



Computational catalysis

Mechanism of the oxidative addition of hypervalent iodonium salts to palladium(II) pincer-complexes[☆]

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ABSTRACT

Oxidative addition of hypervalent iodonium salts to palladium pincer-complexes was studied to rationalize the mechanism of the key-step in related Pd(II)/Pd(IV) based catalytic processes. It was found that this oxidative addition is an exothermic process with a relatively low activation barrier. The activation energy is highly dependent on the organic substituents of the iodonium salts. For example, an ethynyl group is transferred with a considerably lower activation barrier from iodine to palladium, than a phenyl functionality. We have compared the reaction profiles of the oxidative addition of hypervalent iodonium salts and phenyl iodide. The most important difference between the two processes is that the oxidative addition of phenyl iodide is highly endothermic, as the reductive elimination of phenyl iodide from the Pd(IV) species requires a very low barrier. In contrast, the formation of the Pd(IV) species using hypervalent iodonium salts is an irreversible process, which allows ligand exchange and transmetalation reactions generating a productive catalytic cycle. The studies indicate that the most important MO's involved in the oxidation is the antibonding σ^* orbital of the iodonium salt and a non-bonding Pd(4d) orbital, which is perpendicular to the coordination plane of the palladium atom.

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1. Introduction

Palladium-catalyzed redox-reactions represent one of the most important tools in selective organic synthesis [1,2]. Most of these procedures are based on a standard Pd(0)/Pd(II) cycle, such as Heck coupling [3], Suzuki coupling [4–6], allylic substitutions [7,8] etc. However, recently new types of redox-reactions via a Pd(II)/Pd(IV) redox cycle attracted considerable interest in the synthetic community [9–12]. By using this methodology, some notorious problems arising from Pd(0)/Pd(II) catalysis can be solved. An obvious advantage is to avoid formation of Pd(0) intermediates, which are usually instable and may form amorphous Pd(0), so-called palladium black by deactivating the catalyst. This leads to the requirement of using high catalytic loadings of palladium, which is one of the main obstacles to implement many palladium-catalyzed processes in industrial applications. A further problem is that Pd(0) easily undergoes oxidative addition to aryl and allyl halides and allyl acetates, and therefore these functionalities usually does not survive Pd(0) catalyzed reactions [1,2]. There are many further advantages of using Pd(II)/Pd(IV) catalytic processes, such as the very facile reductive elimination of Pd(IV) to Pd(II) species and the easy transmetalation of organometallics to Pd(IV) species [9–12].

In the implementation of Pd(II)/Pd(IV) based redox cycles the main challenge is the generation of the Pd(IV) species under catalytic conditions. Since this oxidation state involves d^6 configuration on palladium, which is a highly oxidized state compared to the d^{10} configuration preferred by this noble metal, the oxidation process is often highly endothermic and therefore difficult to realize [9–12]. However, the oxidation of Pd(II) can be promoted by application of electron-supplying ligands. In this respect, so-called pincer-complexes, such as **1a** and **1b** may represent an interesting choice [13–16]. A further requirement is to find efficient oxidizing agents that are able to oxidize Pd(II) species under catalytic conditions. Currently, one of the simplest way to generate Pd(IV) intermediates under catalytic conditions is application of hypervalent iodonium salts (**2**) [17–20]. In fact, stoichiometric studies by van Koten [13], Canty et al. [15] and our group [16] have demonstrated that NCN pincer-complex **1a** [21–23] and its analogs relatively easily undergo oxidation to palladium(IV) species (Fig. 1).

In a recent study we have shown that hypervalent iodonium salts (**2a–b**) can be employed as aryl sources in Heck coupling type of reactions with alkenes using palladium pincer-complex (such as **1a**) and Pd(OAc)₂ as catalysts (Fig. 2) [24]. These reactions are supposed to proceed via Pd(II)/Pd(IV) catalytic cycle. In order to demonstrate the synthetic potential of the Pd(II)/Pd(IV) based transformations, we concentrated on preparation of functionalized allylic acetates. These functionalities (allylic acetate) would easily undergo oxidative addition in a Pd(0) catalyzed transformation [1] but remained unchanged in the presented process.

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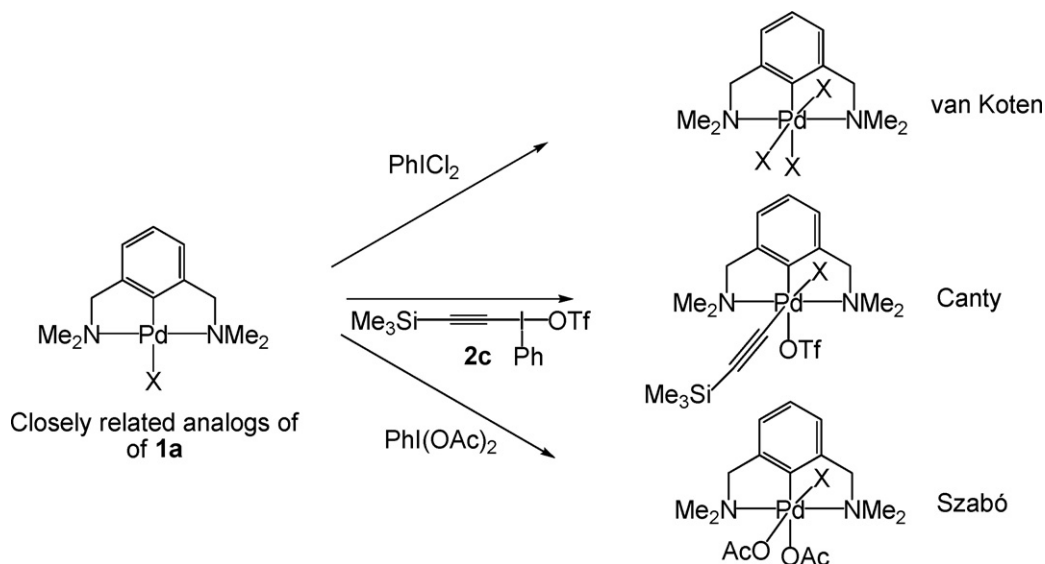


