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DFT studies of isomerization in palladium(IV) chemistry and alkyl halide transfer from palladium(IV) to palladium(II)

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ABSTRACT

A DFT study of alkyl halide exchange from Pd(IV) to Pd(II) centers supports proposals for an S_N2 process in which nucleophilic Pd(II) square-planar complexes attack the axial alkyl group in electrophilic square-pyramidal Pd(IV) centers, leading to transfer of R^+ from Pd(IV) to Pd(II) involving a transition structure of the form $[R_2(bpy)\cdot\cdot R\cdot\cdot PdR_2(bpy)]^+$ (bpy = 2,2′-bipyridine). Computation accounts for the selectivity in benzyl (Bn) over methyl transfer from $PhMeBnPd^{IV}(bpy)Br$ to $Me_2Pd^{II}(bpy)$, giving $PhMePd^{II}(bpy)$ and $BnMe_2Pd^{IV}(bpy)$. Transition structures are formed by the interaction of a d_z2-like HOMO at the Pd(II) nucleophile and the Pd-C σ* LUMO at the cationic Pd(IV) electrophile. Isomerization of octahedral palladium(IV) complexes via halide loss followed by involvement of trigonal-bipyramidal transition structures to facilitate isomerization is also examined. A lower barrier for Bn^+ than Me^+ transfer is attributed to stabilisation of the transition structure by delocalisation of positive charge within the benzyl group, reflected in a higher total charge density for the benzyl group than found for the methyl group.

1. Introduction

Reactions involving alkyl group transfer from higher oxidation state metal centers to lower oxidation state metal centers have become a fundamental aspect of organometallic chemistry [1]. For the platinum group metals, early reports on the transfer of methyl groups from platinum (IV) to platinum (II) [2,3] were extended to Pd(IV)/Pt (II) systems which are more amenable to kinetic and NMR studies of mechanism [4]. This latter work in the Puddephatt laboratory added significant impetus to the developing field of organopalladium(IV) chemistry, and prompted studies of this class of reaction for alkyl halide transfer from Pd(IV) to Pd(II) [5–8]. Typical reactions are illustrated in Scheme 1, where the generation of Pd(IV) species (**2a/2b**, **5a**) by oxidative addition is shown prior to methyl iodide transfer from **2a/2b** to **3** giving **4**, and benzyl bromide transfer from **5a** giving **6a**.

The reaction of **1** with methyl iodide allows isolation of a mixture of complexes **2a/2b** in 1:1 ratio, and this mixture is fully and cleanly converted to **1** and **4** on reaction with **3** in $(CD_3)_2CO$ at −20 °C when studied by NMR spectroscopy. Complex **5a**, isolated in a similar manner to **2a/2b**, is the sole detected isomer for the reaction of **1** with benzyl bromide, and is converted to **1** and **6a** on reaction with **3** in $(CD_3)_2CO$ [6]. The structures of all species, except **5a**, were reliably determined from NMR spectra. Based on NMR spectra for **5a** and X-ray structural studies of the related complex $Me_2(p\text{-}BrC_6H_4CH_2)(phen)Br$ (phen = 1,10-phenanthroline) [9], a structure with "*trans*-BnPdBr" has been assigned (**5a**). Kinetic and NMR studies show retardation of alkyl halide transfer in the presence of additional halide ion [4,6]. In reactions similar to those of Scheme 1 it has been demonstrated that the transfer of methyl iodide from $Me_3Pd(bpy)I$ occurs exclusively to axial sites of $(D_3C)_2Pt(bipyrimidine)$ [4], In view of these observations, mechanisms involving halide dissociation from Pd(IV) followed by nucleophilic attack by the Pd(II) center at an axial alkyl group in a square-pyramidal cation to form a transition state **I** (Scheme 1) have been proposed [5–8]. Transition state **I** allows the "alkyl$^+$" group to migrate from the formerly Pd(IV) center to the Pd(II) center resulting in a reversal of oxidation state for the metal centers in the products.

