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Noncovalent Interactions in a Transition-Metal Triphenylphosphine Complex: a Density Functional Case Study[†]

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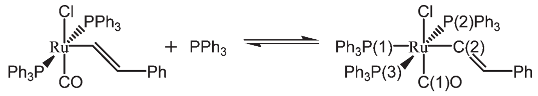
The binding enthalpy of a triphenylphosphine ligand in Ru(CO)Cl(PPh$_3$)$_3$(CH═CHPh) is studied with "standard" (BP86 and B3LYP), dispersion-corrected (B3LYP-D and B97-D), and highly parametrized (M05 and M06 series) density functionals. An appropriate treatment of noncovalent interactions is mandatory because 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 homogeneous 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 (noncovalent) 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 the specific addition of 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.

Scheme 1



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 our 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 noncovalent interactions can take place, e.g., between neighboring phenyl rings of the ligands.

We adopted a computational protocol that can be readily applied to a large number of molecules (as required, e.g., for the modeling of 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 of CH$_2$Cl$_2$ (ΔE_{solv}) by way of single-point calculations using a larger basis set denoted as 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

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[†] Dedicated to Prof. Dr. Walter Thiel on the occasion of his 60th birthday.

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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 the 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 the experiment, with a slight overestimation of Ru−Cl and most Ru−P distances (by 0.01−0.04 Å). When the basis is enlarged from ECP1 to ECP2, the Ru−P bonds are elongated by ca. 0.02−0.06 Å, whereas the Ru−C and Ru−Cl bonds are almost unaffected (compare columns 1 and 2 in Table 1). The largest deviations from the 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 because 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 the experiment, except for the Ru−Cl distance in **1P**, which deviates by ca. 0.07 Å.

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°). 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 (Δ*E*) by the addition of 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 (Δ*E*) range from −40.0 to +2.8 kcal/mol, depending on the choice of the 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 (Δ*H*) 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 Δ*H* values of −21.6 and −17.9 kcal/mol, respectively, in 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 the 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 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	2.3743(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).

Table 2. Computed and Experimental Binding Enthalpies (Δ*H*, kcal/mol), Calculated from the Binding Energy (Δ*E*), Corrected for BSSE (ΔE_{BSSE}), Solvation (ΔE_{solv}), and an Enthalpy Term (ΔE_H, All in kcal/mol)

	Δ*E*	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 the 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 the 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

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

to the single-point results, leaving B97-D still in good agreement with the experiment. Thus, the mostly minor changes in the structural parameters upon variation of basis set and functional (see the previous discussion) do not translate into qualitative changes of the resulting binding enthalpy.

The most important finding of our study is that noncovalent 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 ca. −2 kcal/mol have 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 cancelation between an overestimated interligand 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 the last entry in Table 3): in the latter case, where interligand repulsions are expected to be small, both covalent and noncovalent interactions have important contributions.

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 $\Delta S = -56.5 \pm 7.6$ cal mol^{-1} K^{-1},[7] affording very small ΔG values 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., $\Delta S = -70.7$ 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 the experiment.[18] Thus, not only reasonably accurate geometries but also harmonic frequencies that are useful for evaluating enthalpies and entropies, which are instrumental for comparison with the experiment, can be obtained at the "low" RI-BP86/ECP1 level.

Table 3. Influence of the Nature of the Ligands [P(1), P(2), and P(3)] on the Contribution of the Noncovalent Interactions (ΔE_{disp}, kcal/mol) to the Phosphine Binding Energy (ΔE, kcal/mol) and Corresponding BSSE Energies (ΔE_{BSSE}, kcal/mol)

		ΔE			
P(2), P(3)	P(1)	B3LYP	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

In summary, a DFT study of PPh_3 coordination to the sterically congested complex **1** has revealed the importance of noncovalent interactions, which turn out to be a very important contributor to the total PPh_3 binding enthalpy in this case. Careful validation against the 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 homogeneous catalysis, and represents a significant methodological step toward the study and understanding of the reactivity of "real" catalysts at the molecular level.

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Supporting Information Available: Computational details, absolute RI-BP86/ECP1 energies (Table S1), optimized bond angles (Table S2), and RI-BP86/ECP1 optimized coordinates of **1P**, **1**, and **P**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(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) This follows 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 an 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., $\Delta S = -45.4$ cal mol^{-1} K^{-1} at $T = 203.15$ K and $P = 1354$ atm).