Fig. 1. Oxidation of NCN pincer-complex by hypervalent iodonium salts by van Koten and co-workers, [13] Canty et al. [15] and Szabó and co-workers [16].

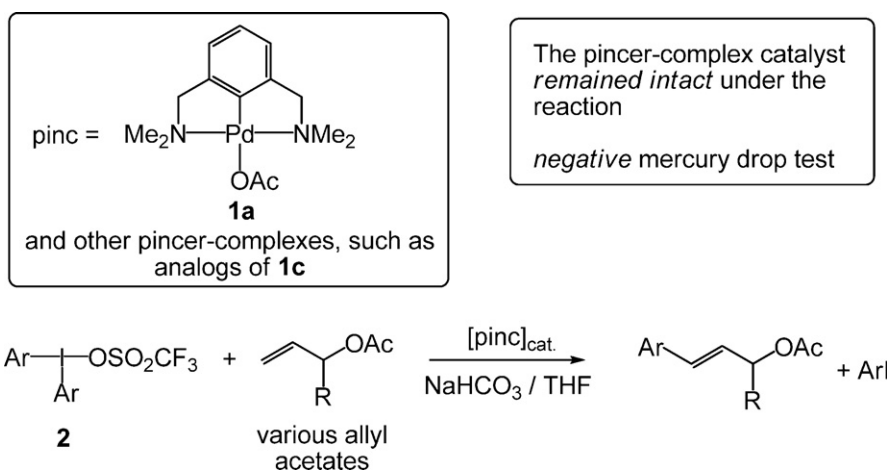


Fig. 2. Heck type coupling of allyl acetates by hypervalent iodonium salts using NCN pincer-complex as direct catalysts [24].

A particularly interesting mechanistic aspect of this study is to show that palladium pincer-complexes may serve as direct catalysts in processes via Pd(IV) intermediates without disintegrating of the pincer structure. In contrast, when phenyl iodide is employed as aryl source in pincer-complex catalyzed Heck coupling with alkenes under harsh conditions, the pincer-complex catalyst was

decomposed by releasing Pd(0) (Fig. 3) [25–27]. An important indication is the positive mercury drop test [28], which shows that the reaction proceeds via Pd(0) species, and thus a Pd(0)/Pd(II) redox cycle is involved in the process.

The present study is aimed to investigate the oxidative addition of hypervalent iodonium salts (2) to palladium(II) pincer-

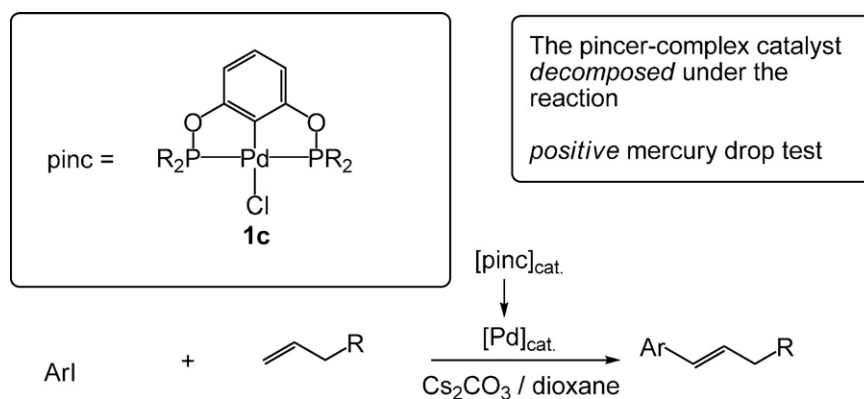


Fig. 3. Heck type coupling of aryl iodides with alkenes catalyzed by pincer-complexes as catalyst precursors reported by Eberhard [25].

