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Iodo-methyl ligand exchange reaction in platinum complexes: A density functional study

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Dedicated to Professor Gyula Pályi on the occasion of his 70th birthday.

Abstract

A theoretical investigation at the gradient-corrected density functional (BP86) level of theory on the iodo-methyl ligand exchange reaction in platinum–diphosphine complexes is discussed. The reaction consists of two elementary steps: the oxidative addition of methyl–iodide, and reductive elimination of ethane from the intermediate $Pt(bdpp)(CH_3)_3I$ complex which is the rate determining step with a free energy of activation of 19.5 kcal/mol in acetonitrile phase. The oxidative addition step takes place with S_N2 mechanism via a transition state with a collinear arrangement of the $I–CH_3–Pt$ moiety.
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1. Introduction

The reactivity of the transition metal–alkyl bond has long been investigated in detail since it is involved in crucial steps of several homogeneous catalytic reactions and has been the target of many treatises and reviews [1,2]. For example, either the hydrogenolysis of a metal–alkyl bond or the reductive elimination of alkane from hydrido-alkyl intermediates could serve as a product forming step in hydrogenation catalysed by various transition metal complexes. Furthermore, the insertion of carbon monoxide into the metal–alkyl bond leading to transition metal-acyl intermediates is a key step of various carbonylation reactions like hydroformylation, hydroethoxycarbonylation or hydrocarboxylation [3,4]. Several further insertion reactions e.g. that of the carbene, formed in situ from ethyl diazoacetate, have been extensively studied with platinum–alkyl complexes [5–9].

Although the detailed mechanistic investigations shed some light on the elementary steps of insertion reactions, less are known about the mechanistic details of the formation of the Pt–alkyl intermediate itself. Various parameters like the platinum–chelate conformation, the conformation and configuration of the chiral ligand itself might have a great impact on the reactivity of the platinum–alkyl complex.

As a part of our ongoing interest in platinum catalysed reactions, several platinum–alkyl/aryl complexes bearing optically active diphosphine, bdpp ((2S,4S)-2,4-bis(diphenylphosphino)pentane) have been synthesised and fully characterised including X-ray crystallography. It has been also found that methyl iodide could serve as iodide source to provide Pt(bdpp)(alkyl/aryl)I complexes selectively [10].

Among the most well-known examples of utilising methyl iodide in transition metal catalysis are the Monsanto and Cativa processes i.e. the production of acetic acid by the

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rhodium- or iridium-catalysed carbonylation of methanol. The mechanism of the reaction was extensively studied using the density functional theory [11–13] including solvation effects. The oxidative addition of methyl–iodide was found to take place by S_N2 mechanism.

In this work, due to the new developments in applying quantum theory, quantum mechanical treatment of methyl iodide activation by platinum–diphosphine complexes resulting in the alkyl-iodo ligand exchange will be described in order to achieve a better understanding of the reaction mechanism. Due to its practical importance, the methyl iodide activation by rhodium has been investigated in detail including computational methods; however, to the best of our knowledge this kind of reaction of platinum–diphosphine complexes has never been described theoretically. As we assumed the phenyl groups of the bdpp ligand to play an important role in the coordination of methyl iodide and influence the geometry of the intermediates occurring throughout the reaction, we did not use the simplified model; which replaces phenyl groups by hydrogen atoms. Although the simplified model using PH_2 groups (for diphosphines) and PH_3 (for monophosphines) usually leads to correct results, in our case it could not be considered as a reliable model due to the expected phenyl interactions.

2. Computational details

Full geometry optimisations have been performed at the density functional level of theory without any symmetry constraints using the GAUSSIAN 03 suite of programs [14] and the LANL2DZ basis set for P, I, and Pt, with the corresponding effective core potential (relativistic for Pt and I) [15] and the valence double-ζ basis set of Dunning and Hay [16]. The density fitting basis sets were generated automatically from the AO primitives by the GAUSSIAN 03 program. The stationary points were characterised by frequency calculations in order to verify that they have zero imaginary frequency for equilibrium geometries and one imaginary frequency for transition states. The NBO analyses were carried out on the stationary points using the NBO 3.1 program [17] as implemented in GAUSSIAN. For all the calculations the gradient-corrected exchange functional developed by Becke [18] was utilised in combination with a correlation functional developed by Perdew [19] and denoted as BP86.

