found for a number of complexes related to **10** containing various alkynyl derived substituents R and different bridging ligands X.[8,14] We conclude that in such cationic dimetallic bis(zirconocene) containing frameworks planar-tetracoordinate carbon is actually more stable by *ca.* 12 kcal mol^{-1} than ordinary trigonal-tricoordinate carbon bearing the same combination of substituents.[11b,17] This is a very large effect, and demonstrates the extraordinary ability of the Group 4 bent metallocenes to induce novel structural and chemical properties in organic and organometallic systems.

In view of the very large energetic stabilization of planar-tetracoordinate carbon in such frameworks resulting from a favorable combination of suitable features of both metal centers involved it is not surprising that the syntheses of a great variety of related organometallic *anti*-van't Hoff–LeBel compounds were achieved in recent years.[13] A few examples originating from our laboratory shall be described here for a representative illustration.

The examples shown so far have all had an alkyl or aryl or even a more bulky metal-centered substituent attached at the planar-tetracoordinate carbon atom in the center of the dimetallabicyclic framework. But we have recently even found a way to prepare such compounds bearing hydrogen at this carbon atom. The new compounds were prepared by a simple protonation route (see Scheme 5).[18] The typical example **13** was obtained by treatment of the neutral doubly alkynyl-bridged bis(zirconocene) complex **12** with the Brønsted acid *N*,*N*-dimethylanilinium tetraphenylborate. A clean protonation of the alkynyl carbon adjacent to zirconium is observed to yield the dimetallabicyclic cationic planar-tetracoordinate carbon complex **13**. Complex **13** was characterized by X-ray diffraction (see Fig. 4) and spectroscopically [^{1}H/^{13}C NMR features of the planar-tetracoordinate C^1–H unit: δ 0.51/157.7 ppm ($^1J_{CH}$ = 103 Hz)]. The low ^{13}C–^{1}H coupling constant indicates an agostic C–H···Zr2 interaction.[16] This is supported by the X-ray crystal structure analysis.



12 **13**

Scheme 5

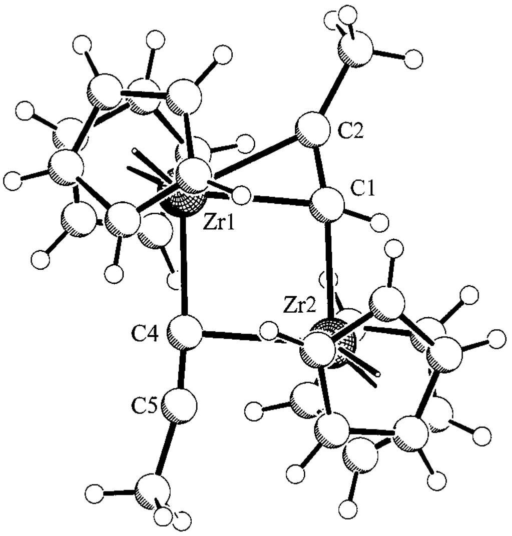


Fig. 4 Molecular structure of **13** (cation only). Selected bond lengths (Å) and angles (°): Zr1–C1 2.377(6), Zr1–C2 2.365(8), Zr1–C4 2.313(6), Zr2–C1 2.274(7), Zr2–C4 2.406(6), Zr2–C5 2.693(8), Zr2–H1 2.14(7), C1–C2 1.255(9), C1–H1 0.91(7), C4–C5 1.199(9), Zr1–C1–Zr2 96.7(2), Zr1–C1–C2 74.1(5), Zr1–C1–H1 166(4).