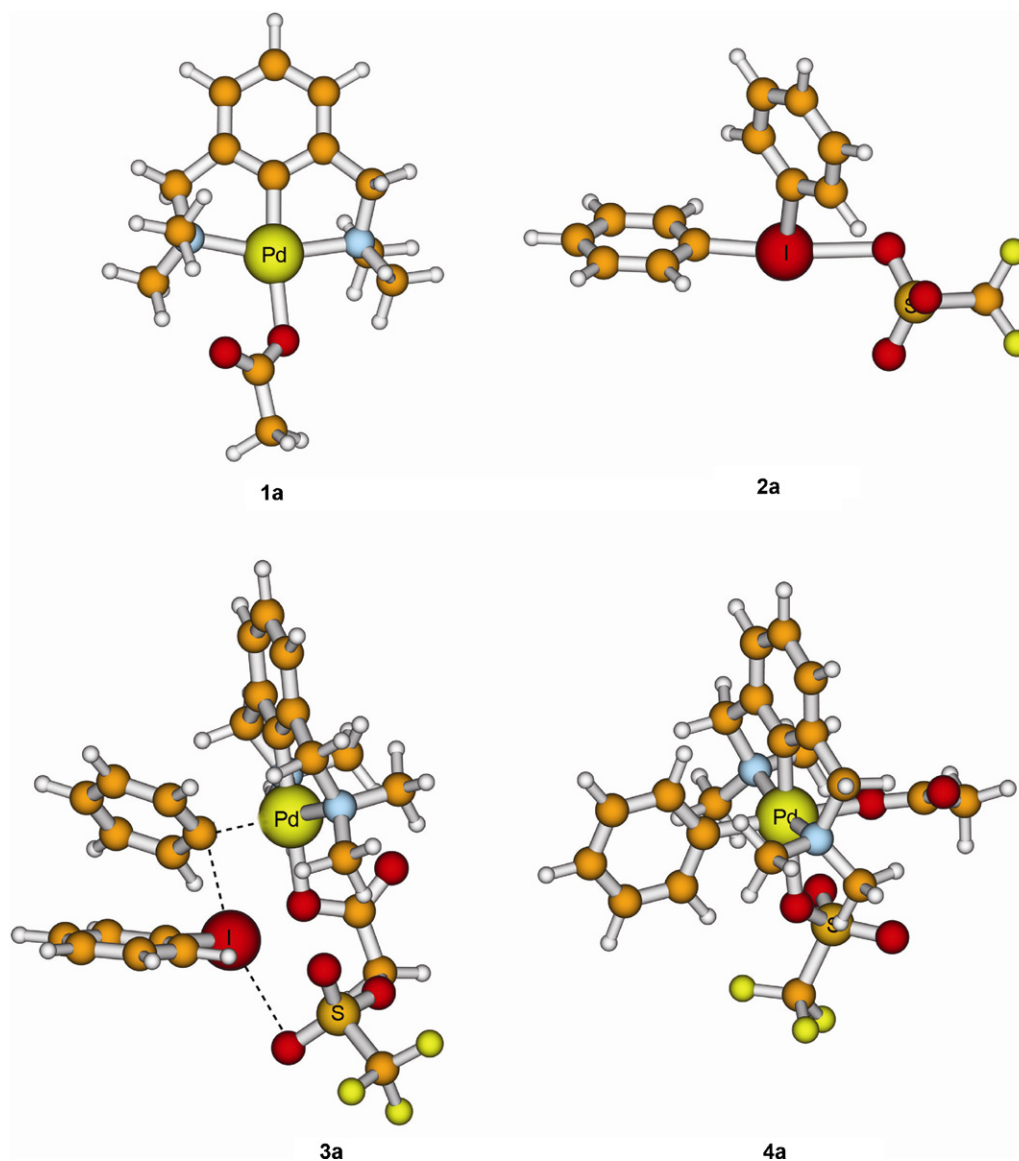


Fig. 4. Selected species involved in oxidation of Pd(II) pincer-complex by hypervalent iodonium salts.

complexes (**1a–b**) (Figs. 4–7). As mentioned above NCN complexes relatively easily form Pd(IV) complexes with iodonium salts (Fig. 1) and they can be employed as catalyst in the reaction of iodonium salts with alkenes (Fig. 2), therefore we used this particular pincer-complex as one of the reactants in the present studies. It should also be added that **1a** is relatively small and structurally well defined because of the terdentate pincer type coordination rendering **1a** to a particularly suitable species for DFT modeling studies. Although, several excellent ab initio and DFT studies are published in the literature on the structure and reactivity of hypervalent iodonium salts [29–35], as far as we know this is the first detailed theoretical study addressing the mechanistic aspects of the oxidation of Pd(II) to Pd(IV) species by iodonium salts. Some of the presented results were very briefly (in a single sentence) discussed in a previous communication [24]. In this paper we give a full account to our results and extend the studies to investigation of the substituent and ligand effects to the oxidative addition reactions. In addition, we compare the oxidative addition of hypervalent iodonium salts and phenyl iodide, in order to rationalize the observed differences of the catalytic activity of pincer-complexes (cf. Figs. 1 and 2) in Heck-type coupling reactions.

2. Results and discussion

The calculated structures of selected palladium and hypervalent iodonium species are given in Figs. 4 and 6, while the calculated reaction profiles for the Pd(II) → Pd(IV) processes are given in Figs. 5 and 7.

