

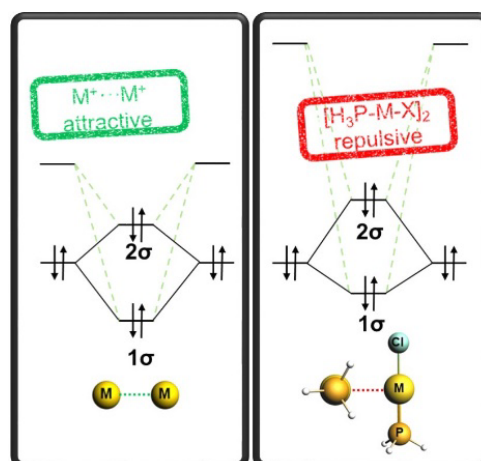
Relevance of Orbital Interactions and Pauli Repulsion in the Metal-Metal Bond of Coinage Metals

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Closed-shell d^{10} - d^{10} interactions are an interesting research target both from an experimental as well as from a theoretical perspective.^[1] From a practical point of view, these interactions can be used for the design of supramolecular (di-, oligo- or polymeric) structures. Furthermore, these structures show very interesting luminescent properties, including mechanochromic or vaporchromic behavior and are discussed as important viable intermediates in gold-catalyzed hydroarylation reactions.^[2] Surprisingly, the bonding mechanism is still a subject of a long-standing debate; while the importance of relativity and dispersion in metallophilicity has been discussed in numerous studies,^[3] the existence of hybridization has also been speculated.^[4] In this talk, a quantitative molecular orbital analysis and energy decomposition of the metallophilic interaction in atomic dimers ($M^+ \cdots M^+$) and molecular perpendicular $[H_3P-M-X]_2$ (where $M = Cu, Ag, Au$ and $X = F, Cl, Br, I$) are discussed. Our research proves, that besides the commonly accepted dispersive interactions, orbital interactions and Pauli repulsion play a crucial role in metallophilicity. While for $M^+ \cdots M^+$ the orbital interaction is larger than the Pauli repulsion, leading to a *net attractive* MO interaction, the bonding mechanism in perpendicular $[H_3P-M-X]$ dimers is different. Here Pauli repulsion is much larger and *two-orbital-four-electron repulsion* is dominant (see Figure).^[5] These results are of utmost importance for the fundamental understanding of metallophilicity and for future design of new materials.



Literature:

[1] a.) P. Pyykkö, *Chem. Soc. Rev.* **2008**, 37, 1967-1997; b.) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, 37, 1931-1951; c.) S. Sculfort, P. Braunstein, *Chem. Soc. Rev.* **2011**, 40, 2741-2760; d.) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, 41, 370-412. [2] a.) C.-M. Che, S.-W. Lai, *Coord. Chem. Rev.* **2005**, 249, 1296-1309; b.) D. L. Phillips, C.-M. Che, K. H. Leung, Z. Mao, M.-C. Tse, *Coord. Chem. Rev.* **2005**, 249, 1476-1490; c.) Z. N. Chen, N. Zhao, Y. Fan, J. Ni, *Coord. Chem. Rev.* **2009**, 253, 1-20. Aponick, A. F., O.N.; Gagné, M.R.; Hammond, G.B.; Jones, A.C.; López, A.C.; Malhotra, D.; Michelet, V.; Paioti, P.H.S.; Shin, S.; Weber, D.; Xu, B. In *Homogeneous Gold Catalysis*; Gagné, M.R.; Weber, D. 1 ed.; Springer International Publishing: Cham, **2015**; Vol. 357, Chapter 6, pp 167-212 (and references herein). [3] a.) P. Pyykkö, Y. F. Zhao, *Angew. Chem. Int. Ed.* **1991**, 30, 604-605; b.) J. Li, P. Pyykkö, *Chem. Phys. Lett.* **1992**, 197, 586-590; c.) P. Pyykkö, J. Li, N. Runeberg, *Chem. Phys. Lett.* **1994**, 218, 133-138. [4] a.) P. K. Mehrotra, R. Hoffmann, *Inorg. Chem.* **1978**, 17, 2187-2189; b.) Y. Jiang, S. Alvarez, R. Hoffmann, *Inorg. Chem.* **1985**, 24, 749-757 [5] M. B. Brands, J. Nitsch, C. Fonseca Guerra, *Inorg. Chem.*, DOI: 10.1021/acs.inorgchem.7b02994.