

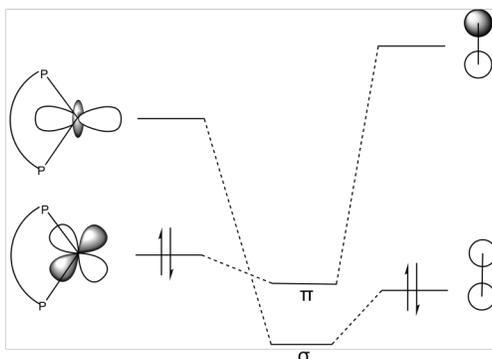
# Quantum Mechanical Analysis of Donor-Acceptor Interactions in Organometallic Complexes

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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<sup>1-4</sup> 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<sub>2</sub> 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.

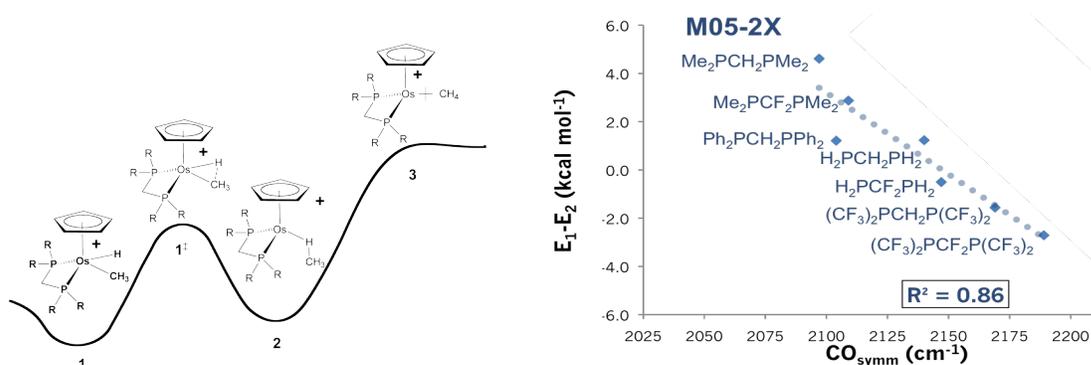


**Figure 1.** Diagram showing Dewar-Chatt-Duncanson model of bonding with  $\sigma$  and  $\pi$  interactions between a metal fragment and a H<sub>2</sub> ligand.

We have used density functional theory (DFT) to investigate the geometries and metal-ligand bonding in nickel complexes of bidentate phosphines, Ni(CO)<sub>2</sub>(R<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PR<sub>2</sub>) and NiH<sub>2</sub>(R<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PR<sub>2</sub>), where  $n = 1, 2,$  or  $3$ ; and R = H, Me, CF<sub>3</sub>, 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)<sub>2</sub>(R<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PR<sub>2</sub>) complexes. This frequency can be estimated from the empirical expression  $\nu(\text{CO}) = 1988 + \sum \chi_B - 4n$ , 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<sup>-1</sup>) – *t*-Bu (0.0), *i*-Pr (0.8), Et (3.0), Me (4.0), Ph (4.3), H (6.3), OMe (10.8), CF<sub>3</sub> (17.8), and F (18.3) – are generally similar to Tolman's electronic parameter  $\chi$  derived from nickel complexes of unidentate phosphines.<sup>5</sup> For the NiH<sub>2</sub>(R<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PR<sub>2</sub>) complexes, the global minimum is a non-classical dihydrogen structure. Natural bond order<sup>6</sup> analyses confirmed that the Ni-H<sub>2</sub> interaction is a three-center two-electron bond. Energy decomposition analysis of these complexes reveals, as expected, electron donating

phosphines increase the  $[\text{Ni}] \rightarrow (\text{H}_2)$   $\pi$  backdonation component of the Ni-H<sub>2</sub> 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 than the molecular H<sub>2</sub> adduct.

We have also used DFT to analyze the effect of ancillary ligands on the hydrogen exchange reaction of  $(\text{C}_5\text{H}_x\text{R}_{5-x})\text{Os}(\text{Y}_2\text{PCZ}_2\text{PY}_2)(\text{CH}_3)\text{H}^+$  where R = Me, F, CF<sub>3</sub>, SiH<sub>3</sub>, or SiMe<sub>3</sub>, 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  $[(\text{C}_5\text{Me}_5)\text{Os}(\text{Me}_2\text{PCH}_2\text{PMe}_2)(\text{CH}_3)(\text{H})]^+$  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<sup>-1</sup>, so that the exchange rate at 400°C is 100 times per second.<sup>7-11</sup> Previous computational studies had shown that a methane tautomer was an intermediate on reaction coordinate.<sup>12,13</sup> There are three important points on the potential energy surface, the methyl hydride **1**, the transition state **1**<sup>‡</sup>, 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.<sup>14</sup> 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 CF<sub>3</sub> or F, decrease the energy of **1**<sup>‡</sup> and stabilize **2** relative to **1** while electron donating ligands such as SiMe<sub>3</sub> increase the energies of **1**<sup>‡</sup> 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  $[(\text{C}_5\text{H}_5)\text{Os}((\text{CF}_3)_2\text{PCH}_2\text{P}(\text{CF}_3)_2)(\text{CH}_3)(\text{H})]^+$ , 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  $\text{Ti}_2\text{Cl}_6[\text{N}(\text{t-Bu})_2]_2$ . The crystal structure of  $\text{Ti}_2\text{Cl}_6[\text{N}(\text{t-Bu})_2]_2$  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.<sup>15,16</sup> 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.

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