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Supporting Information

Chromocene in porous polystyrene:

an example of organometallic chemistry in confined spaces

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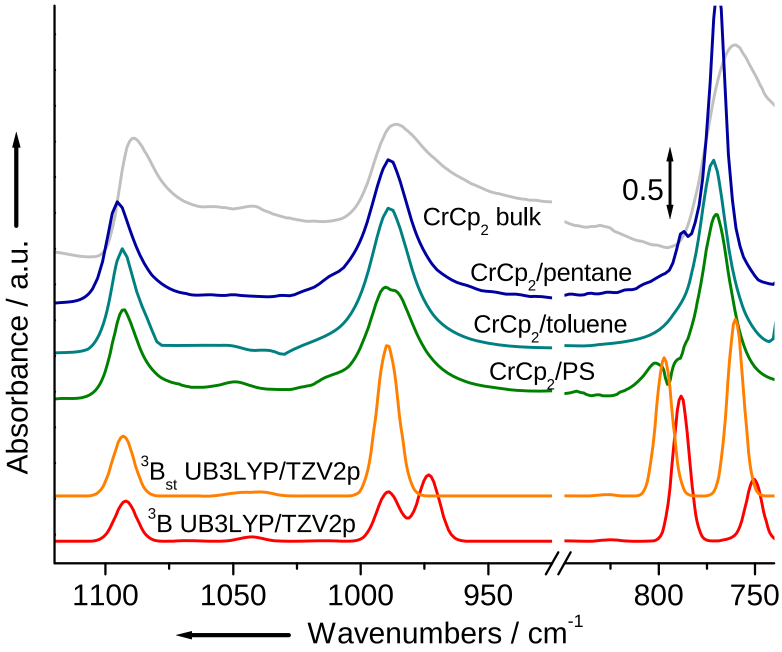

Figure S1. Top: IR spectra, in the 1120-750 cm^{-1} region, of CrCp$_2$/PS compared to that of bulk CrCp$_2$ and to those of CrCp$_2$ in solution of pentane and toluene. The spectrum of CrCp$_2$/PS is background subtracted using as background the spectrum of PS before CrCp$_2$ sublimation. Bottom: computed infrared spectra for the ^{3}B and ^{3}B$_{st}$ chromocene conformers as obtained at the UB3LYP level. A scaling factor of 0.973 has been adopted, in order to align the band around 1100 cm^{-1}.

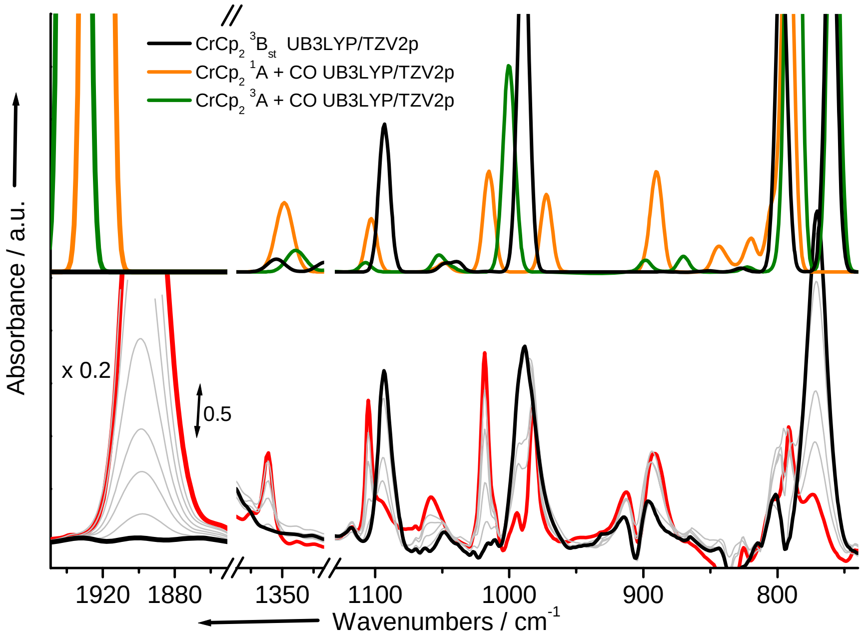

Figure S2. Bottom: from bold black to bold red, evolution of FTIR spectra of the $CrCp_2$/PS system upon increasing P_{CO} at 77 K. The frequency regions of CO stretching (left) and Cp deformations (right) are shown. All spectra are background subtracted using as background the spectrum of PS before $CrCp_2$ sublimation. Top: simulated IR spectra for the $^3Cp_2Cr\cdots CO$ (green) and $^1Cp_2Cr\cdots CO$ (orange) adducts as obtained at the UB3LYP level. A scaling factor of 0.973 has been adopted, in order to align the band around 1100 cm^{-1}.