2.1. Computational methods

All geometries were fully optimized employing a Becke-type [36] three-parameter density functional model B3PW91 [37,38] using a 6-31G* basis set on C, H, N, O, S atoms [39,40]. On Pd, Br and I a LANL2DZ basis [41–43] was employed, which was augmented with one set of diffuse d-functions on Pd (exponent: 0.0628), a diffuse p-function (exponent: 0.0376) and a d-polarization function (exponent: 0.434) on Br and a diffuse p-function (exponent: 0.0308) and a d-polarization function (exponent: 0.294) on I. Harmonic frequencies have been calculated at the level of optimization for all structures to characterize the calculated stationary points and to determine the zero-point energies. The TS structures (**3a–d** and **5**) are characterized by a single imaginary frequency, while

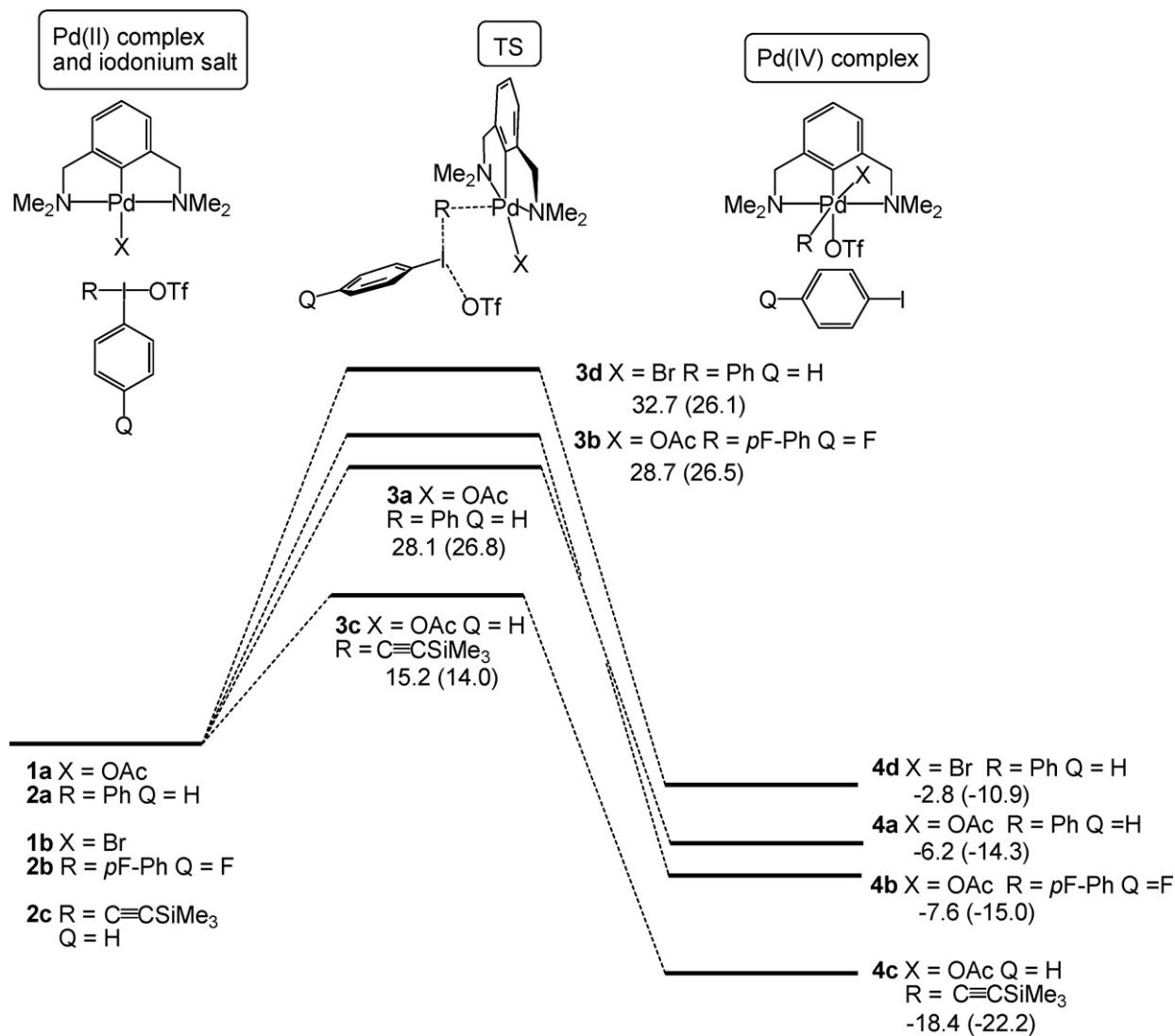


Fig. 5. Reaction profiles for oxidation of NCN complex **1a** with various hypervalent iodonium salts **2a–c**. The energies (kcal mol⁻¹) are corrected with the ZPV and solvation energies, the uncorrected relative energies are given in parenthesis.

