Non-Covalent Interactions in a Transition-Metal Triphenyl-phosphine Complex: a Density Functional Case Study

Nicolas Sieffert and Michael Bühl*

University of St. Andrews. School of Chemistry. North Haugh. St. Andrews. Fife. KY16 9ST. Scotland. United Kingdom. E-mail: buehl@st-andrews.ac.uk.[#]

The binding enthalpy of a triphenylphosphine ligand in $Ru(CO)Cl(PPh_3)_3(CH=CHPh)$ is studied with "standard" (BP86 and B3LYP), dispersion-corrected (B3LYP-D and B97-D), and highly parametrized (M05 and M06 series) density functionals. An appropriate treatment of non-covalent interactions is mandatory as these turn out to account for a large fraction of the metal-ligand interaction energy. Among the tested methods, B97-D and the M06 series of functionals best reproduce the experimental binding enthalpy value of Sponsler et al. (*Inorg. Chem.* **2007**, *46*, 561).

Phosphine ligands are of key importance in homogenous catalysis,[1] and their interaction with metal centers has stimulated numerous experimental and modeling studies.[2, 3] The latter usually apply density functional theory (DFT) in one of its many flavors. The accurate prediction of thermodynamic parameters for metal-ligand bond formation/breaking processes is of key interest and remains a challenging task for modern DFT. Dictated by computational cost, early computational studies usually used simplified model ligands, *e.g.* PH_3 instead of the widely used PPh_3. Evidently, reaction channels that involve phosphine coordination or dissociation are difficult to assess with such models. Now that "real" systems with bulky ligands have become amenable to DFT calculations, a critical evaluation of the corresponding thermodynamic driving forces is possible.

As the systems under study become larger, long-range (non-covalent) interactions tend to become more important. Such interactions have emerged as rather notorious problems for most common DFT methods.[4] Thus, new functionals have been developed that are able to describe long-range dispersion forces, either by specifically adding an empirical R^{-6} term,[5] or by massive parametrization against experiment.[6] In the quest for a reliable protocol to compute transition-metal/ligand binding energies, we have now tested these new functionals for the binding of PPh_3 in a sterically encumbered metal complex prototypical for many homogeneous catalysts.

We chose the binding of PPh_3 (**P**) to the five-coordinate complex $Ru(CO)Cl(PPh_3)_2(CH=CHPh)$ (**1**; see Scheme 1) as test case, because this is a rare example of an equilibrium apparently unperturbed by competing coordination of the solvent, and for which reliable thermodynamic parameters have been measured.[7] This reaction represents a typical case where a bulky ligand binds to a highly coordinated metal complex, and in which multiple non-covalent interactions can take place, *e.g.* between neighboring phenyl rings of the ligands.

Scheme 1.

We adopted a computational protocol that can be readily applied to a large number of molecules (as required, e.g., for modeling whole catalytic cycles). This protocol consists of gas-phase geometry optimizations and frequency calculations at the RI-BP86/ECP1 level (employing the relativistic Stuttgart-Dresden pseudopotentials with their associate valence basis, SDD, on Ru, 3-21G on the Ph groups, and 6-31G** basis elsewhere), and evaluations of energies *(ΔE)*, basis-set superposition errors *(ΔE_{BSSE})*, and solvation effects in a continuum modeling CH_2Cl_2 *(ΔE_{solv})* by way of single-point calculations using a larger basis set denoted ECP2 (i.e. SDD on Ru, 6-31G* on Ph, and 6-311+G** elsewhere). Three groups of functionals were tested, namely *(i)* the conventional BP86[8] and B3LYP[9] combinations, *(ii)* Grimme's dispersion-corrected B3LYP-D and B97-D functionals,[10] and *(iii)* Truhlar's M05 and M06 series.[11] The latter were recently reviewed for a similar reaction,[6, 12] and B97-D was successfully applied to model Ru/PH_3 complexes.[13] In addition, geometries were reoptimized using functionals from groups *(i)* and *(ii)* together with ECP2 basis set. For further details and references, see the Supporting Information (SI).