To estimate the effect of the solvent, single-point calculations on the gas-phase optimised structures were carried out using the polarized continuum model (PCM) [20] using the dielectric constant $\varepsilon_0 = 36.64$ for acetonitrile. Thermochemistry corrections were taken from gas-phase frequency calculations at 298.15 K and 1 atm. We are aware of the drawbacks giving up full geometry optimisation with solvation effects included [11,12], however, these sort of calculations would have not been feasible for the relatively large molecules discussed in our study due to the vast increase of the computational cost.

3. Results and discussion

3.1. Oxidative addition of methyl iodide

Reactant complex in the initial step is $Pt(bdpp)(CH_3)_2$ (**1**). Due to the shape variability of the bdpp ligand
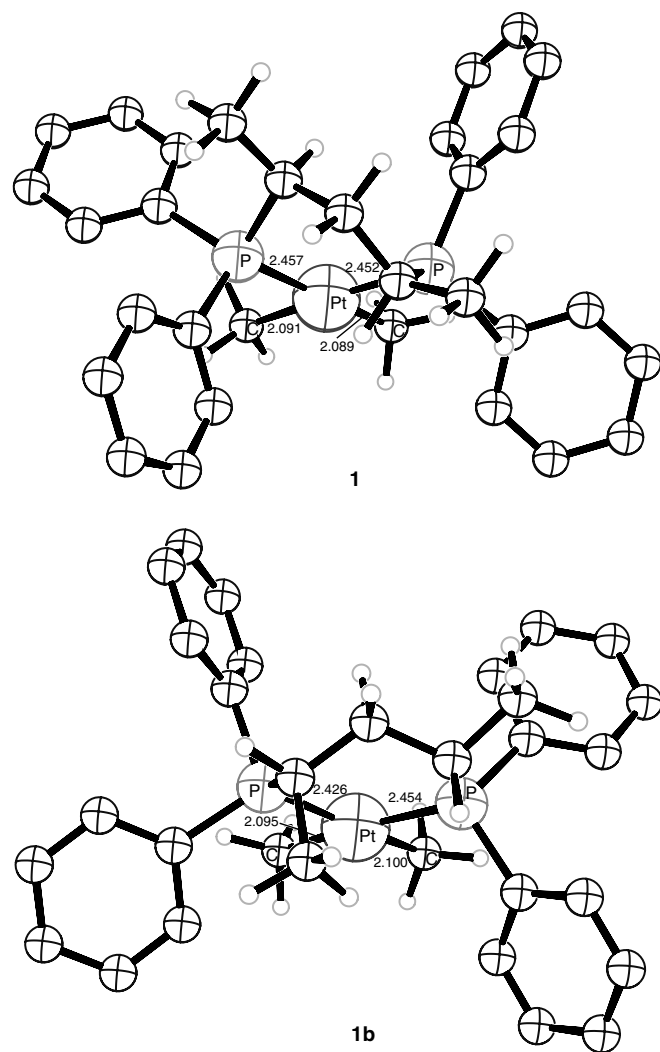

Fig. 1. Optimised structures (bond distances in Å) of two conformers of $Pt(bdpp)(CH_3)_2$.

Table 1
NPA charges of species **1–6**, methyl iodide and ethane at the BP86/LANL2DZ level

Complex	Q_{Pt}	Q_{P1}	Q_{P2}	Q_I	Q_C[a]
1	0.174	0.864	0.869	0.071[b]	−0.811[b]
1b	0.177	0.880	0.860	0.071[b]	−0.811[b]
2	0.170	0.873	0.864	0.034	−0.792
3TS	0.422	0.858	0.846	−0.415	−0.735
4	0.617	0.851	0.843	−0.726	−0.681
5TS	0.347	0.962	0.855	−0.842	−0.679
6	0.094	0.948	0.846	−0.424	−0.646[c]

