Stereo-Electronic Interaction in Complex Molecules: Cyclopropyl Conjugation with Lewis Acidic Centres Across Connecting Carbon-Carbon Triple Bonds

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Supporting Information

Experimental Section.

5a 3.04 g of Dichlorobis(η^5-cyclopentadienyl)zirconium (10.42 mmol) were mixed under argon with 1.50 g cyclopropylethinyllithium (20.83 mmol) and at -30 °C dissolved in 150 ml THF. The reaction mixture was allowed to warm up to room temperature and stirred overnight. Solvent was removed and the remaining solid was dissolved in dichloromethane. The orange suspension was filtered over Celite® to remove the LiCl formed. After removal of the solvent the crude product remained in the flask as a beige product. Single crystals suitable for a single crystal structural analyses were obtained from a concentrated hot solution of **5a** in toluene at room temperature.

Yield: 3.28 g (9.3 mmol, 89.5 %);

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): 129.4 (C2), 129.0 (C1), 110.8 (Cp), 9.5 (C4), 1.9 (C3) ppm;

GHSQC δ_C/δ_H (125/500 MHz; benzene-d_6, 298 K) 110.8/6.08 (Cp), 9.5/0.65, 0.45 (C4/4-H, 4-H'), 1.9/1.19 (C3/3-H) ppm;

GHMBC δ_C/δ_H (150/600 MHz; benzene-d_6; 298 K) 129.4 /0.65, 0.45 (C2/4-H, 4-H'), 129.0/1.19 (C1/3-H), 9.5/1.19, 0.65, 0.45 (C4/3-H, 4-H, 4-H'), 1.9/0.65, 0.45 (C3/4-H, 4-H');

IR $\tilde{\nu}_{\max}$/cm^{-1} 2081, 2058 cm^{-1} (C≡C);

Elemental analysis Found: C, 68.58; H, 5.22. Calc. for $C_{20}H_{20}Zr$: C, 68.32; H, 5.73 %.

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 (±h, ±k, ±l), [$(\sin\theta)/\lambda$] = 0.66 Å^{-1}, 1937 independent (R_{int} = 0.026) and 1595 observed reflections [$I \geq 2\sigma(I)$], 96 refined parameters, R = 0.026, wR^2 = 0.075, CCDC 609890.

5b 5.00 g of dichlorobis(η^5-cyclopentadienyl)hafnium (13.2 mmol) were mixed under argon with 1.90 g cyclopropylethinyllithium (26.4 mmol) and at –30 °C dissolved in 150 ml diethylether. The reaction mixture was allowed to warm up to room temperature and stirred overnight after which the orange solution was filtered over Celite® to remove the LiCl formed. After removal of the solvent the crude product remained in the flask as a beige product. Single crystals suitable for a single crystal structural analyses were obtained from a concentrated hot solution of **5b** in toluene at room temperature.

Yield: 3.63 g (8.27 mmol, 62.8 %);

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;

GHSQC δ_C/δ_H (150/600 MHz; benzene-d_6, 298 K) 109.8/6.00 (Cp), 9.3/0.64, 0.44 (C-4/4-H, 4-H'), 2.0/1.15 (3-H) ppm;

GHMBC δ_C/δ_H (150/600 MHz; benzene-d_6; 298 K) 132.8/0.64, 0.44 (C2/4-H, 4-H'), 109.8/6.00 (Cp), 9.3/0.64, 0.44 (C4/4-H, 4-H'), 2.0/0.64, 0.44 (C3/4-H, 4-H') ppm;

IR $\tilde{\nu}_{\max}$/cm^{-1} 2089 and 2065 cm^{-1} (C≡C);

Elemental analysis Found: C, 54.30; H, 4.50. Calc. for $C_{20}H_{20}Hf$: C, 54.74; H, 4.59 %.