We report here a Density Functional Theory (DFT) examination of the alkyl halide transfer reactions shown in Scheme 1, including probing the presence of isomers (**2a/2b**), absence of mixtures of isomers for the benzyl system (**5a**), interconversion of isomers **2a/2b** to ensure quantitative conversion for methyl iodide transfer, mechanism of alkyl group exchange, and selectivity for benzyl transfer for the reaction of **5a**. The experimental observations listed

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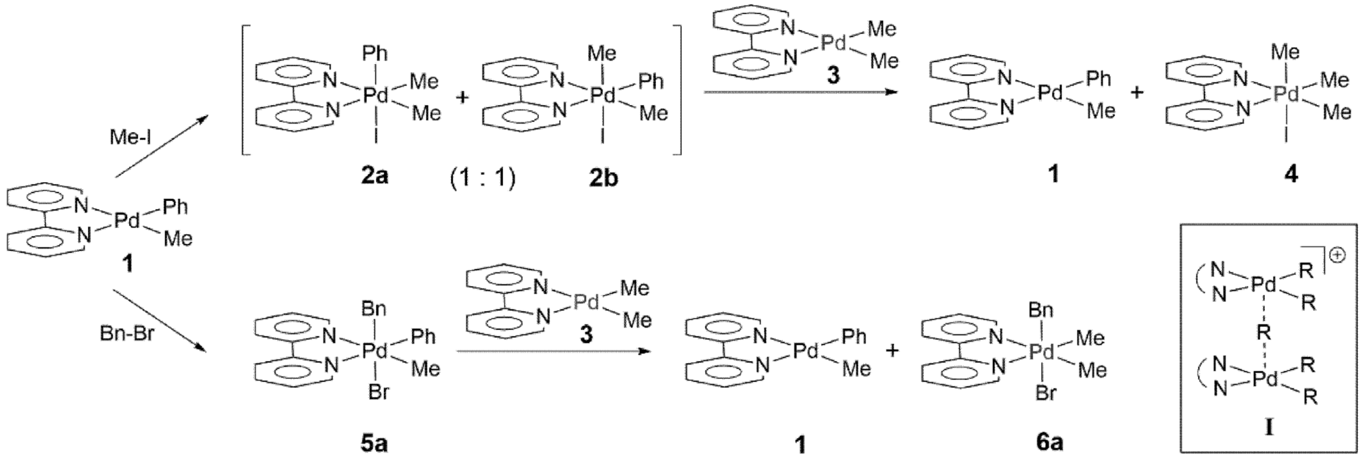


Scheme 1. The synthesis of a 1:1 mixture of isomers of PhMe$_2$Pd^{IV}(bpy)I (**2a**, **2b**) followed by their reaction with Me$_2$Pd (bpy) (**3**), and the synthesis of PhMe$_2$BnPd^{IV}(bpy)I (**5a**) followed by its reaction with Me$_2$Pd^{II}(bpy) (**3**) [6] (bpy = 2,2′-bipyridine, Bn = benzyl). Structure **I** illustrates the proposed transition structure for exchange reactions.