[a] Methyl carbon incoming from methyl iodide.
[b] In methyl–iodide separated.
[c] In ethane after elimination.
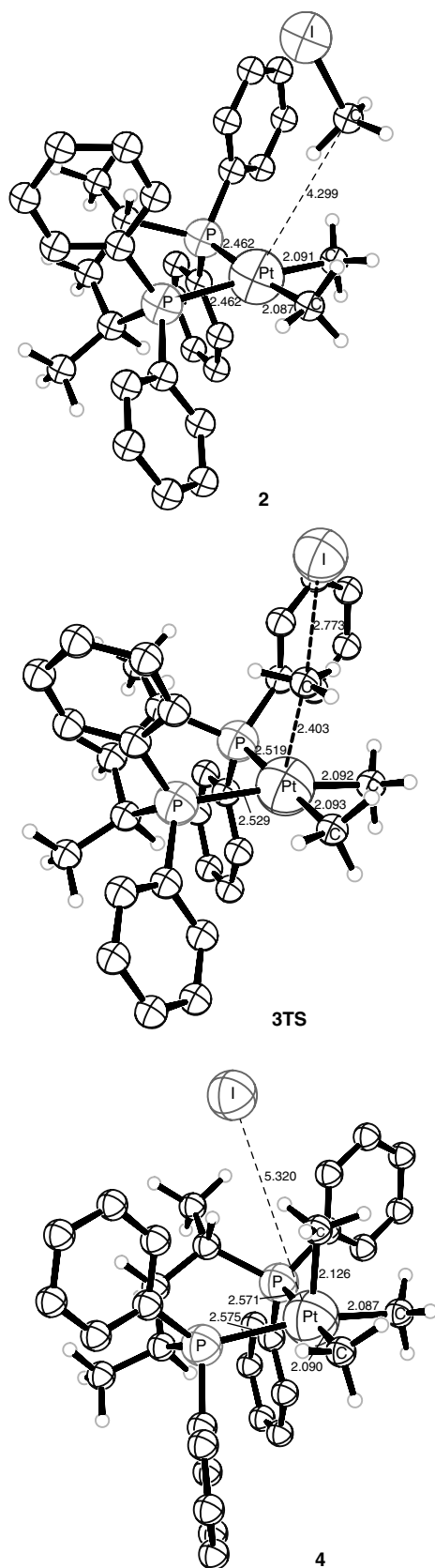
2

3TS

4

Fig. 2. Optimised structures (bond distances in Å) of the adduct of Pt(bdpp)(CH$_3$)$_2$ and MeI (**2**), the transition state of the oxidative addition (**3TS**) and the [Pt(bdpp)(CH$_3$)$_3$]$^+$I$^-$ intermediate (**4**) formed after the oxidative addition.

numerous metallacycle conformers can be assumed when connected to platinum. Some conformers of relevance found in crystal phases were applied for the dimethyl complex. The delta skew-boat conformation, with two equatorial and two axial phenyl groups, was found to be the lowest energy conformer and for the sake of simplicity this conformation was kept for every species throughout this study. However, all the conformers of Pt(bdpp)(CH$_3$)$_2$ examined lied within a range of 2 kcal/mol energy difference. The second most stable one, denoted as **1b** (also presented in Fig. 1 with **1**), possesses an envelope conformation of the metallacycle with an axial, an equatorial and two bisectional phenyl groups. The energy difference between **1** and **1b** was 0.4 kcal/mol.

Approaching to the coordination sphere of **1**, methyl iodide forms the adduct **2**. The energy gain of forming this van der Waals complex is rather low in gas phase, however according to NBO analysis slight repartitioning of the charge distribution occurs in both Pt(bdpp)(CH$_3$)$_2$ and methyl–iodide moieties (see Table 1). When solvation is taken into account, **2** lies above the reactants by 0.3 kcal/mol. Therefore as starting point the two reactants at infinite separation were considered, thus the activation energies were evaluated as the energy difference between **1** plus methyl–iodide together and the transition states.

