Stereo-electronic interaction in complex molecules: cyclopropyl conjugation with Lewis acidic centres across connecting carbon–carbon triple bonds†

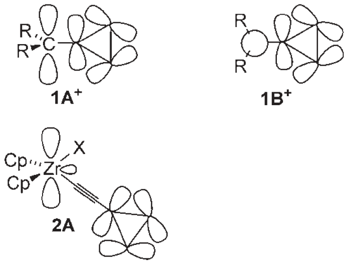
Gereon Dierker, Gerald Kehr, Roland Fröhlich,‡ Gerhard Erker* and Stefan Grimme§*

Received (in Cambridge, UK) 5th June 2006, Accepted 17th July 2006
First published as an Advance Article on the web 8th August 2006
DOI: 10.1039/b607906g

Bis(cyclopropylethynyl)zirconocene shows a bisected conformation in the crystal: the magnitude of the stabilizing conjugation of the Cp_2Zr Lewis acid centre with the cyclopropyl substituent across the connecting C≡C triple bond is assessed by DFT calculations and a comparison with a series of cationic organic and organometallic reference systems.

Electronic interaction between specific subunits essentially determines the properties of complex unsaturated molecules. Correctly predicting and understanding *e.g.* their characteristic structural features requires at least a qualitative and often a quantitative knowledge of their conjugative interaction.[1] The Cp_2Zr unit in diorganyl zirconocenes has unique stereoelectronic properties: The pseudotetrahedrally coordinated 16-electron metal centre features a single well defined low lying acceptor orbital located in the σ-ligand plane, which bisects the Cp–metal–Cp angle[2,3] (see Scheme 1). This posed the question of its electronic interaction with σ-bonded π-systems. Since the electronic *e.g.* Cp_2Zr–acetylide conjugation was expected to be small its experimental detection required the use of a sensitive chemical indicator. We here report about the favourable and easy use of a conformational cyclopropyl detector for an assessment of such electronic interactions.

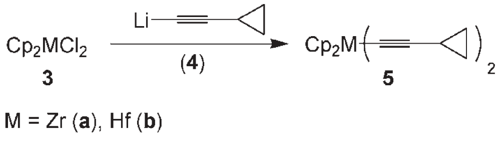
Cyclopropyl carbinyl cations ($\mathbf{1}^+$) are known to favour their bisected form ($\mathbf{1A}^+$) over the "perpendicular" conformation ($\mathbf{1B}^+$) because of the stabilization of the cation in $\mathbf{1A}^+$ by conjugation with the cyclopropyl Walsh orbitals.[4] For realistic plots of such orbitals see *e.g.* the example of $\mathbf{6}^+$ in Fig. 4. In the unfavourable rotamer $\mathbf{1B}^+$ (which actually represents a transition state geometry) this positive electronic interaction is shut off. If there were a sizable electronic conjugation of a Cp_2Zr unit with σ-bonded acetylide ligands[5] then an attachment of a cyclopropyl substituent at the far end of the Cp_2Zr–C≡C-unit should make itself known by the observation of the preferred bisected orientation (**2A**) of this stereoelectronic sensoring group.



Scheme 1

We have prepared bis(cyclopropylethynyl)zirconocene (**5a**)¶ by treatment of Cp_2ZrCl_2 (**3a**) with two molar equivalents of the cyclopropylethynyllithium reagent (**4**) (Scheme 2). Complex **5a** was isolated in *ca.* 90% yield. It shows a ^{1}H NMR Cp singlet at δ 6.08 (10H) and an AA′BB′C pattern at δ 1.19 (2H, CH), 0.65, 0.45 (each 4H) of the cyclopropyl hydrogen atoms. The CC triple bond shows ^{13}C NMR features at δ 129.0 (Zr–C≡) and δ 129.4 (≡C–cyclopropyl). The hafnium complex **5b** was prepared by treatment of Cp_2HfCl_2 with the Li–C≡C–cyclopropyl reagent **4** (*ca.* 60% isolated, ^{13}C NMR of Zr–C≡C: δ 138.1, 132.8).