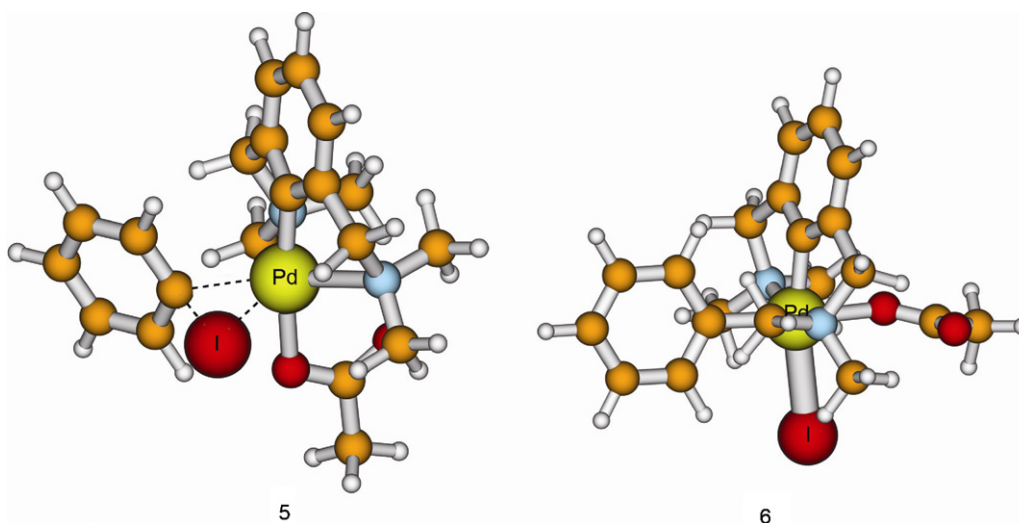


Fig. 6. Transition state (**5**) and oxidized adduct (**6**) obtained for the reaction of **1a** with phenyl iodide.

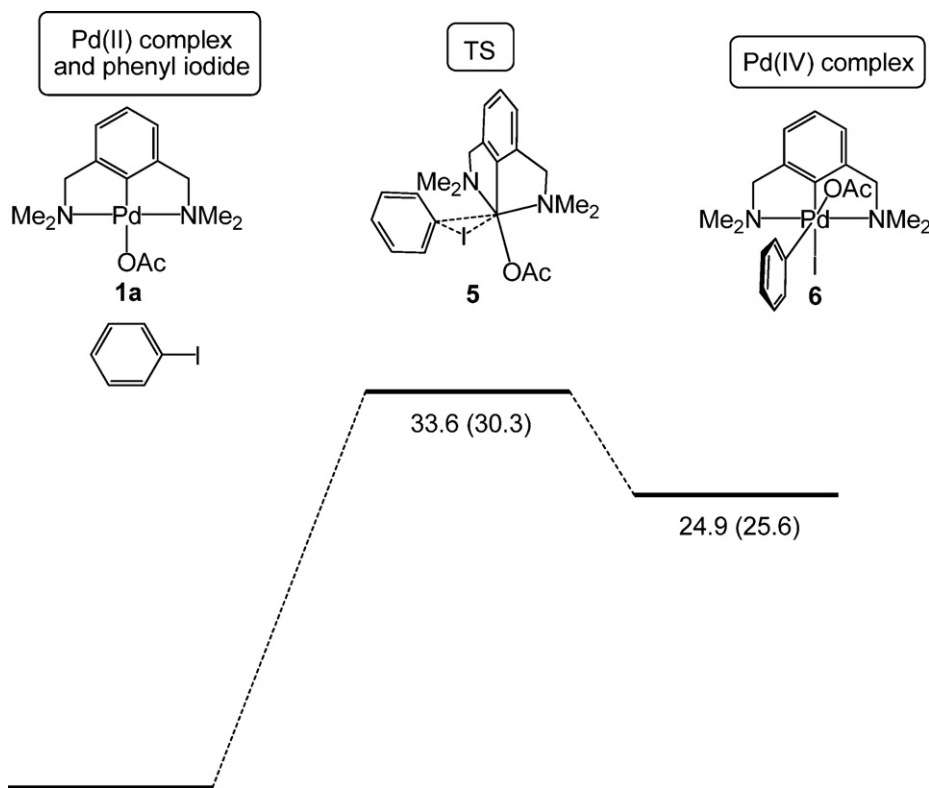


Fig. 7. Reaction profiles for oxidation of NCN complex **1a** with phenyl iodide. The energies are given in kcal mol⁻¹.

the rest of the optimized structures possess only real frequencies. Solvation contributions were calculated by single point calculations at the level of optimization using the CPCM method [44,45] with THF as solvent (this was also the solvent in the experimental studies [24]). The energies given in Figs. 5 and 7 are corrected with the zero-point energies and the solvation. All calculations were carried out by employing the Gaussian03 program package [46].

2.1.1. Oxidation of Pd(II) pincer-complexes by hypervalent iodonium salts

In order to improve the solubility of the palladium-complex in organic solvents in the stoichiometric [15] and catalytic studies [24] benzoate was employed as the counter ion in the NCN pincer-complex. In order to reduce the necessary computational efforts, we employed acetate in **1a** instead of benzoate, which probably has no effect in the oxidation reactions. Except this we did not employ any other simplification or truncation of the experimentally studied species.

Complex **1a** (Fig. 4) shows a typical pincer-complex structure, in which the Pd–N distance is rather short, 2.141 Å. It is interesting to point out that in all studied TS structures (**3a–d** and **5**) and Pd(IV) species (**4a–d** and **6**) the tridentate coordination of the pincer ligand is maintained.

