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Theoretical DFT study of ethylene hydroformylation on platinum complexes with hydrophosphoryl ligands

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The DFT quantum-chemical modeling of the catalytic cycle of alkene hydroformylation on organoplatinum hydride $[(R_2PO)_2H]$-$Pt(PR_3)(H)$ shows that reversible shifts of proton in the $–PR_2OH\cdots O{=}PR_2–$ chain inside quasi-chelate ligand $[(R_2PO)_2H]$ proceed in several reaction steps thus providing fine tuning of electron density in the catalytic centre and acting as a molecular switch.

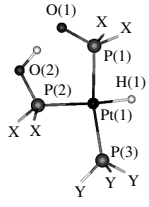
Hydrophosphoryl compounds (HPCs) in solutions easily undergo the tautomeric transition RR′P(H)O ⇆ RR′POH, providing them a unique combination of properties of pentavalent and trivalent phosphorus derivatives.[1–3] Similarly to tertiary phosphines, phosphinous acids RR′POH with late transition metals form stable complexes,[4–6] which act as active catalysts in cross-coupling reactions,[7,8] hydroformylation of alkenes,[9] and hydrophosphinylation of alkynes.[10] However, unlike the complexes of tertiary phosphines, these complexes are air-stable due to the higher oxidative stability of HPCs. Therefore, in the last decade the chemistry of HPC was newly stimulated powerfully in its development. Van Leeuwen and co-authors[9,11] showed that the hydroformylation of hept-1-ene on the complex $[(Ph_2PO)_2H]$-$Pt(PPh_3)(H)$ occurs with regioselectivity higher than 90% under very mild conditions:

$$C_5H_{11}CH{=}CH_2 + CO + H_2 \rightarrow C_5H_{11}CH_2CH_2CHO. \quad (1)$$

We performed the theoretical modeling of the mechanism of this reaction for the complex $[(H_2PO)_2H]Pt(PH_3)(H)$ **2**, in which the Ph groups at the phosphorus atoms are replaced by hydrogen atoms to reduce computational expenses.

All calculations were carried out using the PRIRODA program.[12,13] The generalized gradient approximation (GGA) for exchange-correlation functional by Perdew, Burke and Ernzerhof[14] was employed. The core electrons of C, O, P and Pt were described by effective core potentials.[15] The orbital basis sets of contracted Gaussian-type functions of size $\{3s,1p\}/\{5s,1p\}$ for H, $\{3s,3p,2d\}/\{5s,5p,2d\}$ for C, O and P and $\{5s,5p,4d\}/\{9s,9p,8d\}$ for Pt were used for remaining electrons in conjunction with the density fitting basis sets of uncontracted Gaussian-type functions $\{5s,1p\}$ for H, $\{6s,3p,3d,1f\}$ for C, O and P and $\{10s,6p,6d,5f,5g\}$ for Pt. The full optimization of the geometry of the test structures was performed using analytical gradients and followed by analytical calculations of second derivatives of energy with respect to coordinates in order to characterize the nature of the resulting stationary points (minima or saddle points) on the potential energy surface (PES). Vibrational frequencies, zero-point vibrational energies and thermodynamic data were calculated using ideal gas, rigid rotor and harmonic oscillator approximations. The conjugation of the found transition states with the starting compounds and products was verified by the construction of an intrinsic reaction coordinate (IRC).

Table 1 Selected bond lengths (Å) of **1** and **2** according to the calculation and X-ray diffraction data.[10]



Bond	**1** (X = Ph, Y = Et)	**1**[10] (X = Ph, Y = Et)	**2** (X = Y = H)
Pt(1)–P(1)	2.341	2.280	2.315
Pt(1)–P(2)	2.366	2.313	2.353
Pt(1)–P(3)	2.344	2.301	2.323
O(1)···O(2)	2.455	2.317	2.470
P(1)–O(1)	1.573	1.532	1.563
P(2)–O(2)	1.614	1.569	1.607

A comparison of the geometric parameters calculated for **1** and **2** with the X-ray diffraction data[10] for **1** shows (Table 1) that the calculations satisfactorily reproduce the coordination site geometry. The energy of the $P(2)H_2O(2)H\cdots O(1)P(1)H_2$ hydrogen bond in **2** is 13.1 kcal mol^{-1}. This estimate was obtained by the calculation of the structure in the case of turning the $P(2)H_2OH$ group in **2** about the Pt–P(2) bond by 180°. The local minimum on the PES corresponds to this conformation.