As seen on Fig. 2, the transition state **3TS** shows a nearly linear Pt–C$_{methyl}$–I arrangement corresponding to an S$_N$2 type of reaction which is also supported by the character of the imaginary vibration mode (224i cm^{-1}). The calculated free energies of activation are 23.5 kcal/mol in gas phase and 17.7 kcal/mol in acetonitrile, respectively. The cleavage of the C$_{methyl}$–I bond leads to the tetragonal pyramidal complex **4**, in an endothermic reaction. During this nucleophilic substitution reaction the cen-
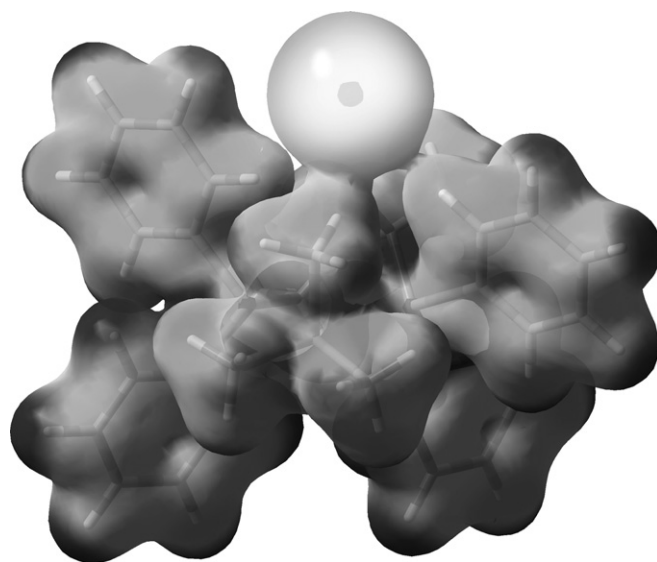