The formation of dimetallic planar-tetracoordinate carbon compounds is even more favorable when a combination of a Group 4 metallocene with a main group metal substituent is used. Such neutral complexes are readily formed from suitable organometallic precursors. A typical preparation involves treatment of dimethylzirconocene (**14**) with *e.g.* the dimethylaluminum(phenylacetylide) dimer (**15**).[19] Probably σ-ligand transfer occurs between zirconium and aluminum, followed by elimination of trimethylaluminum. CC-bond formation eventually leads to the heterodimetallic *anti*-van't Hoff–LeBel compound **16**. The X-ray crystal structure analysis (see Fig. 5) has established the presence of a planar-tetracoordinate carbon atom in the center of the planar complex framework. The general bonding features of this type of complex are very similar to those of the cationic planar-tetracoordinate carbon compounds presented earlier in this account. According to the theoretical discussion on this type of compound, the C2–Al σ-bond probably interacts strongly with the in-plane oriented Cp_2Zr acceptor orbital across the ring. An *ab initio* calculation of a model system of **19**, using Cl_2Zr instead of Cp_2Zr, and $ClAlH_2$ instead of Ph–C≡C–$AlMe_2$ indeed shows an increased energetic stabilization of the planar-tetracoordinate carbon geometry. The dimetallabicyclic planar-tetracoordinate carbon structure was calculated to be by some 34 kcal mol^{-1} energetically favored over its monocyclic isomer containing only conventional trigonally-planar carbon centers. Using boron instead of aluminum resulted in a similarly pronounced calculated stabilization.[11a]

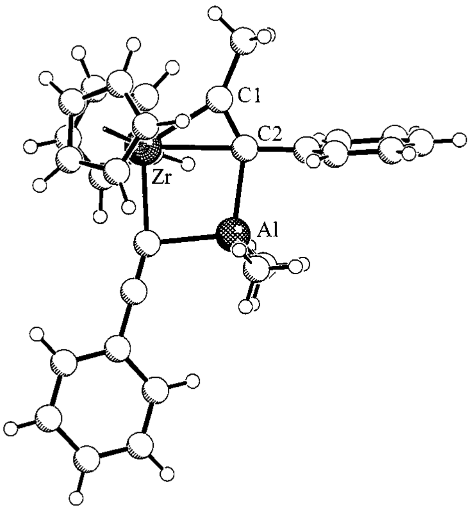
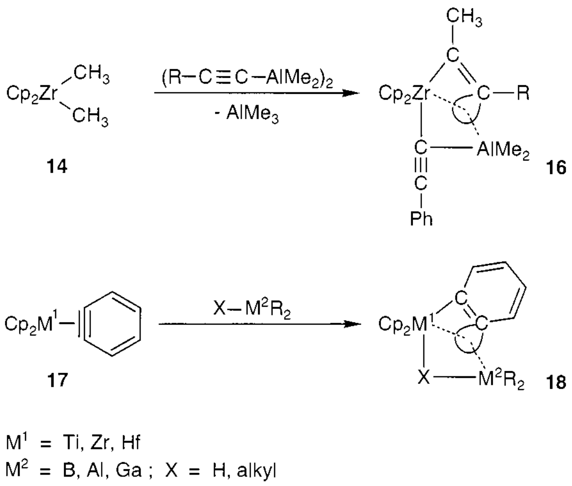


Fig. 5 Structure of **16**.

Various synthetic protocols have been developed[19] for the preparation of a great variety of compounds analogous to the zirconium–aluminum complex **16**, which all contain a planar-tetracoordinate carbon that is stabilized by the combined action of the attached main group and transition metals. Combinations of all of the Group 4 metallocenes with boron, aluminum and gallium building blocks were successfully employed. A major synthetic example of such systems has involved reactive (η^2-alkyne)- and (η^2-aryne)metallocene complexes (*e.g.* **17** → **18**, see Scheme 6).[20] More than a dozen of such dimetallic planar-tetracoordinate carbon compounds were characterized by X-ray diffraction. Much of their chemistry has been reviewed previously.[21] Therefore, additional details of this chemistry will not be discussed here.

