Glenn T. Seaborg Center Seminar

The large influence of the substituents on the Cp' ring on the CO stretching frequencies in Cp3'U(CO): How they report on the participation of f and d orbitals in the U-CO bond

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Quantum calculations of the CO stretching frequencies have been carried out on $(C_5H_4(SiMe_3))_3U(CO)$. Calculations in which the 5f orbitals are explicitly included as valence orbitals reproduce properly the observed lowering of the CO frequency by around 160cm^{-1} compared to free CO. A detailed study of the CO stretching frequency in $(C_5H_5)_3U(CO)$ shows the crucial role of the empty 6d orbitals in determining the lowering of the CO stretching frequency. The empty 6d orbitals receive their density from the Cp' ligands, hence the large influence of the substituent of the ligands on the CO stretching frequency. The calculations of additional Cp'_3UCO complexes (Cp' = C_5Me_4H, C_5Me_5 in progress) with 5f orbitals in the core, reproduce the experimental trends. This model predicts that the CO stretching frequency in $(C_5H_4(SiMe_3)_3)Pu(CO)$, calculated with 5f orbitals in the valence shell, is lower than that for the uranium complex, consistent with the experiment.

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