Fig. 3. The electron density map of **4** with the electrostatic potential mapped onto the surface. Darker regions are more positive, lighter are more negative.
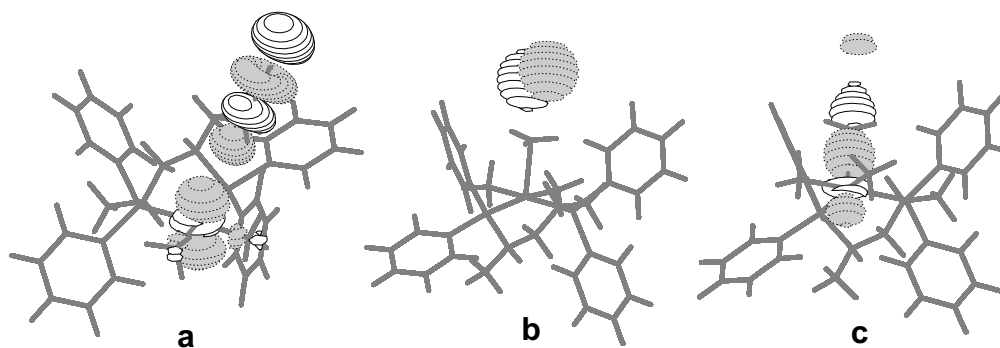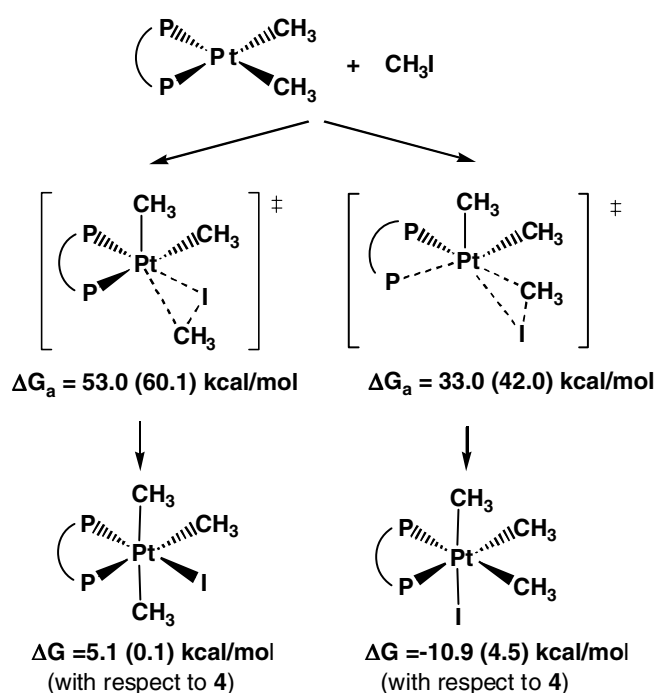
Fig. 4. (a) Frontier orbital interaction between the HOMO of Pt(bdpp)(CH₃)₂ and LUMO of MeI; (b) HOMO of the transition state **3TS**; (c) HOMO-16 of 3TS: the highest energy occupied orbital of bonding character with respect to the forming Pt-C bond.
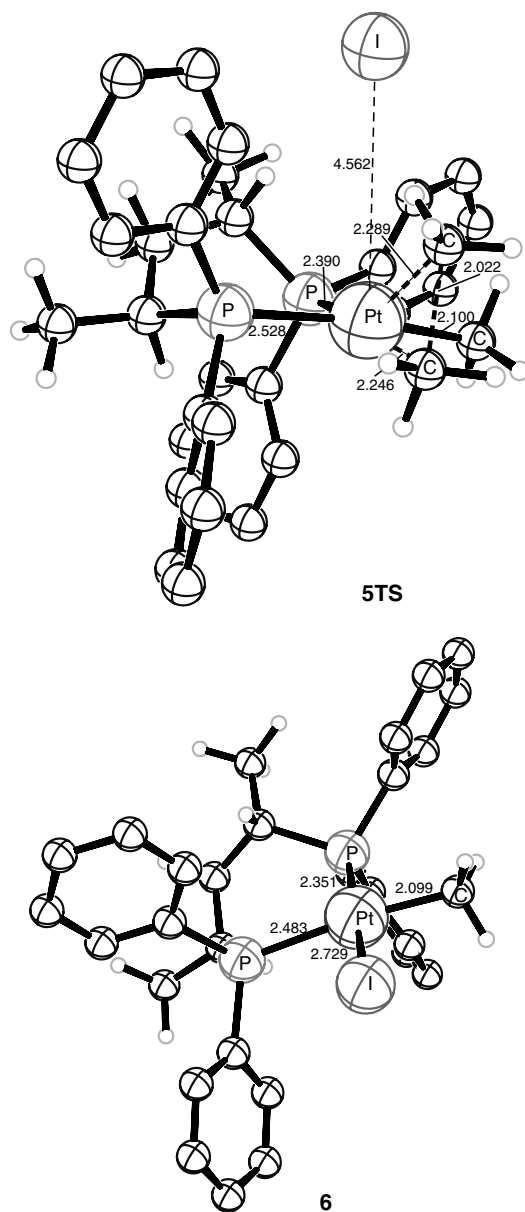

Scheme 1.

Fig. 5. Optimised structures (bond distances in Å) of **5TS**, the transition state of the reductive elimination of ethane from the Pt(bdpp)(CH₃)₃I intermediate, and of the product Pt(bdpp)(CH₃)I (**6**).

tral platinum atom of the 'nucleophilic agent' (i.e. the platinum-bdpp-dimethyl complex) loses from its electron density, as its natural charge increases from 0.170 to 0.617. The methyl carbon belonging originally to methyl iodide becomes also slightly more positive. The splitting iodine has basically an ionic character, however its natural charge (−0.726) is higher than that of the 'pure' anion. The charge donation occurs to the axial methyl group and to two of the phenyl groups belonging to bdpp forming a half-cage and stabilizing the iodine. Fig. 3 presents the electron density map of **4** with the electrostatic potential mapped onto the surface.

