

Supplementary material for the article:

Malenov, D. P.; Antonijević, I. S.; Hall, M. B.; Zarić, S. D. Stacking of Cyclopentadienyl Organometallic Sandwich and Half-Sandwich Compounds. Strong Interactions of Sandwiches at Large Offsets. *CrystEngComm* 2018, 20 (31), 4506–4514.
<https://doi.org/10.1039/c8ce00597d>

Supporting Information

CSD SEARCH DETAILS

The search can yield contacts which have metal of one complex directly interact with Cp ligand of another contact (Figure S1b-e, see Supporting information); these contacts should be excluded, since our goal is to study the contacts between ligands. In that order, additional restrictions were applied – $M_1-\Omega_1-\Omega_2$, $M_2-\Omega_2-\Omega_1$, $M_1-\Omega_1-M_2$ and $M_2-\Omega_2-M_1$ angles must all be larger than 90° (Figure S1a). If any of these angles is smaller than 90° , the contact is excluded (Figures S1b-e).

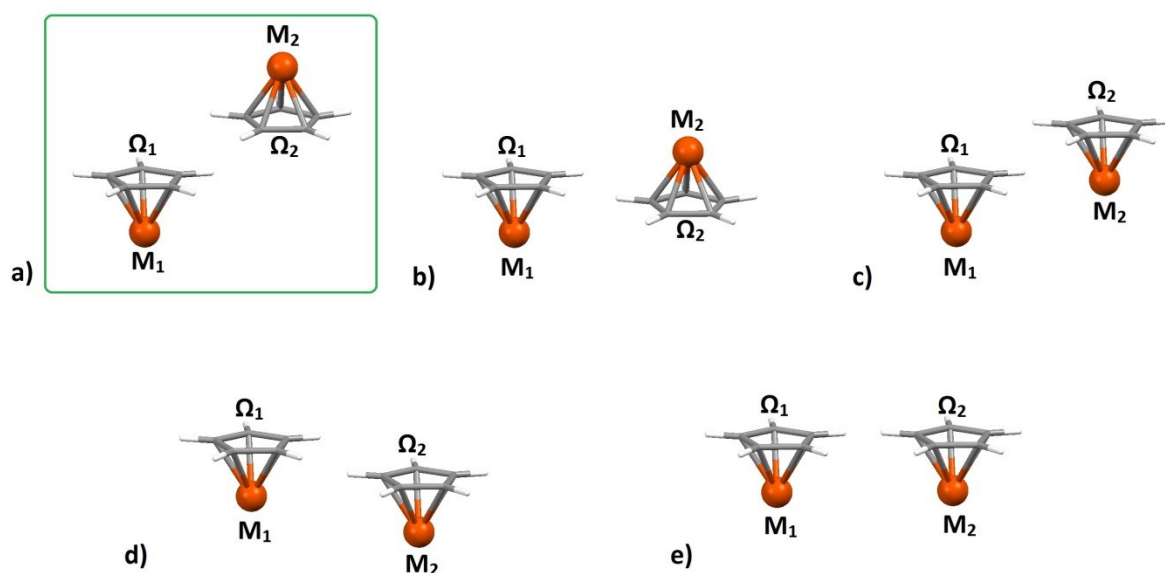


Figure S1. Interaction between two Cp ligands in which one Cp does not interact directly with the metal from another complex (and vice versa) has angles $M_1-\Omega_1-\Omega_2$, $M_2-\Omega_2-\Omega_1$, $M_1-\Omega_1-M_2$ and $M_2-\Omega_2-M_1$ all larger than 90° (a). If any of these angles is smaller than 90° , metal directly interacts with the ligand from another complex, hence these contacts were excluded from the search results: b) $M_1-\Omega_1-\Omega_2 < 90^\circ$, $M_2-\Omega_2-\Omega_1 < 90^\circ$, c) $M_2-\Omega_2-\Omega_1 < 90^\circ$, $M_2-\Omega_2-M_1 < 90^\circ$, d) $M_1-\Omega_1-\Omega_2 < 90^\circ$, $M_1-\Omega_1-M_2 < 90^\circ$, $M_2-\Omega_2-M_1 < 90^\circ$, e) $M_1-\Omega_1-M_2 < 90^\circ$, $M_2-\Omega_2-M_1 < 90^\circ$.