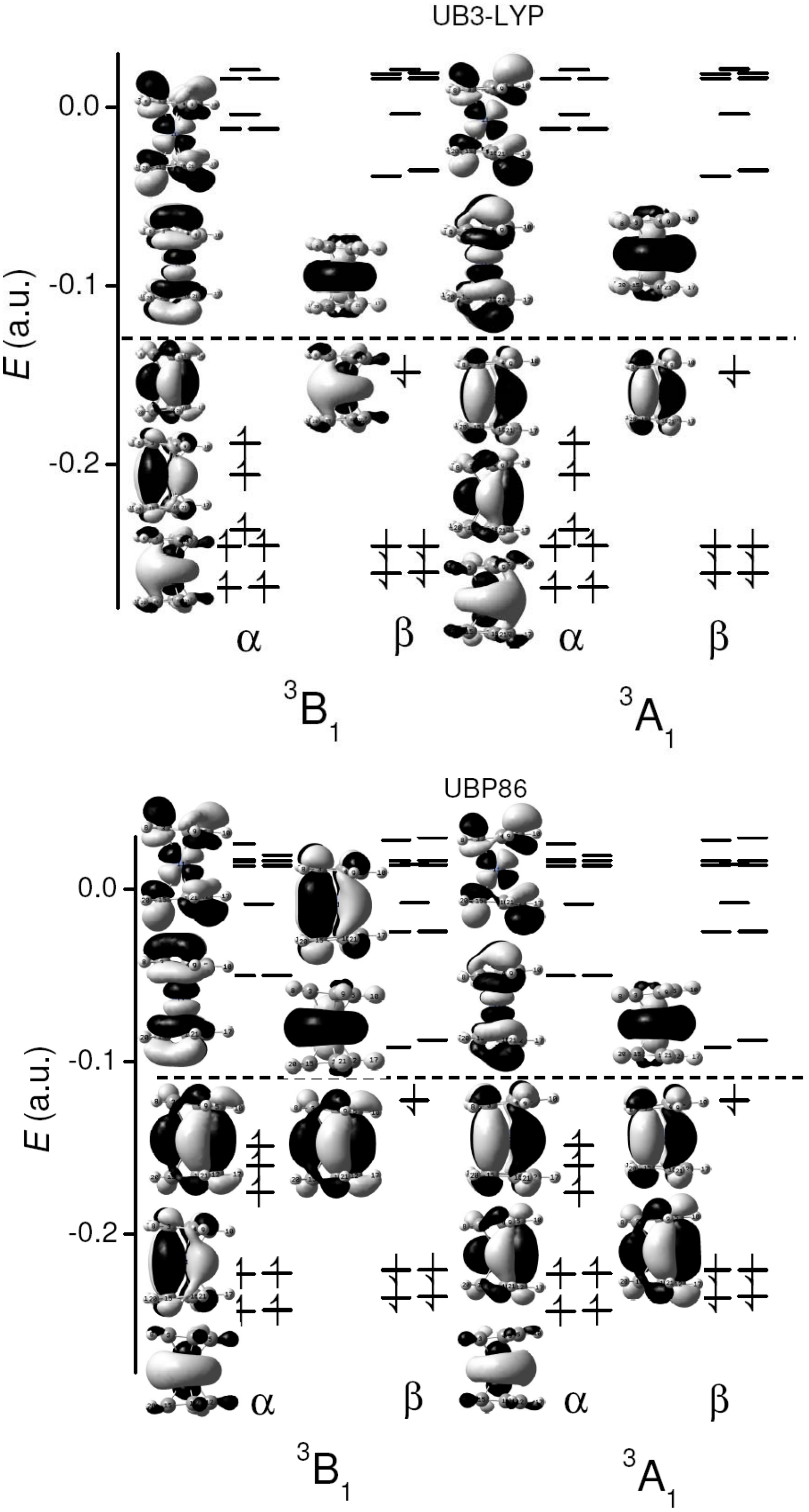

Figure S3. Molecular Kohn-Sham orbital energy level diagram for chromocene and sketches of its molecular orbitals at different level of calculations. Alpha orbitals surfaces reported: LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2. Beta orbitals surfaces reported: LUMO, HOMO.