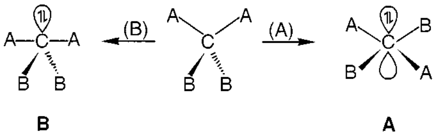
The examples highlighted in this chapter have illustrated that organometallic systems, in which planar-tetracoordinate carbon is stabilized by the combined and mutually supportive action of two suitable metal complex fragments, can be readily prepared and are often very stable and easily isolated. As expected by the straightforward and rapid development of this chemistry many related examples were found and disclosed by other groups,[8,22] demonstrating that 'square-planar carbon' is not at all unusual if certain rules are followed, which lead to the electronic stabilization of this 'unnatural' coordination geometry of carbon. The unique stereoelectronic features of the Group 4 bent metallocenes[2] have been of great help in developing this chemistry.



Scheme 6

4 A stable C_{2v}-methane derivative

Methane derivatives can be distorted principally in two different ways, as depicted in Scheme 7. Following pathway A opens both the A–C–A and the B–C–B angles from tetrahedral to ultimately 180°. Square-planar methane results, as described above. Pathway B in Scheme 7 leads to the opening of only one pair of σ-bonds (here the A–C–A angle). Opening to 180° results in the formation of a C_{2v}-methane isomer. This is characterized by a strong σ-electron deficiency in the linear A–C–A part of the molecule. In addition, opening of the A–C–A angle leads to the development of a doubly occupied sp^2-orbital at the backside of the B–C–B wedge. A further increase of the A–C–A angle leads to 'inverted' methane structures of similar electronic distributions. Thus, C_{2v}-methane derivatives (**B** in Scheme 7) should follow similar rules for their electronic stabilization by organometallic substituents as square planar-methane, except that their attachment must take the specifically altered sequence of orbitals into account, as a carbon centered p-orbital is used for constructing the electron deficient three-center-two-electron σ-system and the lone pair occupies the sp^2-orbital. We have recently prepared a stable organometallic C_{2v}-methane derivative[23] making use of the special bonding features of the bent metallocene Cp_2Zr.



Scheme 7

Complex **20** was prepared by treatment of the (μ-vinyl)bis(zirconocene) complex **19a** with B(C_6F_5)$_3$. Clean addition to the methylene terminus is observed. The resulting neutral dipolar addition product was characterized by X-ray diffraction (see Fig. 6).[23]

The central tetracoordinated carbon atom C1 in **20** exhibits a coordination geometry that corresponds essentially to a distorted C_{2v}-methane derivative. C1 is bonded to two zirconium atoms (C1-Zr1: 2.396(3) Å, C1–Zr2: 2.156(3) Å), a hydrogen (C1–H1: 0.98(3) Å) and a carbon atom (C1–C2: 1.502(3) Å). The bond angles at carbon atom C1 deviate markedly from tetrahedral (Zr2–C1–C2: 145.9(2)°, which corresponds to the enlarged A–C–A angle in structure **B** in Scheme 7, Zr2–C1–H1: 105(2)°, C2–C1–H1: 109(2)°). The remaining framework angles are much smaller (Zr2–C1–Zr1: 101.86(10)°, Zr1–C1–C2: 80.11(14)°, Zr1–C1–H1: 101(2)°). The Zr2–C1 distance is extremely short. To our knowledge it is the shortest bond length between zirconocene and a tetravalent carbon atom observed so

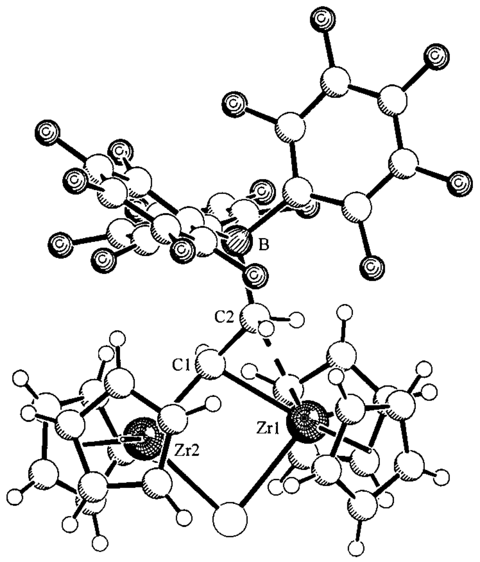


Fig. 6 A view of the molecular structure of the organometallic distorted C_{2v}-methane derivative **20**.