INTERACTION ENERGIES AT CCSD(T)/CBS LEVEL AND THEIR COMPARISON WITH DFT-D ENERGIES

CCSD(T)/CBS energies were compared with energies calculated with two DFT methods. The TPSS-D2 method and def2-TZVP basis set without correction for basis set superposition error (BSSE) gives better agreement with the CCSD(T)/CBS level than B2PLYP-D2 functional with the same basis set. Therefore, TPSS-D2/def2-TZVP level of theory is used for calculations of interaction energy values for all model systems.

Table S1. Interaction energies estimated at CCSD(T)/CBS level for stacking of benzenes with (benzene)tricarbonylchromium and ferrocene and comparison with two DFT-D methods

SYSTEM	offset [Å]	normal distance [Å]	CCSD(T)/CBS [kcal/mol]	TPSS-D2/def2-TZVP (no BSSE correction) [kcal/mol]	B2PLYP-D2/def2-TZVP (no BSSE correction) [kcal/mol]
$(\text{C}_6\text{H}_6)(\text{CO})_3\text{Cr} \parallel \text{C}_6\text{H}_6$	0.0	3.7	-3.45	-3.46	-3.68
	1.5	3.4	-4.19	-4.17	-4.41
	3.0	3.3	-3.03	-3.15	-3.17
	4.5	2.9	-2.47	-2.51	-2.43
	6.0	1.9	-1.47	-1.57	-1.35
$(\text{C}_5\text{H}_5)_2\text{Fe} \parallel \text{C}_6\text{H}_6$	0.0	3.7	-2.22	-2.26	-2.32
	1.5	3.4	-2.83	-2.84	-2.95
	3.0	3.3	-2.31	-2.39	-2.31
	4.5	2.8	-2.15	-2.23	-2.09
	6.0	1.5	-1.40	-1.64	-1.38

ENERGIES OF STACKING INTERACTIONS WITH DIFFERENT ORIENTATION OF Cp HALF-SANDWICH COMPOUNDS

The orientation of Cp ligand (Figure S2) has a significant effect on interaction energies at larger offsets, while at small offsets this effect is not so pronounced (Figure S3). In another orientation that we studied, the interactions in Cp HS-HS system even get repulsive at $r > 5.5$ Å. The reason for that is non-equivalence of hydrogen atoms in Cp ligand due to the geometry of half-sandwich compound and different substituents.