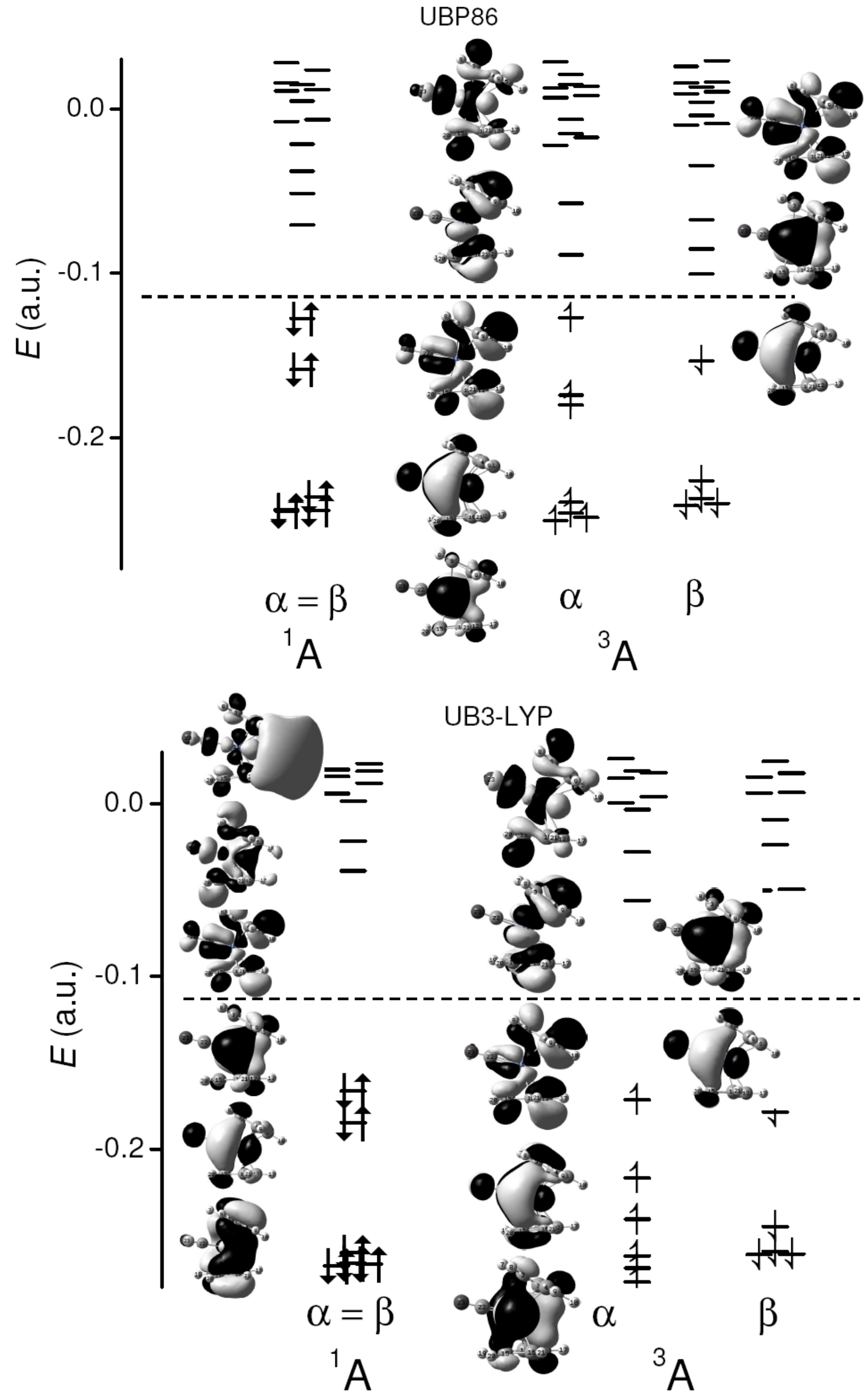

Figure S4. Molecular Kohn-Sham orbital energy level diagram for CO complex with chromocene and sketches of the molecular orbitals of the system. Alpha orbitals surfaces reported: LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2. Beta orbitals surfaces reported: LUMO, HOMO.