The addition of an ethylene molecule to **2** proceeds readily as an entropy-controlled reaction ($\Delta H_{298} = –5.15$ kcal mol^{-1}, $\Delta S_{298} = –41.58$ eu and $\Delta G_{298} = 7.25$ kcal mol^{-1}) to form **3**, in which ethylene is bound to the platinum atom according to the η^2-mode. Remarkably, for ethylene coordination the hydrogen atom in the P(2)–O(2)–H···O(1)–P(1) chain migrates to the O(1) atom.

$$\underset{\mathbf{2}}{\{[(H_2PO)_2H]Pt(PH_3)(H)\}} + CH_2{=}CH_2 \rightarrow \underset{\mathbf{3}}{\{[(H_2PO)_2H]Pt(PH_3)(H)\eta^2(CH_2{=}CH_2)\}} \quad (2)$$

The rearrangement of **3** to η^1-ethyl complex **4** [equation (3)] proceeds through the early transition state with an activation energy of 14.15 kcal mol^{-1}.

$$\mathbf{3} \rightarrow \underset{\mathbf{4}}{\{[(H_2PO)_2H]Pt(PH_3)Et\}} \quad (3)$$

The process is exothermic ($\Delta H_{298} = –12.26$ kcal mol^{-1} and $\Delta G_{298} = –13.89$ kcal mol^{-1}). The insertion of ethylene into the Pt–H bond is accompanied by the backward hydrogen atom transfer in the hydrogen bond chain from O(1) to O(2).

The addition of carbon monoxide to **4** [equation (4)] is barrier-free ($\Delta H_{298} = –10.18$ kcal mol^{-1} and $\Delta G_{298} = –0.41$ kcal mol^{-1}) and affords complex **5**. This reaction is also accompanied by proton transfer in the hydrogen bond chain.

$$\mathbf{4} + CO \rightarrow \underset{\mathbf{5}}{\{[(H_2PO)_2H]Pt(PH_3)(CO)Et\}} \quad (4)$$

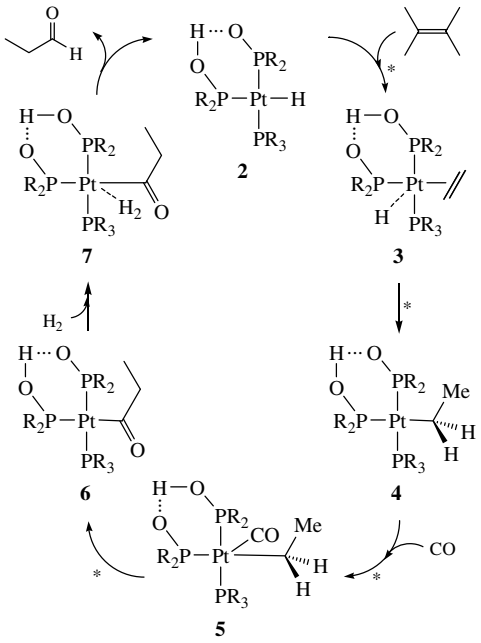


Figure 1 Catalytic cycle of ethylene hydroformylation on complex **2**. Asterisks (*) mark the steps accompanied by proton transfer in the $P(2)H_2O(2)H\cdots O(1)P(1)$ hydrogen bond chain.

After this, the exothermic isomerization of complex **5** to planar-square η^1-acyl complex **6** [equation (5)] occurs (ΔH_{298} = = –8.98 kcal mol^{-1} and ΔG_{298} = –8.86 kcal mol^{-1}), which is the rate-determining step due to the surmounting of the highest barrier in this reaction path (ΔE_a^0 = 17.60 kcal mol^{-1}). The process is also conjugated with proton transfer in the hydrogen bond chain.

$$\mathbf{5} \rightarrow \underset{\mathbf{6}}{\{[(H_2PO)_2H]Pt(PH_3)COEt\}} \quad (5)$$