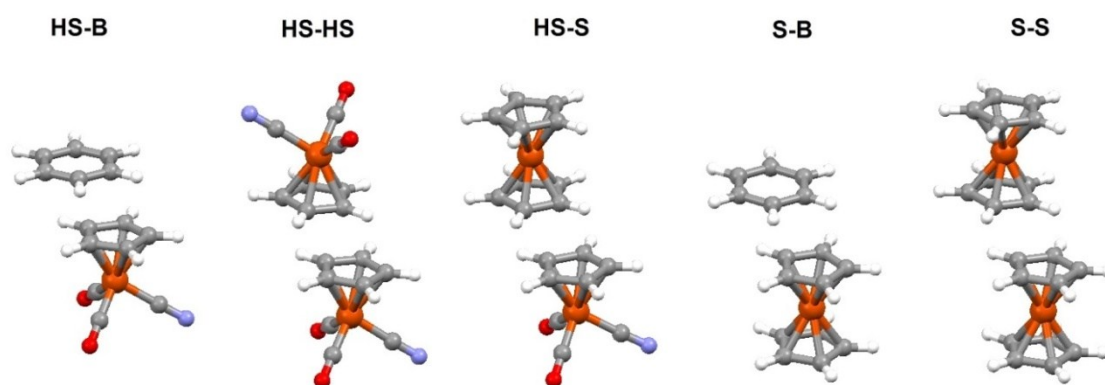


Figure S2. Model systems used for DFT-D calculations with another orientation between molecules, different than in main text (Figure 3): HS-B denotes half-sandwich||benzene, HS-HS half-sandwich||half-sandwich, HS-S half-sandwich||sandwich, S-B sandwich||benzene and S-S half-sandwich dimer. The geometries with $r = 1.5$ Å are presented.

For HS-B system, the effect of different orientation is generally less pronounced than for other systems. The main difference was calculated at $r = 1.5$ Å; the orientation in the main text (Figure 3) has the energy of -4.46 kcal/mol, while in orientation at Figure S2 the energy is -4.71 kcal/mol. The similar difference at large offsets was found in HS-S system, in the orientation from the main text the energy at 1.5 Å is -4.96 kcal/mol, while in orientation at Figure S2 the energy is -5.15 kcal/mol. However, the influence of orientation in HS-S system is more pronounced at 6.0 Å, where in the main text orientation the energy is -1.54 kcal/mol, while in the orientation at Figure S2 the energy is -1.72 kcal/mol.

The differences are most pronounced in HS-HS system. The energies at $r = 0.0$ Å and 1.5 Å are the same, but substantial differences are present at large offsets. At 5.0 Å the orientation in the main text has the energy of -0.82 kcal/mol, while at Figure S2 the interaction in HS-HS system at 5.0 Å is only -0.27 kcal/mol. Moreover, at 6.0 Å interaction at Figure S2 is

repulsive, with interaction energy of +0.29 kcal/mol, while at the same offset in the main text the interaction is attractive.

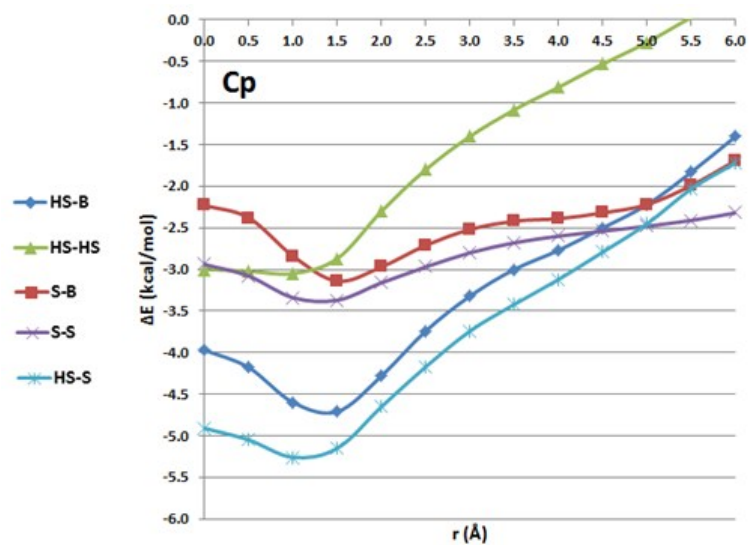


Figure S3. Potential energy curves for half-sandwich||benzene, half-sandwich||half-sandwich, sandwich||benzene, sandwich||sandwich and half-sandwich||sandwich model systems (Figure S2) with Cp ligand at various offset values calculated at TPSS-D2/def2-TZVP level without BSSE correction.