In **2a** the phenyl groups are in cis position to each other and one of the phenyls is trans to the loosely bound triflate (OSO₂CF₃) counter ion. Interestingly, the trans disposition of the phenyl groups is highly unfavoured. Attempts to find a stationary point on the potential energy surface (PES) in the vicinity of the trans-diphenyl form was failed and the optimization is converged directly to **2a**. This type of trans-influence, which is also known in transition-metal chemistry, was pointed out by Zhdankin and co-workers [35].

In the TS state structure **3a** the iodonium species **2a** undergoes fragmentation. One of the I–C bonds of **2a** (2.136 Å) is elongated

to 2.781 in **3a** with simultaneously formation of a new Pd–C bond. The other phenyl group pre-forms a phenyl iodide molecule, while the triflate ion also leaves the iodide (Fig. 4). The activation energy (Fig. 5) is 28.1 kcal mol⁻¹, which is reasonable for a catalytic reaction proceeding at moderately high temperature (50 °C) in THF as solvent [24].

In the final complex (**4a**) the coordination sphere of palladium is expanded from four to six by maintaining the pincer structure with slightly elongated Pd–N distances of 2.200 Å. The formed phenyl iodide molecule does not show any coordination affinity to palladium atom of the oxidized complex. The entire oxidation process is exothermic by 6.2 kcal mol⁻¹ and the (uncorrected) gas-phase value (–14.3 kcal mol⁻¹) indicates a highly exothermic electronic process.

We have briefly studied the substituent effects on the activation energy of the oxidation (Fig. 5). Applying *para*-fluoro-phenyl group in the iodonium salt (**2b**) the activation energy (**3b**) rises by an insignificantly low value of 0.6 kcal mol⁻¹ (28.7 kcal mol⁻¹) compared to the oxidation by the phenyl iodonium salt (**2a**). Interestingly, the entire process is more exothermic by 0.6 kcal mol⁻¹, for the reaction fluoro-phenyl salt compared to the phenyl one. These results are in line with the experimental observations that **2a** and **2b** are about equally efficient reagents in cross-coupling reactions and the similar rate of arylation in the catalytic reaction suggest a similar activation barrier.

Replacement of one of the phenyl groups with a silyl acetylenyl functionality leads to a highly reactive oxidizing species, **2c**. In the most stable ground state structure the silyl acetylenyl group is trans to the triflate (see Fig. 1). Interestingly, in the isomeric iodonium salt, when the phenyl group is trans to the triflate (and the acetylenyl is cis), the relative energy rises by 8.5 kcal mol⁻¹ indicating an unfavorable trans influence of the phenyl group, which was also pointed out by Zhdankin [35]. Considering the TS geometry of the process (e.g. **3a**, Fig. 4), the cis arrangement of the silyl acetylenyl group to triflate predestinates the chemoselectivity of the oxida-

tion process, i.e. that the silyl acetynyl group (and not the phenyl) is transferred from iodide to palladium (Fig. 1) [15]. The activation barrier of the acetynyl transfer ($2c \rightarrow 3c \rightarrow 4c$) process proceeds through a much lower (by $12.9 \text{ kcal mol}^{-1}$) activation barrier than the corresponding oxidative phenylation ($2a \rightarrow 3a \rightarrow 4a$) reaction. In fact, Canty et al. [15] were able to perform this reaction (formation of **4c**) at -40°C (Fig. 1), while the catalytic reaction involving **2a** requires 50°C to proceed. It was reasoned that the difficulty of the experimental generation/observation of **4a** is encumbered by the relatively high temperature (activation energy) required by the oxidative addition of **2a** to **1a** [24]. Although, formation of **4c** is a highly exothermic process, the thermo stability of this complex is rather poor. According to the observations of Canty et al. [15] this complex rapidly decomposes at ambient temperature. Interestingly, the platinum analog of **4c** is stable and even its X-ray structure is available [15].

Replacement of the counter ion in **1a** from acetate to bromide leads to complex **1b**. Oxidative addition of **2a** to **1b** proceeds with a higher activation energy, than with the acetate analog. However, the increase of the barrier by ($4.6 \text{ kcal mol}^{-1}$) is due to the solvent effects, as the gas phase activation energies are identical within $0.7 \text{ kcal mol}^{-1}$. This suggests that somewhat higher catalytic activity is expected for the acetate complex **1a** than for bromide **1b**, which is a more widely used in catalytic applications [23,47–50].

2.1.2. Oxidation of Pd(II) pincer-complexes by phenyl iodide

As mentioned above there has been a debate about the possibility of using pincer-complexes as direct catalysts for coupling of phenyl halides with alkenes via Pd(IV) intermediates (Fig. 3) [25–27,51–53]. Recently, both experimental [25,26] and theoretical [53] studies indicate that this process is difficult to achieve because of the apparent inability of phenyl halides to oxidize Pd(II) to Pd(IV) in pincer-complexes. As the structure of hypervalent iodonium salts and phenyl iodide are similar, it was interesting to compare the oxidation ability of these species toward the palladium atom of pincer-complexes.