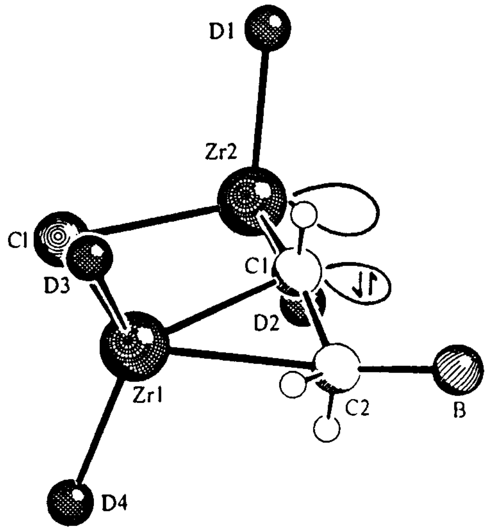


Fig. 7 A projection of the structural framework of **20** (D1–D4 denote the centroids of the Cp-rings). The depicted orbitals at C1 and Zr2 indicate potential electronic stabilization of the coordination geometry towards distorted C_{2v} at carbon atom C1.

far. This probably indicates the presence of an electronic stabilization of the sp^2-C1 lone pair by a favorable in-plane interaction with the ideally located acceptor orbital at the Cp$_2$Zr2 bent metallocene unit (see Fig. 7).

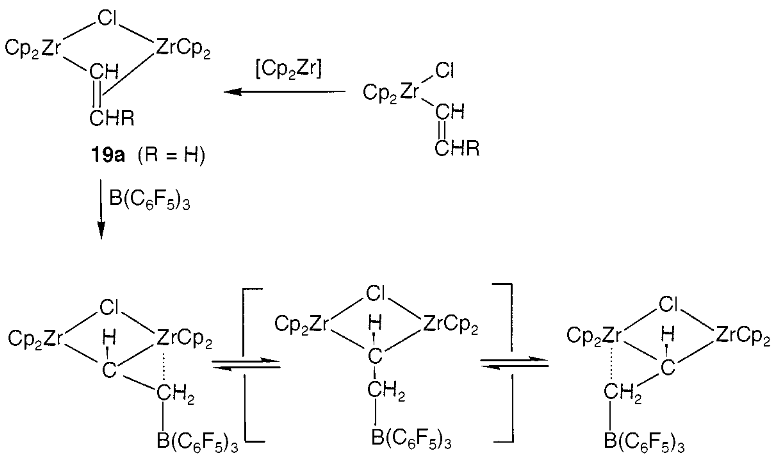
The Cp$_2$Zr^1···C2H$_2$–[B] interaction in **20** is electrostatic. It corresponds to an internal ion pair situation (Zr1–C2: 2.600(3) Å, angles C1–C2–B: 119.2(2)° and Zr1–C2–B: 155.0(2)°), analogous to that found for the internal ion pair structures of the complexes **2** and **4** described in the first chapter of this account[4] (see Fig. 1 and Scheme 1).