Optimized metal-ligand bond distances of **1P** and **1** are collected in Table 1, together with experimental data for analogous complexes.[7, 14] At the RI-BP86/ECP1 level, the distances are in good agreement with experiment, with a

slight overestimation of Ru-Cl and most Ru-P distances (by 0.01 to 0.04 Å). Upon enlarging the basis from ECP1 to ECP2, the Ru-P bonds are elongated by ca. 0.02 to 0.06 Å, whereas the Ru-C and Ru-Cl bonds are almost unaffected (compare columns 1 and 2 in Table 1). The largest deviations from experiment are obtained for B3LYP, where the Ru-P and Ru-Cl distances are clearly exaggerated (by up to 0.24 Å for **1P**). Inclusion of the dispersion correction is beneficial for this functional, since the B3LYP-D optimized Ru-P bond distances agree satisfactorily, within 0.03 Å, with the reference values from the X-ray structures. The Ru-Cl and Ru-C bond distances are only weakly affected by the dispersion correction. The B97-D results are also in good accord with experiment, except for the Ru-Cl distance in **1P**, which deviates by ca. 0.07 Å.

Table 1: Selected bond distances (in Å) for complexes **1P** and **1**.

	BP86 ECP1	BP86 ECP2	B3LYP ECP2	B3LYP-D ECP2	B97-D ECP2	Exp. [a]
			Complex **1P**			
Ru – Cl	2.496	2.500	2.514	2.518	2.533	2.452(2)
Ru – P(2)	2.455	2.469	2.508	2.434	2.444	2.418(2)
Ru – P(3)	2.433	2.470	2.502	2.433	2.437	2.413(3)
Ru – P(1)	2.544	2.612	2.791	2.528	2.546	2.552(2)
Ru – C(1)	1.831	1.827	1.832	1.836	1.826	1.822(10)
Ru – C(2)	2.095	2.082	2.072	2.090	2.087	2.073(8)
			Complex **1**			
Ru – Cl	2.426	2.429	2.452	2.443	2.452	2.444(1)
Ru – P(2)	2.393	2.410	2.435	2.385	2.380	2.389(1)
Ru – P(3)	2.385	2.402	2.429	2.378	2.375	2.3774(9)
Ru – C(1)	1.827	1.825	1.833	1.836	1.828	1.906(6)
Ru – C(2)	2.009	2.002	2.015	2.016	2.008	1.989(4)

a. Experimental values from: Sponsler *et. al.*,[7] (dinuclear complex similar to **1P**) and Ozawa *et al.*[14] (*Complex* **1** with a *p*-OMe group at the styrene).

The dispersion correction has small effects on the other structural parameters: On going from B3LYP to B3LYP-D, bond angles can be affected by up to ca. 3° (Ru-P-C$_{Ph}$, see Table S2 in the SI), and phenyl rings can rotate slightly (by up to 18°, see Figure S1). Overall, for the geometries the RI-BP86/ECP1 level appears to be a good compromise between accuracy and computational cost.

The **P** binding enthalpies (ΔH) have been calculated from the total ECP2 binding energies (ΔE) by adding ΔE_{BSSE} and ΔE_{solv} corrections obtained at the same level, and an enthalpy correction term ΔE_H, evaluated at RI-BP86/ECP1. The results in Table 2 show that the raw binding energies (ΔE) range from -40.0 to +2.8 kcal/mol, depending on the choice of functional. The weakest binding is obtained with BP86, B3LYP and M05, whereas the dispersion-corrected B3LYP-D and B97-D, as well as M06-class functionals lead to the largest bindings (between ca. -30 and -40 kcal/mol). BSSE is quite pronounced in **1P**, ranging from 7.7 kcal/mol (M06-L) to 11.5 kcal/mol (B3LYP),[15] and stems mainly from the contribution of the PPh$_3$ fragment (which accounts for ca. 66% of the total ΔE_{BSSE}). Solvation effects (ΔE_{solv}) are also significant for this reaction and account for 3.9-5.1 kcal/mol. The application of these energy corrections leads to binding enthalpy values (ΔH) ranging from +21.2 kcal/mol (i.e., clearly endothermic) to -21.6 kcal/mol (strongly exothermic). Our results therefore clearly show that the BP86,