A look at the frontier orbitals of the reactants (Fig. 4a) may be helpful in understanding the pattern for the previous reaction. The HOMO of **1** is formed mainly from the valence d_{z^2} orbital of platinum, whereas the LUMO of

methyl–iodide is the $\sigma*$ C–I antibond. Considering the transition state **3TS**, the HOMO (Fig. 4b) is formed basically from the valence p_x orbital of iodine. The highest energy occupied orbital with bonding character is the HOMO-16 (Fig. 4c).
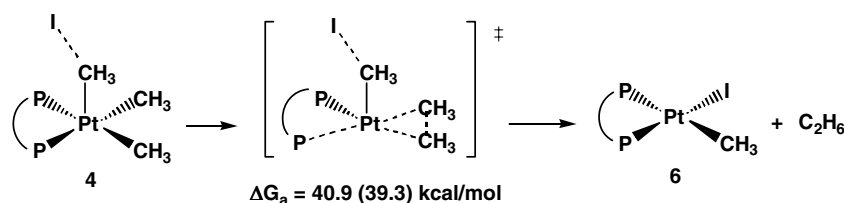
The oxidative addition of methyl–iodide can also take place in a concerted reaction i.e. simultaneous Pt–I and Pt–C_{methyl} bond formation and C_{methyl}–I bond breaking resulting in an octahedral $Pt(bdpp)(CH_3)_3I$ complex (Scheme 1, results obtained in acetonitrile are given in parenthesis). Two transition states (their imaginary vibration frequencies are 280i and 283i cm^{-1}, respectively) were located with the iodine in either the $P_2Pt(CH_3)$ plane or perpendicular to it. In the latter case, the oxidative addition takes place with a simultaneous arm-off dissociation of one of the P–Pt bonds. However, the activation energies are too high in both concerted reactions to consider them as a competitor path to the S_N2 mechanism. In acetonitrile phase both of the octahedral $Pt(bdpp)(CH_3)_3I$ complexes are higher in energy than compound **4**.

### 3.2. Reductive elimination from Pt(bdpp)(CH₃)₃I

The ethane reductive elimination step from **4** proceeds through a three-centred transition state **5TS**, which is depicted on Fig. 5. This transition state structure has an imaginary frequency of 438i cm^{-1}, in which the bonds of platinum and the axial and one of the equatorial methyl groups are elongated and the bond angle is reduced from 89° to 53°. The free energy of activation is 21.3 kcal/mol in gas phase and reduced to 19.5 kcal/mol, when solvation in acetonitrile is taken into account. As ethane dissociates the Pt–I distance decreases, and as product the $Pt(bdpp)(CH_3)I$ complex (**6**) is formed in a highly exothermic reaction. Having a closer look at the results of natural population analysis, there is a charge transfer as iodine passes electron density to platinum turning it almost neutral.

In proceeding from **4**, a concurrent reductive elimination path exists (Scheme 2, free energy of activation calculated with PCM correction is given in parenthesis) involving the two equatorial methyl groups with substantially higher barrier of activation. In the corresponding transition state (with an imaginary frequency of 475i cm^{-1}) one of the Pt–P bonds is dissociated while the position of the axial methyl group and the iodine stabilised by the phenyl groups of the bdpp ligand are preserved. The free energy barrier in this particular case is very close to the value obtained by Ananikov et al. for the C–C reductive elimination of methyl ligands from $Pt(PH_3)_2(CH_3)_2$ [21].
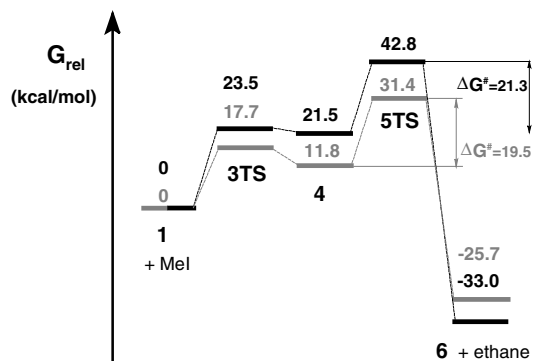