In solution the C^1–H moiety gives rise to a ^{1}H NMR signal at δ 7.12 and a ^{13}C NMR feature at δ 174.7 with $^1J_{CH}$ = 122 Hz. Complex **20** shows temperature-dependent dynamic NMR spectra. At low temperature it exhibits four separate Cp-resonances that broaden and eventually coalesce into two averaged signals upon raising the temperature. This is due to an enantiomerization process of **20** on the NMR timescale by reversible opening of the Cp$_2$Zr1···C2H$_2$–[B] internal ion pair. The activation energy of this process was determined as $\Delta G^{\ddagger}_{enant}$ (273 K) = 12.1 ± 0.5 kcal mol^{-1}. This value is to be compared with the typical dissociation energy of such zirconocene cation–alkylborate anion ion pair interactions[3] of *ca.* 16–18 kcal mol^{-1}. From the comparison of these two values we must conclude that the unusual distorted C_{2v}-methane-like coordination geometry of **20** as such is, despite all favorable electronic factors, still intrinsically by *ca.* 5 kcal mol^{-1} less stable than the normal tetrahedral geometry (which is probably best represented in the transition state geometry **21**‡ of the degenerate rearrangement process as depicted in Scheme 8). It is the additional energy gain of the internal ion pair formation that just tips the balance to favoring the exceptional C_{2v}-methane-like structure of the system **20**.

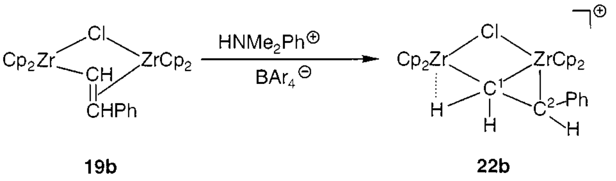
5 Formation of distorted square-pyramidal hypercoordinated carbon compounds by a simple protonation route

Addition of a proton (*e.g.* from HNMe$_2$Ph$^+$BAr$_4$$^-$) to a variety of ($\mu$-alkenyl)bis(zirconocene) complexes **19** under non-nucleophilic conditions takes a different regiochemical course than the B(C$_6$F$_5$)$_3$ addition (see above). Protonation occurs exclusively at the alkenyl methine group with formation of the very unusually structured cationic hypercarbon complex **22** (Scheme 9).[24]

The phenyl-substituted derivative **22b** shows very characteristic NMR features of the μ-η^1:η^2-C1H$_2$C2HPh moiety, that is, bridging uniquely between the two metal centers of the Cp$_2$Zr–Cl–ZrCp$_2$ unit. It features ^{1}H NMR signals at δ 5.17 (C^{2}H), 4.63 and −5.55 with coupling constants of ^3J = 15.6 and 6.6 Hz, ^2J = 5.4 Hz. The corresponding ^{13}C NMR resonances were



Scheme 8



Scheme 9

located at δ92.5 (C1) and δ86.3 ppm (C2). The $^1J_{C2-H}$ coupling constant of 142 Hz is very typical for a metallacyclic three-membered ring and the former signal shows two very different $^1J_{C1-H}$ coupling constants of 131 and 99 Hz. The latter indicates a strong Zr/H–C1 agostic interaction.[16] These NMR patterns are observed throughout the series of complexes **22** with different R groups. They are consistent with a unique distorted square-pyramidal pentacoordinated geometry at the central atom C1. For one example in the series, the $[(MeCp)_2Zr(\mu\text{-}Cl)(\mu\text{-}\eta^1:\eta^2\text{-}C1H_2C2H\text{-}n\text{-}butyl)Zr(MeCp)_2]^+$ complex **22c** this geometry was further supported by an X-ray crystal structure analysis (see Fig. 8).[24] The unique stereochemical properties of both zirconocenes[2] have been used as tools to construct and stabilize the very unusual coordination geometry of the pentacoordinated carbon (C1) in the complexes **22**. This goes so far as to utilize even a C–H bond as a functional group to determine the shape of the coordination polyhedron at the hypercoordinated carbon atom[1a] in the center of these cationic complexes.