B3LYP and M05 functionals fail to reproduce the qualitative trend that the PPh$_3$ binding is an exothermic process. Conversely, the dispersion corrected B3LYP-D and B97-D functionals lead to ΔH values of -21.6 and -17.9 kcal/mol, respectively, in a good agreement with the experimental reference value (-17.5 ± 2.0 kcal/mol).[7] Among the Truhlar functionals, all M06 variants also agree well with experiment, whereas M05-2X, although predicting effectively an exothermic reaction, underestimates the binding enthalpy by ca. 6 kcal/mol. We note that the observed binding enthalpy is best reproduced with B97-D.

Table 2: Computed and experimental binding enthalpies (ΔH, kcal/mol), calculated from the binding energy (ΔE) corrected for BSSE (ΔE_{BSSE}), solvation (ΔE_{Solv}) and an enthalpy term (ΔE_H, all in kcal/mol).

	ΔE	ΔE_{BSSE}	ΔE_{Solv}	ΔE_H [a]	ΔH [b]
Exp.					-17.5 ± 2.0
	Single points on RI-BP86/ECP1 geometries				
BP86	-2.7	10.7	5.0	1.9	14.9
B3LYP	2.8	11.5	5.0	1.9	21.2
B3LYP-D	-40.0	11.5	5.0	1.9	-21.6
B97-D	-35.2	10.4	5.0	1.9	-17.9
M05	-6.7	10.2	4.7	1.9	10.1
M05-2X	-28.2	9.9	4.7	1.9	-11.7
M06	-32.0	11.0	3.9	1.9	-15.2
M06-2X	-30.9	10.1	4.3	1.9	-14.6
M06-L	-33.1	7.7	3.9	1.9	-19.6
M06-HF	-35.8	12.2	5.1	1.9	-16.6
	Full optimizations				
BP86	-3.2	10.4	5.0	1.9	14.1
B3LYP	0.9	10.7	4.4	1.9	17.9
B3LYP-D	-43.6	12.6	4.9	1.9	-24.2
B97-D	-38.2	11.2	5.1	1.9	-20.0

a. Calculated at the RI-BP86/ECP1 level, at -70°C. see SI for details. *b.* $\Delta H = \Delta E + \Delta E_{BSSE} + \Delta E_{Solv} + \Delta E_H$.

The effect of the geometry of the reaction partners on the binding enthalpies was investigated by recalculating the binding enthalpies using the geometries fully optimized with ECP2 basis (see Table 1). The data at the bottom of Table 2 show that BP86 and B3LYP still wrongly predict an endothermic reaction, and that the B3LYP, B3LYP-D and B97-D enthalpies are shifted by ca. -3 kcal/mol with respect to the single-point results, leaving B97-D still in good agreement with experiment. Thus, the mostly minor changes in structural parameters upon varying basis set and functional (see discussion above) do not translate into qualitative changes of the resulting binding enthalpy.

The most important finding of our study is that non-covalent interactions appear to be a very important contributor to the total binding enthalpy. This is apparent from the B3LYP and B3LYP-D results in Table 2, which suggest that dispersion interactions involving a single PPh$_3$ ligand can sum up to ca. 43 kcal/mol, an unexpectedly large value. Much smaller effects had been observed for PH$_3$ binding in model complexes, e.g. in RuCl$_2$(PH$_3$)$_2$(=CH$_2$), where a PH$_3$ binding energy of ca. 20 kcal/mol and a dispersion correction of only -2 kcal/mol has been computed.[13] For comparison, we have repeated our B3LYP and B3LYP-D calculations using PH$_3$ and PMe$_3$ as **P** ligands (see the first three entries in Table 3). The resulting dispersion contribution is small for PH$_3$ and gradually increases with the bulkiness of the ligand (-5.9, -17.9 and -42.8 kcal/mol for PH$_3$,