The obvious difference between the TS of the oxidation by iodonium salt (**3a**, Fig. 4) and by phenyl iodide (**5**, Fig. 6) is the behavior of the iodide ion. In **3a** iodide have a very weak (if any) interaction with palladium ($\text{Pd-I} = 3.471 \text{ \AA}$), while in **5** the palladium–iodide interaction ($\text{Pd-I} = 2.758 \text{ \AA}$) is the major component of the reaction coordinate. It is interesting to point out that the activation energy (Fig. 7) of the oxidative addition of phenyl iodide ($33.6 \text{ kcal mol}^{-1}$) is only $5.5 \text{ kcal mol}^{-1}$ higher than with iodonium salt **2a** ($28.1 \text{ kcal mol}^{-1}$). The major difference between the two processes is the stability of the formed Pd(IV) species. The oxidation of palladium by phenyl iodide is highly endothermic by $24.9 \text{ kcal mol}^{-1}$ (**6**), while the corresponding reaction with iodonium salt **2a** is exothermic by $6.2 \text{ kcal mol}^{-1}$. Thus the major obstacle of generating Pd(IV) species from phenyl iodide is probably the reversibility of the oxidation process, i.e. that the reductive elimination of phenyl iodide from Pd(IV) complex **6** is much easier than the oxidative addition of phenyl iodide to Pd(II) complex **1a**.

An obvious advantage to employ iodonium salts for oxidation of Pd(II) species is that the iodine atom of **2** is in a thermodynamically unfavoured high oxidation state. The accumulated high energy is released by formation of phenyl iodide, and furthermore the reverse reaction, the recombination of the hypervalent iodonium salt by reductive elimination of the Pd(IV) complex **4**, is thermodynamically unfavorable.

Blacque and Frech [53] have carried out DFT studies to explore the possibility of the oxidative addition of aryl bromides to PCP-type of palladium pincer-complexes. Interestingly, these authors have found that the activation barrier of this process for coordinatively saturated (16 electron) pincer-complexes is unexpectedly high, $60\text{--}70 \text{ kcal mol}^{-1}$. Therefore, Blacque and Frech considered

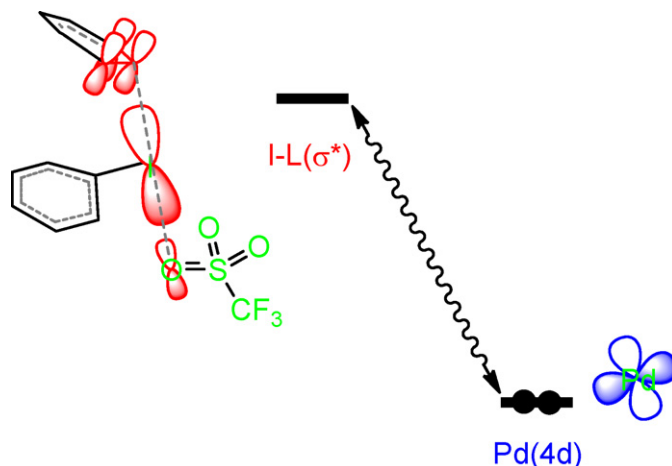


Fig. 8. Qualitative MO diagram on the major electronic interactions of the oxidation.

[53] the possibility of dissociation of the counter ion prior to oxidative addition, which led to lower barriers of $40\text{--}45 \text{ kcal mol}^{-1}$. In contrast to these results, our modeling studies indicate that the activation energy of the oxidative addition of phenyl iodide to coordinatively saturated pincer-complex **1a** requires a relatively low activation energy (Fig. 7). The difference is probably due to the fact that NCN ligand of **1a** is a stronger electron-donor than the PCP-type of ligands studied by Frech and Blacque, which leads to lower barrier to oxidative additions. An additional factor for obtaining a lower activation barrier in the present study is that we employed phenyl iodides instead of phenyl bromides to oxidize the pincer-complexes.

2.1.3. Implications of the present study for the designing of new Pd-catalyzed reactions

Although, the above studies are performed for pincer-complexes the basic conclusions can be extended to any other palladium complex. As shown in Section 2.1.1 hypervalent iodonium salts are excellent oxidants for Pd(II) species. The activation energy of the oxidation is highly dependent on the type of the substituent on iodide and on the ligand effects on palladium.

A simplified qualitative description can be given (Fig. 8) for the oxidation of Pd(II) by hypervalent iodine by considering the electronic interactions between one of the lone-pair d-orbitals of palladium and the low-lying σ^* level of the hypervalent iodine salt [18,20,54]. Electron-pair transfer from Pd(4d) to the antibonding σ^* MO of the iodonium(III) salt leads fragmentation of the I(III) salt, which is clearly reflected by TS structure **3a**. This lone-pair MO of the Pd(II) precursor does not participate in ligand coordination, and thus it is perpendicular to the coordination plane of palladium imposing a stereo electronic constrain to the oxidation process (**3a**, Fig. 4). Any electronic effects lowering the σ^* MO in the hypervalent iodonium salt leads to amplification of the interaction with Pd(4d). Thus highly electronegative groups increase the oxidation potential of the iodonium salt. For example, **2c** with an $\text{I-C}(\text{sp})$ bonded ethynyl substituent is more reactive than **2a** with a phenyl substituent possessing an $\text{I-C}(\text{sp}^2)$ bonding structure, as shown by the presented study (Fig. 5). Similarly, electronic effects increasing the Pd(4d) level leads to enhanced interactions with $\text{I-L}(\sigma^*)$. This can be achieved by implementing electron donating ligands on palladium.