Single crystals of the zirconium complex **5a** were obtained from toluene. The structure features a pseudotetrahedral bent metallocene complex with pertinent central bond angles of 105.1(1)° (C1–Zr–C1*) and 132.2° [Cp(centroid)–Zr–Cp (centroid)], Zr–C(Cp) bond lengths range from 2.481(2) Å to 2.524(3) Å. The Zr–(sp)carbon σ-bond length to the linear acetylide ligand (angles Zr–C1–C2: 179.0(2)°, C1–C2–C3: 177.0(2)°) amounts to 2.239(2) Å. The C≡C triple bond length (C1–C2) is typical at 1.213(2) Å (C2–C3: 1.446(2) Å). The proximal C–C single bond lengths in the cyclopropyl group are longer (C3–C4: 1512(2) Å, C3–C5: 1.511(3) Å) than the distal cyclopropyl C–C linkage (C4–C5: 1.481(3) Å). The C–C–C bond angles inside the three-membered ring are close to the theoretical value. The cyclopropyl ring in complex **5a** is oriented in a bisected conformation, which is as expected for a maximal possible conjugation between the acceptor orbital at the zirconocene Lewis acid centre and the cyclopropane Walsh orbitals. In the crystal complex **5a** is C_2-symmetric with the Zr atom on a twofold axis. Consequently, both the cyclopropyls are suitably oriented for conjugation with Zr across the connecting C≡C triple bond, while they are pointing toward opposite Cp–ligand faces (Fig. 1).



Scheme 2

Organisch-Chemisches Institut, Universität Münster, Corrensstraße 40, 48149, Münster, Germany. E-mail: erker@uni-muenster.de; grimmes@uni-muenster.de; Fax: +49 (0) 251 83-36503

† Electronic supplementary information (ESI) available: Spectroscopic data, details of X-ray crystal structure analysis and quantum chemical calculations. See DOI: 10.1039/b607906g

‡ X-ray crystal structure analyses

§ DFT calculations

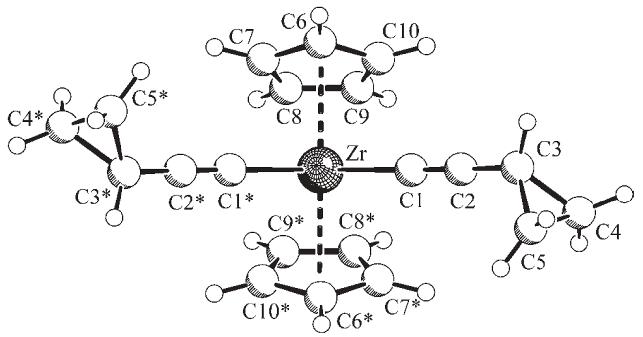


Fig. 1 Molecular structure of complex **5a** (* in the atom labels indicates that these atoms are at equivalent positions (1 − *x*, *y*, ½ − *z*)).

The structure of the hafnium complex **5b**|| is close to C_s-symmetric (but not crystallographically). The bonding features are similar to those of its congener **5a**. In **5b** both cyclopropyl rings are again found in bisected conformations relative to the central Cp_2Hf unit, only that both three-membered rings are rotated toward the same Cp-ring (Fig. 2).

The conformational position of the cyclopropyl ring has qualitatively revealed the presence of an electronic conjugation with the bent metallocene core across the connecting C≡C triple bond. Remaining to be answered is the question of how large in energy this conjugative stabilization actually is. This was investigated by DFT calculations[6] of the example **5a** and a series of suitable organic cations for comparison. First, the 3-cyclopropylpropargyl cation was looked at. It was found that the bisected form (**6A**$^+$, see Fig. 3) was preferred over the "perpendicular" rotamer (**6B**$^+$) by 15.5 kcal mol^{-1} (for a depiction of the essential orbitals see Fig. 4). Even if the primary carbenium ion centre is connected by a butadiynylene unit (–C≡C–C≡C–) we still observe a very large stabilizing effect of 9.7 kcal mol^{-1} favouring the bisected isomer **7A**$^+$. However, this effect is decreased upon the attachment of additional stabilizing substituents at the carbenium ion centre. The corresponding cyclopropyl diphenylpropargyl cation still has the bisected isomer (**8A**$^+$) favoured over the 90° rotated "switched off isomer" (**8B**$^+$), but only by 4.9 kcal mol^{-1}.

The DFT calculation finds the neutral C_2-symmetric zirconocene bisected conformer **5aA** as the global minimum with acceptable accuracy (compared to experimental data from the corresponding X-ray crystal structure analysis) of its structural parameters [Zr–C1: 2.215 Å, C1–C2: 1.237 Å, cyclopropyl bond lengths C3–C4 1.529 Å, C3–C5 1.528 Å, C4–C5 1.498 Å, angles C1–Zr–C1* 102.7°, Zr–C1–C2 175.4°, C1–C2–C3 179.4°], but it is only separated by a mere 1.0 kcal mol^{-1} per cyclopropyl group (2.1 kcal mol^{-1} for a simultaneous rotation of both cyclopropyl rings) from its non-conjugated cyclopropyl rotameric isomer **5aB** (see Fig. 5). The conjugational effect is slightly larger in the hypothetical $[Cp_2Zr–C≡C–cyclopropyl]^+$ cation (**9**$^+$): here the bisected form (**9A**$^+$) is by 3.4 kcal mol^{-1} favoured over its "perpendicular" rotamer (**9B**$^+$).

