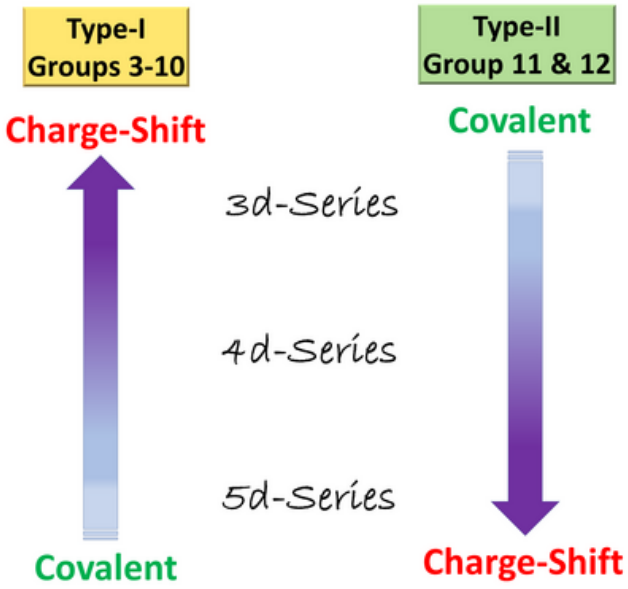
A Unified Understanding of Metal–Metal Bond in Transition Metal Complexes

Start Time: Wednesday, July 8, 2020

End Time:



Covalent vs Charge-Shift Nature of the Metal–Metal Bond in Transition Metal Complexes: A Unified Understanding

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In a joint approach UniSysCat-PI Martin Kaupp and collaboration partners of the group of Sason Shaik at Hebrew University in Jerusalem present a general conceptualization of the nature of metal–metal (M–M) bonding in transition-metal (TM) complexes across the periods of TM elements, by use of ab initio valence-bond theory. The calculations reveal a dual-trend: For M–M bonds in groups 7 and 9, the 3d-series forms charge-shift bonds (CSB), while upon moving down to the 5d-series, the bonds become gradually covalent. In contrast, M–M bonds of metals having filled d-orbitals (groups 11 and 12) behave oppositely; initially the M-M bond is covalent, but upon moving down the Periodic Table, the CSB character increases. These trends originate in the radial-distribution-functions of the atomic orbitals, which determine the compactness of the valence-orbitals vis-à-vis the filled semicore orbitals. Key factors that gauge this compactness are the presence/absence of a radial-node in the valence-orbital and relativistic contraction/expansion of the valence/semicore orbitals. Whenever these orbital-types are spatially coincident, the covalent bond-pairing is weakened by Pauli-repulsion with the semicore electrons, and CSB takes over. Thus, for groups 3–10, which possess $(n-1)s^2(n-$

1)p^6 semicores, this spatial-coincidence is maximal at the 3d-transition-metals which consequently form charge-shift M–M bonds. However, in groups 11 and 12, the relativistic effects maximize spatial-coincidence in the third series, wherein the $5d^{10}$ core approaches the valence 6s orbital, and the respective Pauli repulsion generates M–M bonds with CSB character. These considerations create a generalized paradigm for M–M bonding in the transition-elements periods, and Pauli repulsion emerges as the factor that unifies CSB over the periods of main-group and transition elements.

For more information: *J. Am. Chem. Soc.*2020 https://doi.org/10.1021/jacs.0c03957