Table S1. Structures and relative energies (ΔE) for the different chromocene conformers (triplet spin state). All the distances are reported in Å. The notation of the carbon atoms is that used Figure 3.

	Eclipsed ^{3}B		Staggered $^3B_{st}$		Eclipsed ^{3}A		Staggered $^3A_{st}$	
	UBP86	UB3LYP	UBP86	UB3LYP	UBP86	UB3LYP	UBP86	UB3LYP
Cr-Cp	1.800	1.838	1.803	1.841	1.800	1.838	1.803	1.841
Cr-C_5	2.112	2.143	2.124	2.152	2.237	2.259	2.230	2.254
Cr-C_1(C_4)	2.155	2.182	2.160	2.186	2.194	2.218	2.192	2.218
Cr-C_2(C_3)	2.225	2.248	2.220	2.244	2.124	2.154	2.134	2.161
C_5-C_1(C_5-C_4)	1.445	1.431	1.444	1.431	1.425	1.415	1.425	1.415
C_1-C_2(C_4-C_3)	1.431	1.420	1.431	1.420	1.438	1.426	1.438	1.426
C_2-C_3	1.422	1.413	1.422	1.413	1.447	1.433	1.446	1.432
C_5-H	1.0848	1.076	1.0851	1.0760	1.0864	1.077	1.0863	1.0771
C_1(C_4)-H	1.0853	1.076	1.0854	1.0763	1.0858	1.077	1.0858	1.0766
C_2(C_3)-H	1.0862	1.077	1.0861	1.0770	1.0849	1.076	1.0852	1.0761
$\angle$Cp,H (°)	-2.744	2.400	-2.491	-2.220	2.828	2.371	2.996	177.499
$\angle$Cp-Cr-Cp (°)	177.742	178.773	179.998	179.993	177.816	178.783	180.000	179.996
Δ*E* (kJ/mol)	0	0	2.6635	1.5938	0.0087	-0.0016	2.6570	1.5925

Cr-Cp denotes the distance from the metal atom to the center of cyclopentadienyl ring. $\angle$Cp,H denotes the angle of the C_5-H bond out of the cyclopentadienyl ring; this angle is defined to be positive when the C-H bonds are bent toward the metal atom. $\angle$Cp-Cr-Cp is the angle between the Cr atom and the center of the centers of mass of the two cyclopentadienyl rings. Positive values of Δ*E* indicate a lower stability.

Even if the difference in energy is almost inexistent, the geometry of the ^{3}A and ^{3}B states is quite different: in particular, the tilt of the two Cp rings with respect to the D_{5h} symmetry (perfectly parallel Cp rings) is opposite in the two cases. Moreover, in the ^{3}B conformer the most near C atoms belonging to differ rings are the two tops of the pentagons (C_5 and C_{12} atoms in Figure 3), whereas in the ^{3}A conformer they are the most far. The larger the C-Cr distance (i.e. the local distance between the Cp rings), the smaller the corresponding C-C bonds; as a consequence, the succession of the C-C bonds in the rings results to be completely reversed in the ^{3}A and ^{3}B conformers. Among them, the ^{3}B geometry seems to be more suitable to interact with incoming molecules.

Conversely, in the $^3A_{st}$ and $^3B_{st}$ conformers the Cp rings are almost perfectly parallel each other (all the Cp-Cr-Cp angles of 180°), although a little slipping, along the C_5CrC_{12} plane in the $^3A_{st}$ conformer and along the plane passing through C_1 and C_4 and orthogonal to it in the $^3B_{st}$ conformer, exists . Also in the staggered case, an inverse succession of the C-C bonds is observed in the Cp rings of the two conformers.