PMe$_3$, and PPh$_3$, respectively), whereas the "uncorrected" binding energy (ΔE/B3LYP) increases (from -20.3 to +2.8 kcal/mol when going from PH$_3$ to PPh$_3$; see Table 3).[16] These results therefore show that an increasing bulkiness of the ligands has a dramatic effect on the contribution of the dispersion term (E_{disp}). Whether the latter strictly corresponds to dispersion interactions, still remains to be investigated. At present it cannot be excluded that the remarkable efficiency of the B3LYP-D functional rather stems from an error cancellation between an overestimated inter-ligand repulsion from B3LYP and an exaggerated "dispersion" term from the empirical correction (E_{disp}). This interpretation would be supported by the elongated Ru-P distances found in **1P** at the B3LYP/ECP2 level (see Table 1), and by the computed binding energy of the PPh$_3$ ligand to a Ru(CO)Cl(CH=CHPh)(PH$_3$)$_2$ fragment (see last entry in Table 3): in the latter case, where inter-ligand repulsions are expected to be small, both covalent and non-covalent interactions have important contributions.

Table 3: Influence of the nature of the ligands (P(1), P(2) and P(3)) on the contribution of the non-covalent interactions (ΔE_{disp}, kcal/mol) to the phosphine binding energy (ΔE, kcal/mol), and corresponding BSSE energies (ΔE_{BSSE}, kcal/mol).

P(2), P(3)	P(1)	ΔE B3LYP	ΔE B3LYP-D	[ΔE_{disp}]	ΔE_{BSSE}
PH$_3$	PH$_3$	-20.3	-26.3	[-5.9]	2.1
PMe$_3$	PMe$_3$	-16.9	-34.7	[-17.9]	3.6
PPh$_3$	PPh$_3$	2.8	-40.0	[-42.8]	11.5
PH$_3$	PPh$_3$	-23.6	-42.6	[-19.0]	7.9

Interestingly, our findings are consistent with those of Truhlar et al. who found that the binding energy of the tris(cyclohexyl)phosphine ligand in the real Grubbs II catalyst is underestimated by -25.7 and -27.6 kcal/mol with BP86 and B3LYP, respectively.[12b] Accurate binding energies were obtained with the M06 and M06-L functionals, in which the dispersion effects are taken into account.[12]

The binding entropy for the system in Scheme 1 has been determined as ΔS = -56.5 ± 7.6 cal mol^{-1} K^{-1},[7] affording very small ΔG value at ambient temperature. When standard molar entropies are evaluated from RI-BP86/ECP1 harmonic frequencies in the gas phase (at 1 atm), much more negative values are obtained (e.g. ΔS = −70.7 cal mol^{-1} K^{-1} at -70°C), essentially because translational entropies are much larger in the gas phase than in solution. Computing these entropies at a higher pressure can be a simple way of modeling the translational degrees of freedom in a condensed phase. Using a pressure of 1354 atm,[17] the computed ΔS values range from -56.4 cal mol^{-1} K^{-1} (at -70°C) to -55.5 cal mol^{-1} K^{-1} (at +20°C), in excellent accord with experiment.[18] Thus, not only reasonably accurate geometries can be obtained at the "low" RI-BP86/ECP1 level, but also harmonic frequencies that are useful for evaluating enthalpies and entropies, which are instrumental for comparison with experiment.