OPTIMAL NORMAL DISTANCES AT EACH OFFSET VALUE FOR SYSTEMS CONTAINING COORDINATING BENZENE/Cp

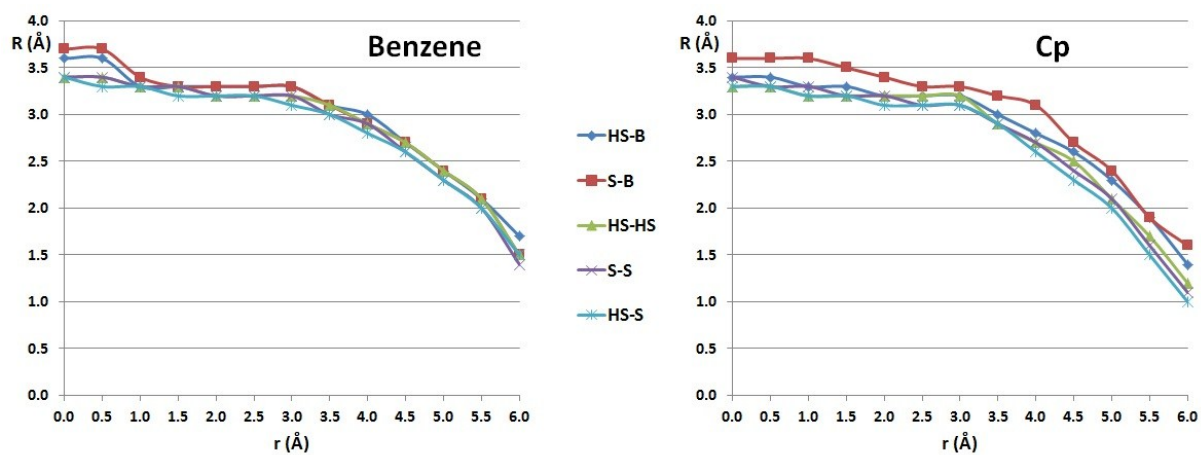


Figure S4. Normal distances corresponding to the strongest interactions at each offset value (see Figure 4 in the Main Text); the energies and normal distances were determined at TPSS-D2/def2-TZVP level (without BSSE correction).

SUPRAMOLECULAR STRUCTURES FOR BENZENE HALF-SANDWICH||HALF-SANDWICH INTERACTIONS

In crystal structures shown on Figure S4 coordinated benzene in half-sandwich has bidentate and planar ligand. These ligands can not participate in formation of additional interactions with another half-sandwich molecule like in structures with voluminous and branched ligand. Stacking interaction at large offsets is formed along with the much stronger stacking at small offsets but is not pronounced in crystals structures.

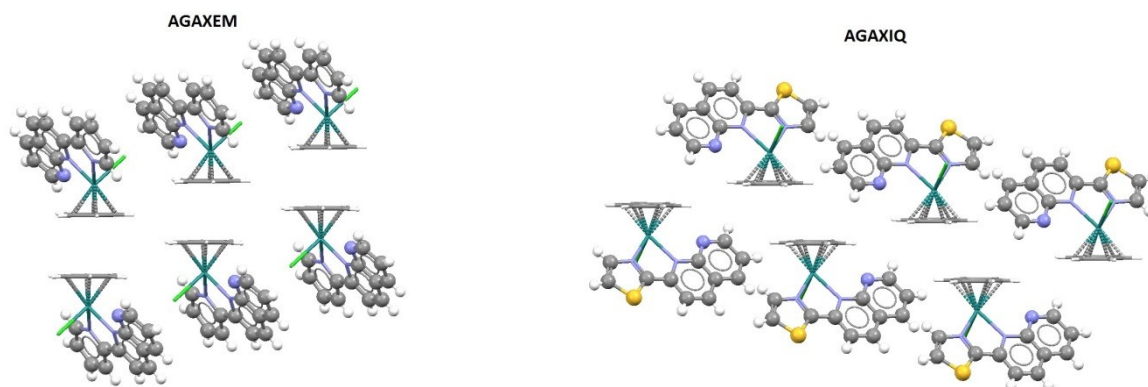


Figure S5. Stacking interactions in crystal structures of substituted benzene half-sandwiches. Bidentate and planar ligands cannot form additional interactions so the frequency of stacking interaction at large offsets is not pronounced.