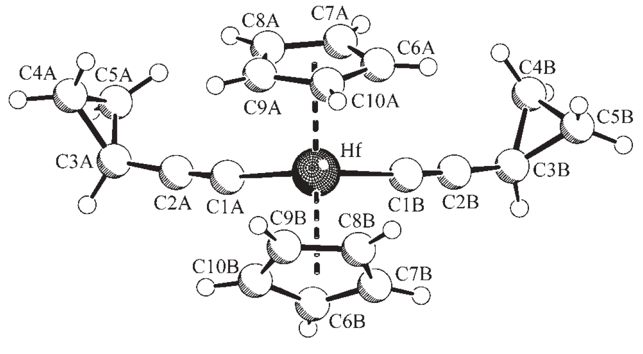


Fig. 2 Molecular structure of complex **5b**. Selected bond lengths (Å) and angles (°): Hf–C1A: 2.182(4), Hf–C1B: 2.170(5), C1A–C2A: 1.203(6), C1B–C2B: 1.209(7), Hf–C1A–C2A: 172.3(4)°, Hf–C1B–C2B: 175.5(5)°, C1A–C2A–C3A: 175.7(5)°, C1B–C2B–C3B: 178.0(6)°, for additional values see the Supporting Information.†

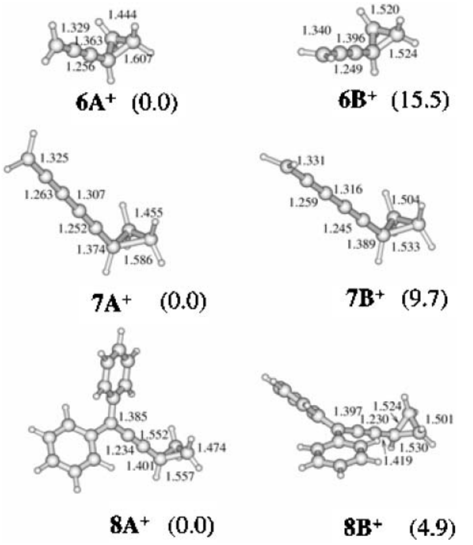


Fig. 3 DFT calculated structures and relative energies (kcal mol^{-1}) of favoured bisected (**A**$^+$) and unfavoured perpendicular (**B**$^+$) isomers of several ω-cyclopropylpropargyl cations.

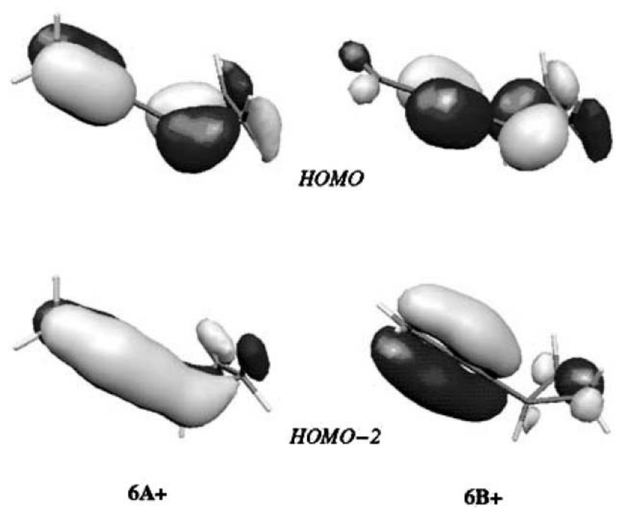
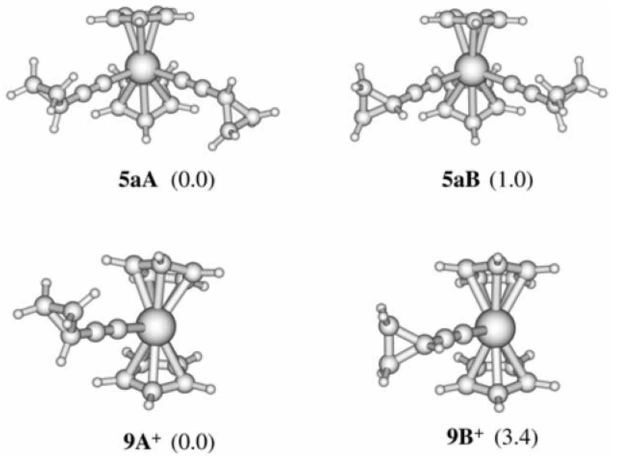


Fig. 4 Highest occupied molecular orbitals (DFT/PBE) of the cation **6**$^+$ showing the favorable conjugative interaction of the CH_2-CC π unit with cyclopropyl-π-type orbitals in **6A**$^+$ compared to non-bonding (HOMO-2) or even anti-bonding (HOMO) interactions in **6B**$^+$.