In summary, DFT study of the PPh$_3$ coordination to the sterically congested complex **1** has revealed the importance of non-covalent interactions, which turn out to be a very important contributor to the total PPh$_3$ binding enthalpy in this case. Careful validation against experiment[7] shows that the enthalpy is well reproduced by functionals designed to capture dispersion effects (specifically B97-D and the M06 series), and that realistic geometries and entropic corrections can be obtained at less elaborate levels. This allows us to propose a cost-effective computational protocol, i.e. optimizing the structures at a lower level of theory and refining the enthalpic parameters by performing higher-level single points. This methodology is readily applicable to complicated, multistep reactions, as encountered *e.g.* in homogenous catalysis, and represents a significant methodological step forward toward the study and understanding of the reactivity of "real" catalysts at the molecular level.
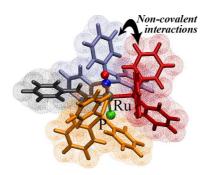
Supporting Information Available: Computational details, absolute RI-BP86/ECP1 energies (Table S1), optimized bond angles (Table S2), superimposed B3LYP and B3LYP-D structures (Figure S1), and RI-BP86/ECP1 optimized coordinates of **1P**, **1** and **P**. This material is available free of charge on the Internet at http://pubs.acs.org.

References

\# Dedicated to Prof. Dr. Walter Thiel on the occasion of his 60th birthday

(1) See for instance: Börner, A. (Ed.), *Phosphorus Ligands in Asymmetric Catalysis: Synthesis and Applications*, Wiley-VCH, Weinheim, 2008.

(2) Dias, P. B., de Piedade, M. E. M., Simões, J. A. M. *Coord. Chem. Rev.* **1994**, *135-136*, 737.

(3) E.g. Torrent, M.; Sola, M.; Frenking, G. *Chem. Rev.* **2000**, *100*, 439.

(4) E.g.: Grimme, S. *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 4460.

(5) Schwabe, T., Grimme, S. *Acc. Chem. Res.* **2008**, *41*, 569.

(6) Zhao, Y., Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.

(7) Seetharaman, S. K., Chung, M.-C., Englich, U., Ruhlandt-Senge, K., Sponsler, M. B. *Inorg. Chem.* **2007**, *46*, 561.

(8) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. (c) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.

(9) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C., Yang, W., Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(10) (a) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463. (b) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.

(11) (a) Zhao, Y., Schultz, N. E., Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364; (b) Zhao, Y., Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101; (c) Zhao, Y., Truhlar, D. G. *J. Phys. Chem. A* **2006**, *110*, 13126.

(12) (a) Zhao, Y.; Truhlar, D. G. *Org. Lett.* **2007**, *9*, 1967. (b) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2009**, *5*, 324.

(13) Piacenza, M., Hyla-Kryspin, I., Grimme, S. *J. Comput. Chem.* **2007**, *28*, 2275.

(14) Maruyama, Y., Yamamura, K., Sagawa, T., Katayama, H., Ozawa, F. *Organometallics* **2000**, *19*, 1308.

(15) A smaller BSSE is to be expected by increasing the size of the basis set on the phenyl rings, a feature that would dramatically increase the computational cost.

(16) We also note that with PH$_3$ and PMe$_3$ as model ligands, the corresponding BSSEs are also significantly smaller (2.1 and 3.6 kcal/mol, respectively; see Table 3).

(17) Following the argument in Martin, R. L.; Hay, P. J.; Pratt, L. R. *J. Phys. Chem. A* **1998**, *102*, 3565-3573, where this simple procedure has been proposed as adjustment for the concentration of water molecules in the liquid, and where the necessary pressure value has been derived from the experimental density of liquid water.

(18) Because they are dominated by low-lying vibrational modes, the computed entropies are associated with considerable uncertainty. If, for instance, all harmonic frequencies below an arbitrary threshold of 100 cm^{-1} are treated as rotations , the corresponding binding entropy is reduced by 11 cal.mol^{-1}.K^{-1} (i.e. ΔS = -45.4 cal.mol^{-1}.K^{-1} at T = 203.15K and P = 1354 atm).

Graphical abstract

To reproduce the binding enthalpy of triphenylphosphine in a bulky ruthenium complex computationally, density functionals need to be employed that account implicitly or explicitly for dispersion. Such non-covalent interactions are thus indicated to be important contributors to the total binding in such systems.