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 (±h, ±k, ±l), [$(\sin\theta)/\lambda$] = 0.67 Å^{-1}, 3760 independent (R_{int} = 0.038) and 3475 observed reflections [$I \geq 2\sigma(I)$], 191 refined parameters, R = 0.020, wR^2 = 0.049, CCDC 609891.

X-ray crystal structure analysis. Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction (R.H. Blessing, *Acta Cryst.* **1995**, *A51*, 33-37; R.H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421-426), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

Quantum chemical calculation. The calculations have been performed with the TURBOMOLE suite of programs [a]. The structures **5-9** have been fully optimized at the density

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[#] *X-ray crystal structure analyses*
§ *DFT calculations*

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. The structures of rotamers **B** have been obtained as transition states for the CH_2 group (CPh_2 in the case of **8**) rotation around the C2-C3 axis. The barriers correspond to pure electronic (zero-point exclusive) energies. The transition states have been characterized by harmonic vibrational calculations and in all cases one imaginary mode has been obtained. 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 from the DFT/PBE barrier of 15.5 kcal/mol. Additional tests (single point calculations) for the reliability of our DFT-PBE/TZVP computations have been performed for the rotational barrier of **5aA**, that is most crucial due to its small value (about 1 kcal/mol). With a larger TZVPP AO basis set (additional (df), (pd) and (f) polarization functions on C, H and Zr atoms, respectively) we found negligible changes of the barrier (<0.1 kcal/mol). With B3LVP density functional we obtain 0.8 kcal/mol as a barrier which als deviates insignificantly from the corresponding PBE value.

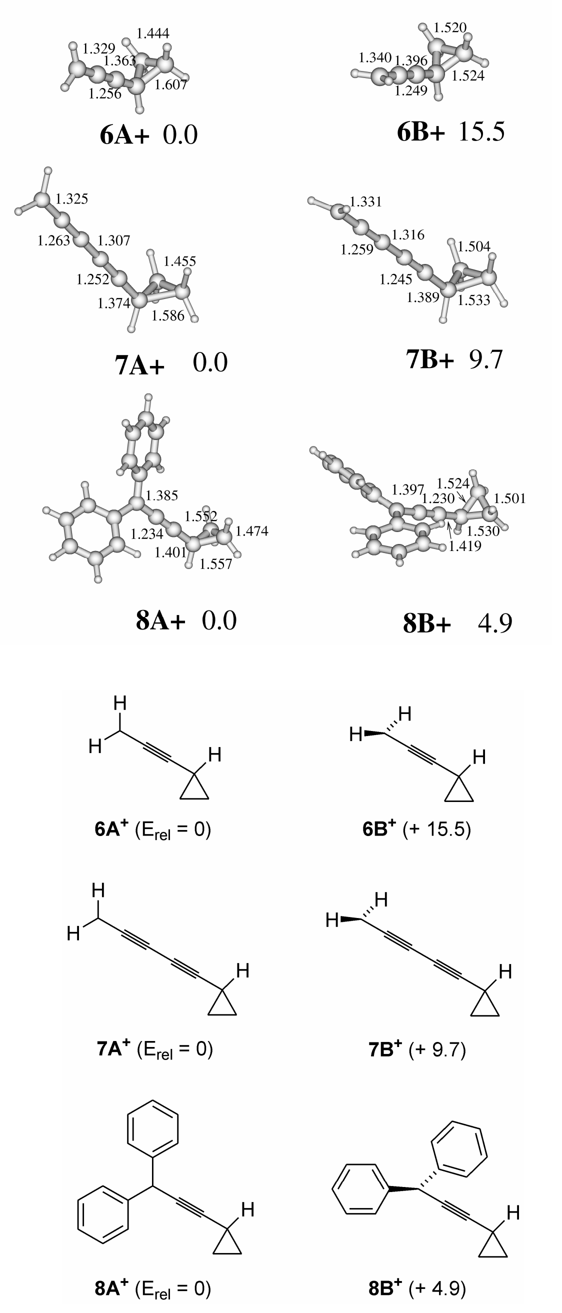

Fig. 3 DFT calculated structures and relative energies (kcal mol^{-1}) of favoured bisected ($\mathbf{A}^+$) and unfavoured parallel ($\mathbf{B}^+$) isomers of several ω-cyclopropylpropargyl cations.