We conclude that carbocation centres can strongly electronically interact with a neutral cyclopropyl substituent that is connected by



5aA (0.0) **5aB** (1.0)

9A$^+$ (0.0) **9B$^+$** (3.4)

Fig. 5 DFT calculated structures and relative energies (kcal mol^{-1}) of the zirconocene systems **5a** and **9$^+$**.

a chain of sp-hybridized carbon atoms over remarkable distances. In the DFT calculated system (**7A$^+$**) this conjugation has remained very effective (−9.7 kcal mol^{-1}) across a carbon atom separation of *ca.* 6.5 Å. As expected this conjugational effect is decreased with an increased generic carbocation stabilization by additional substituents. Surprisingly, the stabilization of a cationic zirconocene unit (in **9$^+$**) by "bisected" cyclopropyl conjugation across a connecting C≡C triple bond is almost as pronounced (−3.9 kcal mol^{-1}) as DFT calculated for the organic diphenyl-substituted carbon analogue (**8$^+$**: −4.9 kcal mol^{-1}). Even in the neutral bis(cyclopropylethynyl) zirconocene (**5a**) this conjugative effect is still structurally prevailing as demonstrated by DFT calculation as well as by experiment, but its magnitude has become small at only *ca.* −1 kcal mol^{-1} per cyclopropylethynyl σ-ligand. Nevertheless, this effect appears to be sufficiently pronounced to determine the structural features of the pair of respective zirconocene (**5a**) and hafnocene complexes (**5b**).

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Notes and references

¶ *Crystal data for* **5a**: **5a** was obtained in 89% yield (3.28 g) from the reaction of 3.04 g (10.4 mmol) Cp_2ZrCl_2 with 1.50 g (20.8 mmol) of **4** in 150 mL THF (−30 °C to rt). Elemental analysis: Found: C, 68.58; H, 5.22. Calc. for $C_{20}H_{20}Zr$: C, 68.32; H, 5.73%; IR $\tilde{\nu}_{max}$/cm^{-1} 2081, 2058 cm^{-1} (C≡C); δ_H (600 MHz; benzene-d_6; 298 K) 6.08 (10 H, s, Cp); 1.19 (2 H, m, 3-H), 0.65 (4 H, m, 4-H), 0.45 (4 H, m, 4-H′) ppm; δ_C (150 MHz; benzene-d_6, 298 K): δ = 129.4 (C2), 129.0 (C1), 110.8 (Cp), 9.5 (C4), 1.9 (C3) ppm. Single crystals were obtained from a concentrated hot solution of **5a** in toluene at room temperature. Crystal data for $C_{20}H_{20}Zr$, M = 351.58, orthorhombic, space group *Pbcn* (No. 60), a = 14.261(1), b = 6.462(1), c = 17.607(1) Å, V = 1622.6(3) Å^3, D_c = 1.439 g cm^{-3}, μ = 0.669 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 198(2) K, 10858 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(sin\theta)/\lambda]$ = 0.66 Å^{-1}, 1937 independent (R_{int} = 0.026) and 1595 observed reflections [$I \geqslant 2\sigma(I)$], 96 refined parameters, R = 0.026, wR^2 = 0.075, CCDC 609890. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607906g

