A DFT study of the Electronic Structure of the Metal-Phosphine Bond in the group 6 Complexes $M(CO)_5PR_3$ (M= Cr, Mo, W; R= H, F, Cl, Me)

Karin Wichmann and Gernot Frenking
Fachbereich Chemie, Philipps-Universität-Marburg, D-35032 Marburg

Phospine ligands play an important role in organometallic chemistry, since they are present in many transition metal complexes. Hence, the nature of the donor and acceptor orbitals of the PR_3 ligand is of great interest.
We chose a series of group 6 $M(CO)_5PR_3$ complexes to carry out a systematic study of the M-PR_3 bonding situation in order to distinguish between steric and electronic effects, between covalent and Coulomb interactions and between σ- and π-contributions. The compounds have been optimized at the BP86 level of density functional theory and the M-PR_3 bond has been analyzed in detail using an energy decomposition scheme.
The analysis of the M-PR_3 bond shows a significant influence of the rests R. While the π/σ-ratio seems not to be substantially dependent on the metal, it is clearly affected by the donor/acceptor properties of R: the π-contribution to the orbital interaction is higher for the ligands with the electronegative elements F and Cl than for the ligands PH_3 and PMe_3.