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## MS22-P02

## Experimental charge density for $\sigma$ hole interactions

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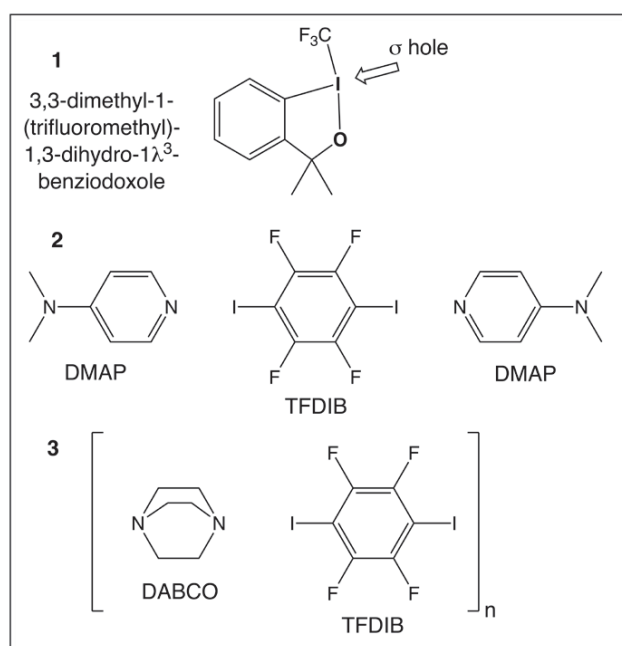
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Halogen bonds and  $\sigma$  hole interactions do not only play an important role in crystal engineering but are also relevant for understanding chemical reactivity.

3,3-dimethyl-1-(trifluoromethyl)-1,3-dihydro-1 $\lambda^3$ ,2-benziodoxole, **1**, commonly known as “Togni reagent” [1], is used for the electrophilic transfer of the trifluoromethyl group by reductive elimination. The  $\sigma$  hole associated with the hypervalent iodine atom is essential for this reactivity. [2] Based on high resolution X-ray diffraction, we have determined the experimental electron density for **1**. In the crystal, it interacts with a neighbouring molecule via O $\cdots$ I contacts of 2.9809(6) Å. We compare **1** with two cocrystals **2** and **3** (see Scheme) in terms of electrostatic potential and QTAIM properties in the bond critical point (bcp) for the  $\sigma$  hole interaction. In **2**, tetrafluorodiiodobenzene (TFDIB) interacts with two molecules of dimethylaminopyridine (DMAP); the N $\cdots$ I halogen bond is as short as 2.6622(4) Å. With respect to its electronic properties, it resembles a coordinative bond [3]. **3** consists of infinite chains in which diaminobicyclooctane (DABCO) and TFDIB alternate; the N $\cdots$ I contacts are significantly longer but still much shorter than O $\cdots$ I in the case of the Togni reagent. The bcps for the halogen bonds in **3** fall in the range of electron depletion associated with the  $\sigma$  hole on iodine; consequently, the electron density in the bcps is surprisingly small.

In conclusion, the three examples documented in this contribution underline the very wide range of  $\sigma$  hole interactions.



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## MS22-P03

## Property studies for the heterobimetallic phosphido-bridged W and Mo complexes through charge density analysis

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The chemical bonds and reactions of the  $(\text{Cp})(\text{CO})_2\text{W}(\text{m-PPh}_2)\text{Mo}(\text{CO})_5$  (1) and  $(\text{Cp})(\text{CO})_3\text{W}(\text{m-PPh}_2)\text{Mo}(\text{CO})_5$  (2) complexes were calculated by density functional theory (DFT) method to gain an insight into the property of heterobimetallic metal-metal bond. Based on quantum theory of atoms in molecules (QTAIM), all chemical bonds of optimized geometry will be characterized by bond critical point (BCP) and its associated topological properties, and these results are further compared with single crystal charge density experimental data. Using exchange functional PBE0-D3BJ can provide better calculation results whether it performed through the ZORA approximation of all-electron relativistic method or the pseudopotential method. In complex 1, the characters of the CO on Mo semibridges to W can be confirmed by the BCP between C and W ( $r_c \sim 0.20 \text{ e}/\text{\AA}^3$ ). Based on fragment charge analysis of DFT calculations,  $\text{Mo}(\text{CO})_5$  fragment of complex 1 (-0.092) is more positive than that of complex 2 (-0.184), and  $\text{CpW}(\text{CO})_2$  fragment of complex 1 (0.208) is more negative than  $\text{CpW}(\text{CO})_3$  fragment of complex 2 (0.321). These results imply that a dative metal-metal bonding is formed by the electron donation from Mo to W. On the other hand, an intermediate without metal-metal bonding between Mo and W can be formed from complex 1 through semibridging CO transferring from Mo to W, and the transition state of this reaction can be located. This result explains the phenomenon of phosphine addition to Mo cis-site, which is observed in our previous publications.

**Keywords:** heterobimetallic, metal-metal bond, DFT