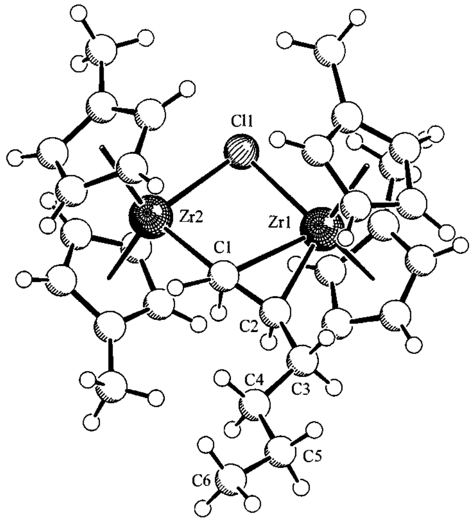


Fig. 8 Molecular structure of **22c** (cation only). Carbon atom C1 is distorted square-pyramidally coordinated with C1 being only located *ca.* 0.17 Å above the basal plane.

This example shall conclude our compilation of uncommon coordination geometries at carbon, as they can be stabilized and determined in their specific structural characteristics by using the well defined special stereoelectronic features of the Group 4 bent metallocene moieties.[2] We are expecting that the application of these and similar organometallic tools will increase the number of stable and isolable compounds that contain very unusual and uncommon coordination geometries at carbon and help to make many of such structurally and chemically new types of organic and organometallic compounds available by design.

6 Acknowledgements

Most of the work described here was done by a group of very talented graduate students (recent work by Jörg Schottek, Wolfgang Ahlers, Jörn Karl, Dirk Röttger, and earlier work by Markus Albrecht). Dr Roland Fröhlich and his team did most of the X-ray crystal structure analyses. A very stimulating collaboration is acknowledged with the groups of Professor Rolf Gleiter (calculations), Professor Paul Binger and Professor Friedrich Bickelhaupt (F. B. and G. E. thank the Alexander von Humboldt foundation for a joint Max-Planck research award under which the internal ion pair work was done.) G. E. gratefully acknowledges generous financial support of this work by the Fonds der Chemischen Industrie, the Alfried Krupp von Bohlen und Halbach-foundation, the Deutsche Forschungsgemeinschaft, the Volkswagen-foundation and the Wissenschaftsministerium NRW.

7 References

1 (*a*) G. A. Olah, G. K. S. Prakash, R. E. Williams, L. D. Field and K. Wade, *Hypercarbon Chemistry*, Wiley, New York, 1987; G. K. S. Prakash, P. v. R. Schleyer, Eds., *Stable Carbocation Chemistry*, Wiley, New York, 1997, and references cited therein; (*b*) F. Scherbaum, A. Grohmann, G. Müller and H. Schmidbaur, *Angew. Chem.*, 1989, **101**, 464; *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 463.

2 H. H. Brintzinger and L. S. Bartell, *J. Am. Chem. Soc.*, 1970, **92**, 1105; W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729; J. C. Green, *Chem. Soc. Rev.*, 1998, **27**, 263.

3 X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10015; P. A. Deck and T. J. Marks, *J. Am. Chem. Soc.*, 1995, **117**, 6128.

4 J. Karl, G. Erker, R. Fröhlich, F. Zippel, F. Bickelhaupt, M. Schreuder Goedheijt, O. S. Akkerman, P. Binger and J. Stannek, *Angew. Chem.*, 1997, **109**, 2914, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2771.

5 W. Luef and R. Keese, *Adv. Strain Org. Chem.*, 1993, **3**, 229; J. E. Lyons, D. R. Rasmussen, M. P. McGrath, R. H. Nobes and L. Radom, *Angew. Chem.*, 1994, **106**, 1722; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1667.

6 R. Hoffmann, R. W. Alder and C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, 1970, **92**, 4992.

7 J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger and J. A. Pople, *J. Am. Chem. Soc.*, 1976, **98**, 5419; K. Sorger, P. v. R. Schleyer, R. Fleischer and D. Stalke, *J. Am. Chem. Soc.*, 1996, **118**, 6924, and references cited therein.

