Theoretical Insight into 20-Electron Transition-Metal Complexes $(C_5H_5)_2TM(E_1E_2)_2$ (TM = Cr, Mo, W; E_1E_2 = CO, N_2, BF): Stabilities, Electronic Structures, and Bonding Nature

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June 8, 2021

Abstract

A systematic first-principles study is performed to investigate the 20-electron transition metal complexes $(C_5H_5)_2TM(E_1E_2)_2$ (TM = Cr, Mo, W; E_1E_2 = CO, N_2, BF). The bond dissociation energy (De) based on $(C_5H_5)_2TM(E_1E_2)_2$ - $(C_5H_5)_2TM(E_1E_2)$ + E_1E_2 indicates much lower thermodynamic stability of $(C_5H_5)_2TM(N_2)_2$ because of poor binding ability of N_2 ligands. For the thermodynamic stable $(C_5H_5)_2TM(E_1E_2)_2$ complexes (TM = Cr, Mo, W; E_1E_2 = CO, BF), their 20-electron nature is derived from their occupied nonbonding molecular orbital mainly donated by ligands. Furthermore, charge transfer from TMs to the C_5H_5 ligands is revealed by the atoms in molecules (AIM) theory, leading to the positive charges of the TM atoms. On the other hand, the nature of the TM-E_1 bond has been thoroughly analyzed by the energy decomposition analysis (EDA) method. The absolute value of interaction energies ($|\Delta E_{\text{int}}|$) between $(C_5H_5)_2TM(E_1E_2)$ and E_1E_2 has the same trend as the corresponding bond dissociation energy and Wiberg bond orders of TM-E_1 bonds, following the order W > Mo > Cr with same ligands and BF > CO with same TM. Additionally, the largest contribution to the ΔE_{int} values is the repulsive term ΔE_{Pauli}. Similar contributions from covalent and electrostatic terms to the TM-E_1 bonds were found, which can be described as the classic dative bond with nearly same σ and π contributions. The stronger σ donations and π backdonations in $(C_5H_5)_2TM(BF)_2$ than in $(C_5H_5)_2TM(CO)_2$ indicate much more stability of $(C_5H_5)_2TM(BF)_2$.

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