

A Direct Measure of Metal-Ligand Bonding Replacing the Tolman Electronic Parameter

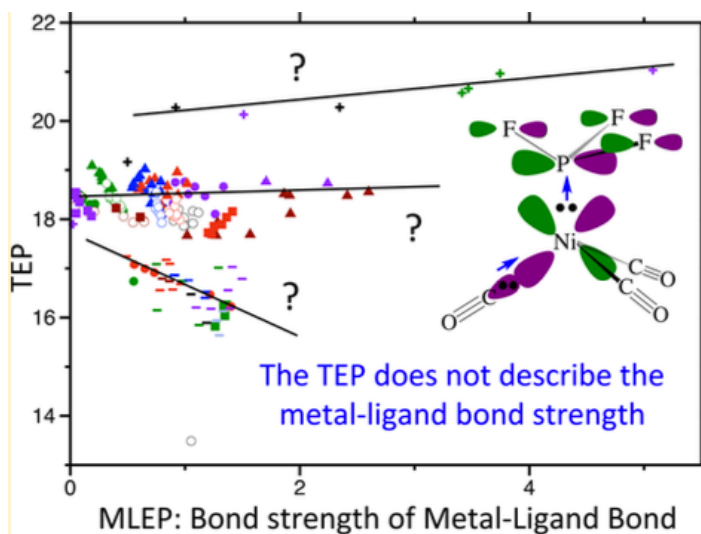
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Abstract: The prediction of the catalytic activity of transition metal complexes is a prerequisite for homogeneous catalysis. The Tolman Electronic Parameter (TEP) was derived to provide this information. It is based on the CO stretching frequencies of metal-tricarbonyl complexes $L-M(CO)_3$ with varying ligands L. It has been used in hundreds of cases as is documented by as many publications.

We show [1] that the TEP is misleading as *i*) it is not based on mode-decoupled CO stretching frequencies and *ii*) a quantitatively correct or at least qualitatively reasonable relationship between the TEP and the metal-ligand bond strength does not exist. This is demonstrated for a set of 181 nickel-tricarbonyl complexes using both experimental and calculated TEP values. Even the use of mode-mode decoupled CO stretching frequencies does not lead to a reasonable description of the metal-ligand bond strength.

A reliable descriptor replacing the TEP is obtained with the help of the metal-ligand local stretching force constant. For the test set of 181 Ni-complexes, a direct metal-ligand electronic parameter (MLEP) in the form of a bond strength order is derived, which reveals that phosphines and related ligands (amines, arsines, stibines, bismuthines) are bonded to Ni both by σ -donation and π -back donation. The strongest Ni-L bonds are identified for carbenes and cationic ligands. The new MLEP quantitatively assesses electronic and steric factors and it can be determined for any metal or transition metal complex, whether it contains CO ligands or not.



References:

[1] Dieter Cremer, Elfi Kraka, "Generalization of the Tolman electronic parameter: the metal-ligand electronic parameter and the intrinsic strength of the metal-ligand bond", *Dalton Trans.*, **2017**, DOI: 10.1039/c7dt00178a.