‖ *Crystal data for* **5b**: The reaction of 5.00 g (13.2 mmol) Cp_2HfCl_2 with **4** (1.90 g, 26.4 mmol) in 150 mL diethylether (−30 °C to rt) gave 3.63 g (63%) of **5b**. Elemental analysis: Found: C, 54.30; H, 4.50. Calc. for $C_{20}H_{20}Hf$: C, 54.74; H, 4.59%; IR $\tilde{\nu}_{max}$/cm^{-1} 2089 and 2065 cm^{-1} (C≡C); δ_H (500 MHz; benzene-d_6; 298 K) 6.00 (10 H, s, Cp), 1.15 (2 H, m, 3-H), 0.64 (4 H, m, 4-H), 0.44 (4 H, m, 4-H′) ppm; δ_C (125 MHz; benzene-d_6; 298 K) 138.1 (C1), 132.8 (C2), 109.8 (Cp), 9.3 (C4), 2.0 (C3) ppm. Single crystals were obtained from a concentrated hot solution of **5b** in toluene at room temperature. Crystal data for $C_{20}H_{20}Hf$, M = 438.85, orthorhombic, space group $Pna2_1$ (No. 33), a = 8.815(1), b = 14.432(1), c = 12.700(1) Å, V = 1615.7(2) Å^3, D_c = 1.804 g cm^{-3}, μ = 6.447 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 198(2) K, 12698 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(sin\theta)/\lambda]$ = 0.67 Å^{-1}, 3760 independent (R_{int} = 0.038) and 3475 observed reflections [$I \geqslant 2\sigma(I)$], 191 refined parameters, R = 0.020, wR^2 = 0.049, CCDC 609891. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607906g

1 W. R. Roth, O. Adamczak, R. Breuckmann, H.-W. Lennartz and R. Boese, *Chem. Ber.*, 1991, **124**, 2499.

2 J. L. Petersen and L. F. Dahl, *J. Am. Chem. Chem.*, 1975, **97**, 6416.

3 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Chem.*, 1976, **98**, 1729; J. C. Green, *Chem. Soc. Rev.*, 1998, **27**, 263.

4 C. U. Pittmann, Jr. and J. A. Olah, *J. Am. Chem. Chem.*, 1965, **87**, 2998; N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln and R. E. Fruit, Jr., *J. Am. Chem. Chem.*, 1965, **87**, 3000; D. S. Kabakoff and E. Namanworth, *J. Am. Chem. Chem.*, 1970, **92**, 3234; G. A. Olah, C. L. Jeuell, D. P. Kelly and R. D. Porter, *J. Am. Chem. Chem.*, 1972, **94**, 146; Reviews: H. G. Richey, Jr., in *Carbonium Ions*, ed. G. A. Olah and P. v. R. Schleyer, Wiley, New York, 1972, **vol. 3**, p. 1201; K. B. Wiberg, B. A. Hess, Jr. and A. J. Ashe, III, in *Carbonium Ions*, ed. G. A. Olah, P. v. R. Schleyer, Wiley, New York, 1972, **vol. 3**, p. 1295; H. C. Brown and P. v R. Schleyer, *Nonclassical Ion Problem*, Plenum Press, New York, 1977, p. 76.

5 See for a comparison: B. Temme, G. Erker, R. Fröhlich and M. Grehl, *Angew. Chem.*, 1994, **106**, 1570, (*Angew. Chem., Int. Ed. Engl*, 1994, **33**, 1480); W. Ahlers, G. Erker and R. Fröhlich, *Eur. J. Inorg. Chem.*, 1998, 889; W. Ahlers, G. Erker, R. Fröhlich and U. Peuchert, *J. Organomet. Chem.*, 1999, **578**, 115.

6 The calculations have been performed with the TURBOMOLE suite of programs [a]. The structures **5–9** have been fully optimized at the density functional (DFT) level employing the non-empirical PBE density functional [b], a Gaussian AO basis of valence-triple-zeta quality including polarization functions (TZV(d,p)) [c] and the resolution-of-the-identity (RI) approximation to represent the Coulomb operator [d]. For zirconium a [5s3p3d] AO basis set and a scalar-relativistic effective core potential with 28 core electrons [e] has been used. For the model system **6**, comparative calculations have been performed at the SCS-MP2[f] level of theory which, however, deviates by less than 1 kcal mol^{-1} from the DFT/PBE barrier of 15.5 kcal mol^{-1}. (Further more details see Supporting Information†) [a] TURBOMOLE (Vers. 5.7):(*a*) R. Ahlrichs, M. Bär, H.-P. Baron, R. Bauernschmitt, S. Böcker, M. Ehrig, K. Eichkorn, S. Elliott, F. Furche, F. Haase, M. Häser, H. Horn, C. Huber, U. Huniar, M. Kattannek, C. Kölmel, M. Kollwitz, K. May, C. Ochsenfeld, H. Öhm, A. Schäfer, U. Schneider, O. Treutler, M. von Arnim, F. Weigend P. Weis and H. Weiss, Universität Karlsruhe 2004. See also http://www.turbomole.com; (*b*) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; (*c*) A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571; (*d*) K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283; (*e*) D. Andrae, U. Haeussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123; (*f*) S. Grimme, *J. Chem. Phys.*, 2003, **118**, 9095.