8 For a general review see: D. Röttger and G. Erker, *Angew. Chem.*, 1997, **109**, 840; *Angew. Chem., Int. Ed. Engl.*, 1997, **36,** 812.

9 W. Ahlers, B. Temme, G. Erker, R. Fröhlich and F. Zippel, *Organometallics*, 1997, **16,** 1440.

10 G. Erker, R. Noe, C. Krüger and S. Werner, *Organometallics*, 1992, **11**, 4174.

11 (*a*) R. Gleiter, I. Hyla-Kryspin, S. Niu and G. Erker, *Angew. Chem.*, 1993, **105**, 753; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 754; (*b*) D. Röttger, G. Erker, R. Fröhlich, M. Grehl, S. J. Silverio, I. Hyla-Kryspin and R. Gleiter, *J. Am. Chem. Soc.*, 1995, **117**, 10503.

12 W. Ahlers, G. Erker, R. Fröhlich and U. Peuchert, *Chem. Ber.*, 1997, **130**, 1069.

13 P. Binger, F. Sandmeyer, C. Krüger, J. Kuhnigk, R. Goddard and G. Erker, *Angew. Chem.*, 1994, **106,** 213, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 197; P. Binger, F. Sandmeyer, C. Krüger and G. Erker, *Tetrahedron*, 1995, **51**, 4277; D. Röttger, G. Erker, R. Fröhlich and S. Kotila, *Chem. Ber.*, 1996, **129**, 1; D. Röttger, G. Erker and R. Fröhlich, *J. Organomet. Chem.*, 1996, **518**, 221.

14 D. Röttger, doctoral dissertation, Univ. Münster, 1995.

15 R. F. Jordan, *Adv. Organomet. Chem.*, 1991, **32**, 325.

16 M. Brookhart, M. L. H. Green and L.-L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1.

17 G. Erker and D. Röttger, *Angew. Chem.*, 1993, **105**, 1691; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1623.

18 J. Schottek, G. Erker and R. Fröhlich, *Eur. J. Inorg. Chem.*, 1998, 551.

19 G. Erker, M. Albrecht, C. Krüger and S. Werner, *Organometallics*, 1991, **10**, 3791; G. Erker, M. Albrecht, S. Werner, M. Nolte and C. Krüger, *Chem. Ber.*, 1992, **125**, 1953.

20 G. Erker, M. Albrecht, C. Krüger, S. Werner, P. Binger and F. Langhauser, *Organometallics*, 1992, **11,** 3517; G. Erker, M. Albrecht, C. Krüger and S. Werner, *J. Am. Chem. Soc.*, 1992, **114**, 8531.

21 G. Erker, *Comments Inorg. Chem.*, 1992, **13,** 111; M. Albrecht, G. Erker and C. Krüger, *Synlett*, 1993, 441.

22 For typical examples see: F. A. Cotton and M. Millar, *J. Am. Chem. Soc.*, 1977, **99**, 7886; S. L. Buchwald, E. A. Lucas and W. M. Davis, *J. Am. Chem. Soc.*, 1989, **111**, 397; 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.*, 1989, **101**, 1547; *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1523; A. Gunale, H. Pritzkow, W. Siebert, D. Steiner and A. Berndt, *Angew. Chem.*, 1995, **107**, 1194; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1111; I. Hyla-Kryspin, R. Gleiter, M.-M. Rohmer, J. Devemy, A. Gunale, H. Pritzkow and W. Siebert, *Chem. Eur. J.*, 1997, **3**, 294; A. Gunale, D. Steiner, D. Schweikart, H. Pritzkow, A. Berndt and W. Siebert, *Chem. Eur. J.*, 1998, **4**, 44.

23 J. Schottek, G. Erker and R. Fröhlich, *Angew. Chem.*, 1997, **109**, 2585; *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2475.

24 J. Schottek, D. Röttger, G. Erker and R. Fröhlich, *J. Am. Chem. Soc.*, 1998, **120**, 5264.

Review 7/08611C