The above mentioned electronic interactions are represented for example in the HOMO-1 of TS structure **3a** (Fig. 9). The HOMO has a pure lone-pair character for the oxygen atoms of the triflate, and therefore it is not characteristic for the bond forming and cleaving process of the oxidation.

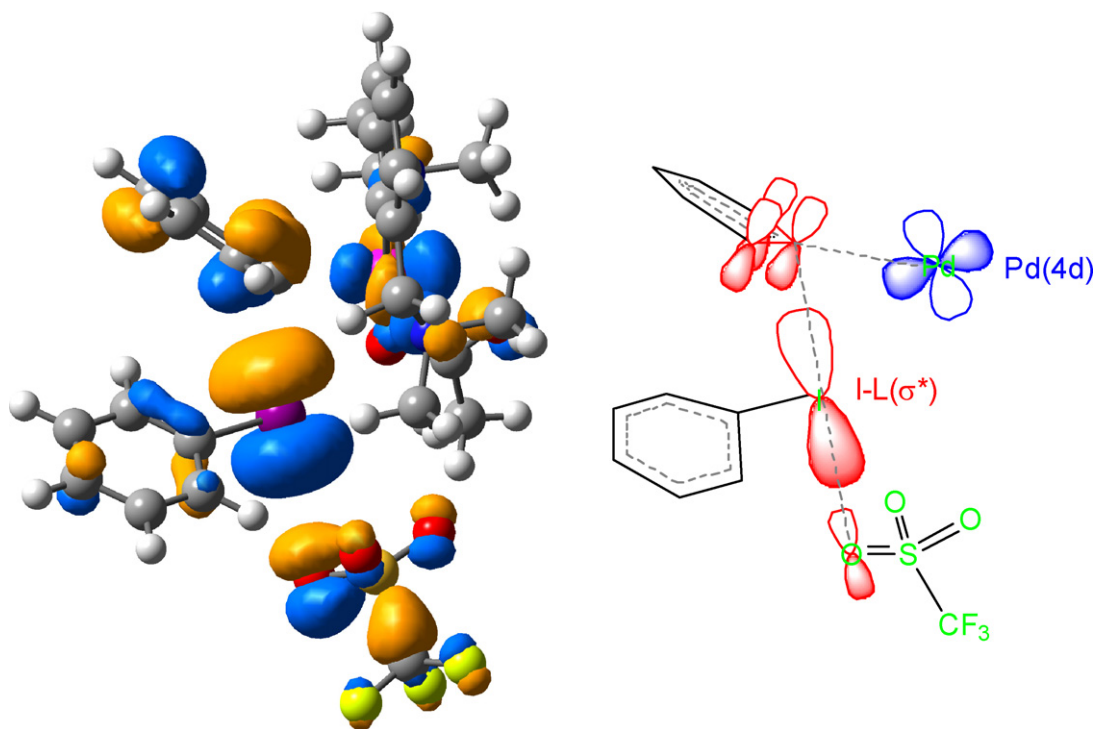


Fig. 9. HOMO-1 of TS structure **3a**. The most important interactions are highlighted on the right side.

A further important advantage of using hypervalent iodonium salts in palladium chemistry is that the oxidative addition to the Pd(II) species is an irreversible process, accordingly the formed Pd(IV) species are able to undergo ligand exchange or transmetalation reactions instead of a reverse reductive elimination reaction. In this way a productive Pd(II)/Pd(IV) catalytic cycle can be created, which is much less viable with traditional reagents, such as phenyl iodide.

3. Conclusions

In this study we have shown that hypervalent iodonium salts are excellent oxidants for Pd(II) complexes. The reaction proceeds via a relatively low activation barrier, and the oxidation is an exothermic and irreversible process. The activation barrier and the exothermicity of the oxidative transfer of the organic functionality from iodine to palladium are dependent on the electronic structure of the organic ligand. For example, an ethynyl group is transferred with a much lower activation barrier than a phenyl group. Phenyl iodide oxidizes Pd(II) to Pd(IV) with a higher barrier than hypervalent iodonium salts, and the reaction is highly endothermic. The oxidative addition of phenyl iodide to Pd(II) precursors requires much higher activation energy than the reductive elimination of phenyl iodide from the resulted Pd(IV) species. The above studies indicate that the reactivity of hypervalent salts can be tuned by altering of the σ^* (LUMO) level of these species. Lowering the σ^* level facilitate the oxidation and the transfer of the organic functionality from iodine to palladium.

The irreversible fragmentation of the hypervalent iodonium salts under the oxidation process is probably the most important advantage of using these species in Pd(II)/Pd(IV) redox cycle based processes. Probably other oxidants that are able to perform similar type of irreversible fragmentation under double electron transfer (electron pair) constrains may serve as efficient oxidant in the Pd(II) to Pd(IV) process, as hypervalent iodonium salts does.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.03.014.

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