Additional information to Fig. 3. The "conjugational length" of $\mathbf{7A}^+$ ist 6.5 Å. DFT calculated bond length (Å) and angles (°).

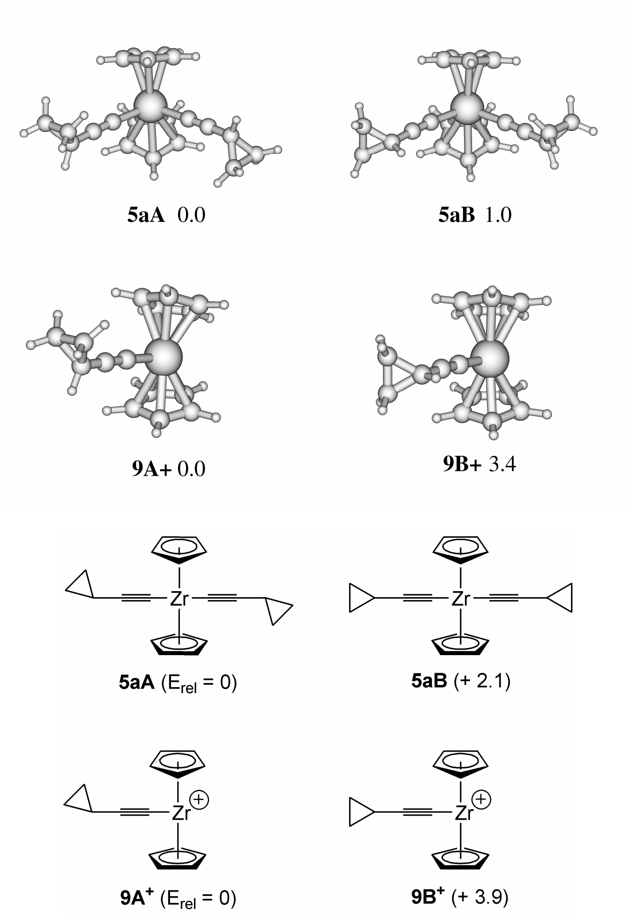

Fig. 4 DFT calculated structures and relative energies (kcal mol^{-1}) of the zirconocene systems **5a** and $\mathbf{9}^+$.

Additional information to Fig. 4. DFT-Data **5aA**: Zr-C1 2.215, C1-C2 1.237, C2-C3 1.431, C3-C4 1.529, C4-C5 1.498, C5-C3 1.528, C1-Zr-C1* 102.7, Zr-C1-C2 175.4°, C1-C2-C3 179.4°. DFT-Data **5aB**: Zr-C1 2.219, C1-C2 1.236, C2-C3 1.435, C3-C4 1.524, C4-C5 1.503, C5-C3 1.524, C1-Zr-C1* 102.3, Zr-C1-C2

173.6°, C1-C2-C3 178.7°. DFT-Data **9A**$^+$: Zr-C1 2.139, C1-C2 1.247, C2-C3 1.411, C3-C4 1.545, C4-C5 1.482, C5-C3 1.545, Zr-C1-C2 177.9°, C1-C2-C3 179.2°. DFT-Data **9b**$^+$: Zr-C1 2.145, C1-C2 1.243, C2-C3 1.424, C3-C4 1.527, C4-C5 1.500, C5-C3 1.527, Zr-C1-C2 176.1°, C1-C2-C3 179.2°.

[a] TURBOMOLE (Vers. 5.7): 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 und 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.

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[e] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta,* 1990, **77**, 123.

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