The oxidative addition of a hydrogen molecule to **6** [equation (6)] affords octahedral *cis*-dihydride **7**. This is an entropy-controlled process (ΔH_{298} = –2.01 kcal mol^{-1}, ΔG_{298} = 9.69 kcal mol^{-1} and ΔE_a^0 = 12.41 kcal mol^{-1}).

$$\mathbf{6} + H_2 \rightarrow \underset{\mathbf{7}}{\{[(H_2PO)_2H]Pt(H)_2(PH_3)COEt\}} \quad (6)$$

The catalytic cycle is completed by the exothermic (ΔH_{298} = = –0.86 kcal mol^{-1} and ΔG_{298} = –14.25 kcal mol^{-1}) step of the reductive elimination of propanal (ΔE_a^0 = 15.51 kcal mol^{-1}):

$$\mathbf{7} \rightarrow \mathbf{2} + EtCHO \quad (7)$$

Van Leeuwen *et al.*[9] proved the structures of **2**, **4** and **6** to exist for the process in benzene or toluene by NMR spectroscopy. Our detailed study of the PES and a possible alternative route for the catalytic process shows that the above catalytic cycle (Figure 1) is optimum in terms of kinetic and thermodynamic characteristics. This cycle agrees well with that proposed by Van Leeuwen and co-authors[9,11] on the basis of experimental data.

Hydrogenation often proceeds as a side process in alkene hydroformylation. Hydrogenation can occur due to the oxidative addition of a hydrogen molecule to **4** followed by the elimination of an ethane molecule. The calculation showed that the addition of H_2 to **4** proceeds with an activation energy of 14.15 kcal mol^{-1} due to which dihydride **8** is formed. The process is controlled by the entropy factor and is endothermic (ΔH_{298} = 1.44 kcal mol^{-1}, ΔS_{298} = –32.55 eu and ΔG_{298} = 11.14 kcal mol^{-1}).

$$\mathbf{4} + H_2 \rightarrow \underset{\mathbf{8}}{\{[(H_2PO)_2H]Pt(PH_3)(H)_2Et\}} \quad (8)$$

Ethane is eliminated further from **8** with an activation energy of 13.93 kcal mol^{-1} as a strongly exothermic reaction (ΔH_{298} = = –18.61 kcal mol^{-1} and ΔG_{298} = –30.25 kcal mol^{-1}).

$$\mathbf{8} \rightarrow \mathbf{2} + C_2H_6 \quad (9)$$

Since carbon monoxide adds to **4** barrier-free and exothermally [equation (4)], whereas the addition of molecular hydrogen [equation (8)] is related to the surmounting of a noticeable barrier (14.15 kcal mol^{-1}) and is endothermic, the contribution of hydrogenation as a competing process under mild conditions should not be significant if the reaction medium contains no excess hydrogen. This conclusion is completely confirmed by experimental data.[9,11]

Thus, the results of the theoretical simulation show that the high efficiency of complexes like **1** and **2** as the catalysts of homogeneous alkene hydroformylation is due to the following factors.

(1) The free coordination site in these planar-square 16-electron platinum complexes provides a possibility to coordinate alkene in the first step without the energetically unfavourable dissociation of a metal–ligand bond.

(2) The high energy of the $P(2)H_2O(2)H\cdots O(1)P(1)$ hydrogen bond results in the formation of a bidentate ligand in the coordination sphere of the metal. This ligand fixes the geometry of a catalytic centre rigidly to enhance the regioselectivity of the process.

(3) The proton in the $P(2)H_2O(2)H\cdots O(1)P(1)$ chain is highly mobile and, hence, easily migrates in it, thus providing the fine tuning of electron density in the catalytic centre in each reaction step and, therefore, acts as a molecular switch (Figure 2).

These regularities can be used for the structure optimization of catalytic complexes like **1** and **2**.

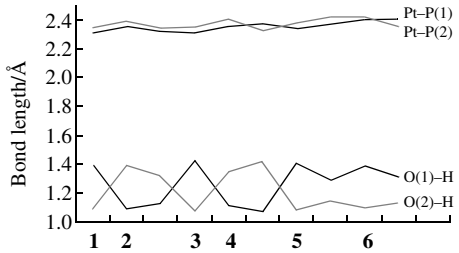


Figure 2 Changes in the bond lengths of the test molecules.

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