Quantum Mechanical Analysis of Donor-Acceptor Interactions in Organometallic Complexes

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Donor-acceptor interactions are ubiquitous in chemistry. In many instances, particularly in organometallic chemistry, donor-acceptor interactions have both a sigma and pi component. In the now-classical Dewar-Chatt-Duncanson model\(^1\) a filled ligand donor orbital donates in a sigma fashion into an empty metal orbital and a filled metal orbital donates in a pi fashion into an empty ligand orbital, as illustrated for metal-H\(_2\) bonding in Figure 1. The interaction can be tuned by altering the energies of the metal orbitals, which can be accomplished by changing the ligands attached to the metal center.

![Figure 1. Diagram showing Dewar-Chatt-Duncanson model of bonding with \(\sigma\) and \(\pi\) interactions between a metal fragment and a H\(_2\) ligand.](image)

We have used density functional theory (DFT) to investigate the geometries and metal-ligand bonding in nickel complexes of bidentate phosphines, Ni(CO)\(_2\)(R\(_2\)P(CH\(_2\))\(_n\)PR\(_2\)) and NiH\(_2\)(R\(_2\)P(CH\(_2\))\(_n\)PR\(_2\)), where \(n = 1, 2, \) or \(3\); and \(R = H, Me, CF_3, Et, i-Pr, t-Bu, Ph, OMe, \) or \(F\). The net donor/acceptor properties of the phosphine ligands can be deduced from the computed frequency of the symmetric CO stretch of the Ni(CO)\(_2\)(R\(_2\)P(CH\(_2\))\(_n\)PR\(_2\)) complexes. This frequency can be estimated from the empirical expression \(\nu(CO) = 1988 + \sum \chi_B - 4n\), where the sum is over the four phosphorus bound substituents, \(\chi_B\) is a substituent-dependent parameter, and \(n\) is the number of carbon atoms in the backbone (\(1 \leq n \leq 3\)). The deduced values of \(\chi_B\) (in units of cm\(^{-1}\)) – t-Bu (0.0), i-Pr (0.8), Et (3.0), Me (4.0), Ph (4.3), H (6.3), OMe (10.8), CF\(_3\) (17.8), and F (18.3) – are generally similar to Tolman’s electronic parameter \(\chi\) derived from nickel complexes of unidentate phosphines.\(^5\) For the NiH\(_2\)(R\(_2\)P(CH\(_2\))\(_n\)PR\(_2\)) complexes, the global minimum is a non-classical dihydrogen structure. Natural bond order\(^6\) analyses confirmed that the Ni-H\(_2\) interaction is a three-center two-electron bond. Energy decomposition analysis of these complexes reveals, as expected, electron donating
phosphines increase the [Ni]→(H₂) π backdonation component of the Ni-H2 bond, and increase the equilibrium H-H distance. For the most strongly donating phosphines, a second local minimum can be located on the potential energy surface: a classical dihydride structure. But even for phosphines bearing t-butyl substituents, this dihydride is always higher in energy that the molecular H₂ adduct.

We have also used DFT to analyze the effect of ancillary ligands on the hydrogen exchange reaction of (C₅HₓRₓ)Os(Y₂PCZ₂PY₂)(CH₃)H⁺ where R = Me, F, CF₃, SiH₃, or SiMe₃, or H; x = 1-5; Y = H, Me, Ph, or F; and Z = H or F. Gross and Girolami had previously reported that in the complex [(C₅Me₅)Os(Me₂PCH₂PMe₂)(CH₃)(H)]⁺ there is a rapid hydrogen exchange between the hydride ligand and the hydrogens on the methyl group. The barrier for this exchange was measured to be 8-9 kcal mol⁻¹, so that the exchange rate at 400°C is 100 times per second.⁷-¹¹ Previous computational studies had shown that a methane tautomer was an intermediate on reaction coordinate.¹²,¹³ There are three important points on the potential energy surface, the methyl hydride 1, the transition state 1‡, the methane tautomer 2, and the fragment molecule, 3. (Figure 2) In a benchmark study of basis sets and DFT methods, we find that correlation consistent basis sets of triple zeta or higher and dispersion corrected DFT methods such as M05-2X produced results consistent with experimental data.¹⁴ The steric and electronic properties of the ligands affect the relative energies of these structures on the potential energy surface: electron withdrawing substituents on the phosphine ligands such as CF₃ or F, decrease the energy of 1‡ and stabilize 2 relative to 1 while electron donating ligands such as SiMe₃ increase the energies of 1‡ and 2 relative to 1 whereas changing the substituents on the cyclopentadienyl ring has a smaller effect on these relative energies. In fact, we predict that for [(C₅Hₓ)Os((CF₃)₂PCH₂P(CF₃)₂)(CH₃)(H)]⁺, the methane tautomer is the global minimum with a large barrier for dissociation of methane, a prediction that is in need of experimental testing. The energy of 3 relative to 1 was found to be correlated to the steric bulk of R or Y.

Figure 2. a) Critical points on the potential energy surface for hydride exchange and reductive elimination of methane. b) Energy of 2 relative to 1 with M05-2X.
Short distances between an electron deficient metal center and carbon-hydrogen bonds have been often assigned to be agostic, i.e., attractive 3-center-2-electron bond interactions. We employed M05-2X, B3LYP, and PBE0 DFT methods to analyze an apparently agostic interaction in the compound Ti$_2$Cl$_6$[N(t-Bu)$_2$]$_2$. The crystal structure of Ti$_2$Cl$_6$[N(t-Bu)$_2$]$_2$ exhibited a very close contact (2.634 Å) between the electron poor titanium center and one of the methyls of the di-(tertbutyl)amide ligand. To ascertain whether or not this close contact was due to an agostic interaction between Ti and the C-H atoms, we optimized the gas phase structure of the complex and related model compounds. These calculations revealed that decreasing the steric bulk of the amido ligand (by replacing the non-interacting tert-butyl ligand with a smaller alkyl group) caused the Ti-H distances to increase significantly. Natural bond order (NBO) analysis of the gas phase structure showed that there were no bonding interactions between titanium and the apparently agostic methyl group.

References

(8) Brumaghim, J. PhD, University of Illinois at Urbana-Champaign, 1994.
(16) Spicer, C., University of Illinois at Urbana-Champaign, 2008.