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(η5-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-d6; 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-d6; 298 K) 129.4 (C2), 129.0 (C1), 110.8 (Cp), 9.5 (C4), 1.9 (C3) ppm;

δ_H (150 MHz; benzene-d6; 298 K) 110.8/6.08 (Cp), 9.5/0.65, 0.44 (C2/4-H, 4-H'), 2.0/0.64, 0.44 (C3/4-H, 4-H') ppm;
δ_H (500 MHz; benzene-d6; 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-d6; 298 K) 138.1 (C1), 132.8 (C2), 109.8 (Cp), 9.3 (C4), 2.0 (C3) ppm;

GHSQC δ_c/δ_H (150/500 MHz; benzene-d6; 298 K) 110.8/6.08, 9.5/0.65, 0.44 (C4/H-4-H''), 1.9/1.19 (C3/H-3-H) ppm;
GHMBC δ_c/δ_H (150/500 MHz; benzene-d6; 298 K) 129.4/0.65, 0.45 (C2/H-2-H'), 129.0/1.19 (C1/H-1-H), 9.5/1.19, 0.65, 0.45 (C4/H-4-H', 1.9/0.65, 0.45 (C3/H-3-H, 4-H'');

IR ν max/cm⁻¹ 2081, 2058 cm⁻¹ (C=C);

Elemental analysis Found: C, 68.58; H, 5.22. Calc. for C20H20Zr: C, 68.32; H, 5.73 %.

Crystal data for C20H20Zr, M = 351.58, orthorhombic, space group Pna21 (No. 33), a = 14.432(1), b = 8.815(1), c = 12.700(1) Å, V = 1615.7(2) Å³, D_c = 1.804 g cm⁻³, μ = 6.447 mm⁻¹, Z = 4, λ = 0.71073 Å, T = 198(2) K, 10858 reflections collected (±h, ±k, ±l), (sinθ/λ) = 0.66 Å⁻¹, 1937 independent (Rint = 0.026) and 1595 observed reflections [I ≥ 2σ(I)], 96 refined parameters, R = 0.026, wR² = 0.075, CCDC 609890.


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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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 \(\text{CH}_2\) 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 also deviates insignificantly from the corresponding PBE value.

**Additional information to Fig. 3.** The “conjugational length” of \(7A^+\) is 6.5 Å. DFT calculated bond length (Å) and angles (°).

**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 175.4°, C1-C2-C3 179.4°.
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 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°.