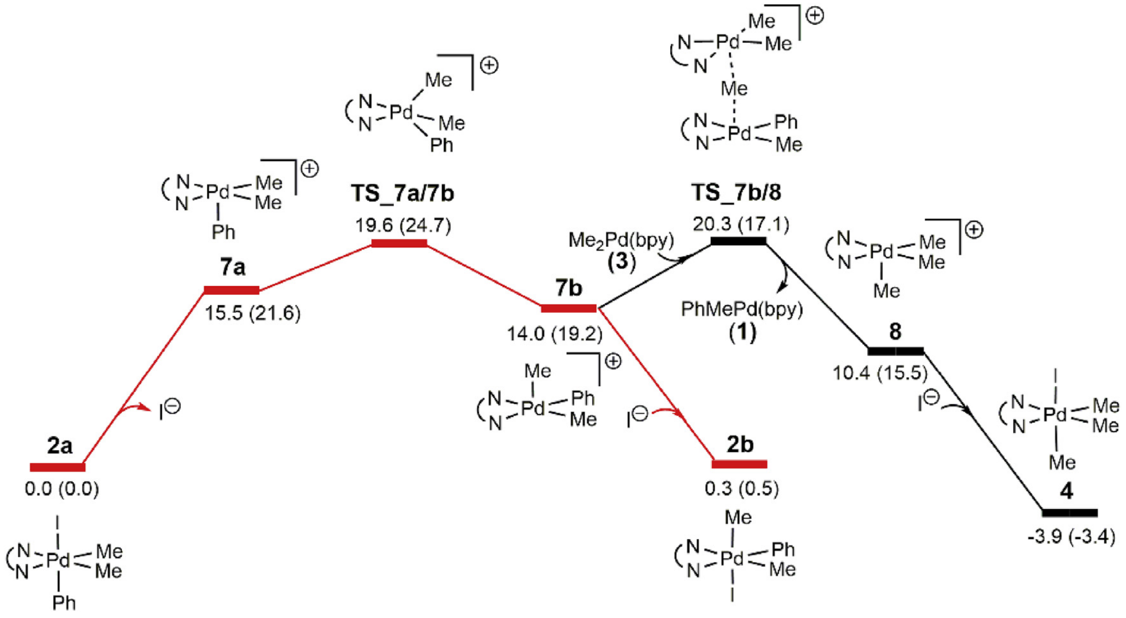
here provide several benchmarks to evaluate the validity of computation.

2. Results and discussion

Isomers of PhMe$_2$Pd(bpy)I (**2a/2b**) were found to have essentially identical energies (Scheme 2), consistent with experimental results obtained on the synthesis of **2a/2b**. As five-coordinate cations are known to be intermediates in oxidative addition to Pd(II) substrates [10], the isomer **2a** may be formed via isomerization of initially formed [PhMe$_2$Pd(bpy)]$^+$ (**7b**), and a transition structure for this process (**TS_7a/7b**) was found after potential energy scans. The isomerization process is also required for the observed quantitative conversion of **2a/2b** on reaction with Me$_2$Pd(bpy) (**3**) to give **1** and **4**. A transition structure was identified for methyl group transfer (**TS_7 b/8**) leading to cation **8**, and coordination of iodide follows to give product **4**. Attempts to identify a transition structure in which iodide is retained as a ligand were unsuccessful. The products are of lower energy than the reactants. The five-coordinate cations are square-pyramidal and the nature of the transition structures **TS_7a/7b** and **TS_7 b/8** is discussed below.

The preference for products **1** and **4** over reactants **2a/b** and **3** is attributed to the higher observed stability of the Pd(IV) product **4** compared with Pd(IV) reactants **2a/2b** [4], e.g. **4** can be isolated and an X-ray structure obtained but **2a/2b** decompose by reductive elimination at 0 °C. We note also, that the reductant **3** has a HOMO that is 0.08 eV higher than that for **1**, so that **3** should be more easily oxidized that **1**, consistent with reaction proceeding from **2a/2b** to **4** rather than the reverse reaction.

Computed isomerization of PhMeBnPd(bpy)Br (**5a**) and its reaction with Me$_2$Pd(bipy) (**3**) are shown in Scheme 3, in this case requiring two transition structures (**TS_9a/9b**, **TS_9a/9c**) to generate three isomers (**5a-c**). In accord with experiment, one structure (**5a**) is lower in energy than **5b** and **5c**, and corresponds to



Scheme 2. Energy profiles for (a) in red, isomerization of PhMe$_2$Pd(bpy)I (**2a**, **2b**) via iodide dissociation, transition structure **TS_7a/7b**, and recoordination of iodide; and (b) in red and black, reaction of the mixture of reagents **2a** and **2b** with Me$_2$Pd(bpy) (**3**) via **7b** and transition structure **TS_7 b/8** to form PhMePd(bpy) (**1**) and Me$_3$Pd(bpy)I (**4**). Energies ΔG (ΔH) in kcal/mol relative to **2a**.