Scheme 2.
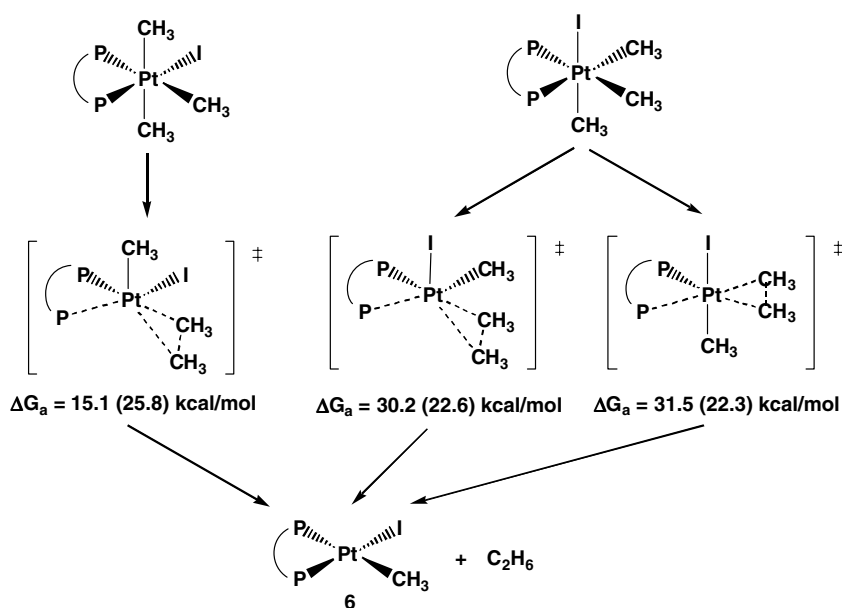
Scheme 3.

Fig. 6. Free energy profile of the iodide–methyl exchange reaction. Results in acetonitrile are shown in grey.

Although the oxidative addition pathways leading to the octahedral Pt(bdpp)(CH$_3$)$_3$I complexes are less preferred, their reductive elimination reactions were also examined (Scheme 3, the solvated free energies of activation are given in parenthesis). Also in these cases the reductive elimination takes place with a simultaneous arm-off dissociation of one of the P–Pt bonds.

When iodine is located perpendicular to the P$_2$Pt(CH$_3$) plane, two different routes are possible; with one 'in plane' and one 'perpendicular', and with both of the 'in plane' methyl groups involved in the elimination process. The free energy barriers of activation are quite close in the two cases, but higher than calculated for the elimination of **4**. The imaginary frequency of the corresponding transition states are 501i and 463i cm^{-1}, respectively.

Interestingly, the free energy barrier (with the transition state having a single 424i cm^{-1} imaginary frequency) for the C–C coupling process of the Pt(bdpp)(CH$_3$)$_3$I complex possessing the iodine 'in plane' differs significantly in gas phase and in acetonitrile. However, the barrier is still higher, than in case of the **4 → 5TS → 6** pathway, when PCM corrections are applied.

The free energy profile of the preferred reaction path is shown on Fig. 6 also including the solvation effects.

4. Conclusions

In this paper, a density functional investigation at the BP86/LANL2DZ level of theory has been carried out. Real complexes, without replacing the phenyl rings of the chelating phosphine ligand by hydrogen, were considered. The results obtained in the present study can be summarized as follows:

(i) In agreement with other transition metal reactions utilizing methyl–iodide (i.e. Monsanto/Cativa process) the oxidative addition proceeds by an S$_N$2 reaction mechanism via a transition state in which the arrangement of the I–CH$_3$–Pt moiety is nearly collinear. Three-centred, concerted transition states, leading to octahedral Pt(bdpp)(CH$_3$)$_3$I complexes, were

also characterized, although the corresponding free energies of activation are too high compared to the proposed mechanism, therefore they are ruled out.

(ii) The reaction intermediate is a tetragonal pyramidal complex cation of the [Pt(bdpp)(CH$_3$)$_3$]$^+$I$^-$ ion pair with the iodine remaining in the outer coordination sphere and stabilised by the axial methyl group and the phenyl rings. During the reductive elimination process ethane dissociates through a three-centred transition state and the square-planar Pt(bdpp)-(CH$_3$)I is formed as result.

(iii) Including solvation effect a different reaction profile has been obtained. The rate determining step in gas phase is the oxidative addition of methyl–iodide, whilst in acetonitrile it is the reductive elimination of ethane.

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