

# Theoretical studies of the oxidative addition of PhBr to Pd(PX<sub>3</sub>)<sub>2</sub> and Pd(X<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PX<sub>2</sub>) (X = Me, H, Cl)

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## Abstract

The density functional theory calculations were used to study the influence of the substituent at P on the oxidative addition of PhBr to Pd(PX<sub>3</sub>)<sub>2</sub> and Pd(X<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PX<sub>2</sub>) where X = Me, H, Cl. It was shown that the C<sub>ipso</sub>–Br activation energy by Pd(PX<sub>3</sub>)<sub>2</sub> correlates well with the rigidity of the X<sub>3</sub>P–Pd–PX<sub>3</sub> angle and increases via the trend X = Cl < H < Me. The more rigid the X<sub>3</sub>P–Pd–PX<sub>3</sub> angle is, the higher the oxidative addition barrier is. The exothermicity of this reaction also increases via the same sequence X = Cl < H < Me. The trend in the exothermicity is a result of the Pd(II)–PX<sub>3</sub> bond strength increasing faster than the Pd(0)–PX<sub>3</sub> bond strength upon going from X = Cl to Me. Contrary to the trend in the barrier to the oxidative addition of PhBr to Pd(PX<sub>3</sub>)<sub>2</sub>, the C<sub>ipso</sub>–Br activation energy by Pd(X<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PX<sub>2</sub>) decreases in the following order X = Cl > H > Me. This trend correlates well with the filled d<sub>π</sub> orbital energy of the metal center. For a given X, the oxidative addition reaction energy was found to be more exothermic for the case of X<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PX<sub>2</sub> than for the case of PX<sub>3</sub>. This effect is especially more important for the strong electron donating phosphine ligands (X = Me) than for the weak electron donating phosphine ligands (X = Cl).

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**Keywords:** Density functional theory calculations; Oxidative addition; Palladium

## 1. Introduction

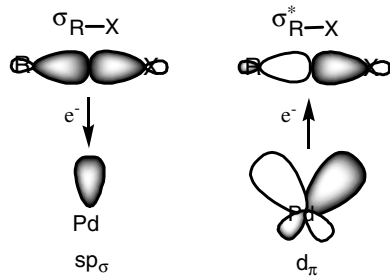
It has been established that oxidative addition of organic halides (RX) to Pd(0)L<sub>n</sub> (n = 1, 2) species is the first step in the many Pd-catalyzed cross-coupling reactions, where L is typically a phosphine ligand and X is a halide [1–3]. The generally accepted mechanism involves the concerted addition of RX to Pd(0)L<sub>n</sub> via a three center transition state leading to the fission of R–X bond and the generation of Pd–R and Pd–X bonds [4]. As shown in Scheme 1, in the transition state, the filled σ<sub>R–X</sub> orbital of RX interacts with the vacant sp<sub>σ</sub>-hybridized orbital of metal. There is also a second interaction between the filled

d<sub>π</sub> orbital of metal and the vacant σ<sub>R–X</sub><sup>\*</sup> orbital of RX leading to the breaking of the R–X bond. Thus, one can expect that a strong σ-donor phosphine ligand, which can increase the electron density of metal, would facilitate oxidative addition reaction through the stronger charge transfer from the d<sub>π</sub> orbital of metal to the σ<sub>R–X</sub><sup>\*</sup> orbital of RX.

Recently, many experimental [5] and theoretical [6–8] works have been employed to investigate the activation of the C–X bonds by coordinatively unsaturated active species Pd(0)L<sub>n</sub>. However, a proper understanding of how the electronic feature of ancillary ligand L influences the reactivity of RX is still lacking. To provide a deeper insight into how the L ligand affects the oxidative addition reaction of organic halides, we investigate the model oxidative addition reaction between PhBr and Pd(PX<sub>3</sub>)<sub>2</sub> (X = Me, H, Cl) with the aid of B3LYP density functional theory

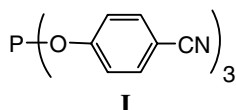
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Scheme 1.

(DFT) calculations. The representative set of  $PX_3$  includes the ligand with gradually changing donor and acceptor characters. The  $\sigma$ -donor character of  $PX_3$  varies as follows:  $PMe_3 > PH_3 > PCl_3$  while the  $\pi$ -acceptor character of  $PX_3$  increases in the order  $PMe_3 < PH_3 < PCl_3$  [9]. According to Tolman's map [10],  $PCl_3$  was chosen to electronically model weak bases such as  $P(OC_6H_4CN)_3$  (**I**). We also theoretically investigated the effect of different chelating phosphine ligands on oxidative addition of PhBr to  $Pd(X_2PCH_2CH_2PX_2)$  ( $X = Me, H, Cl$ ).



## 2. Computational detail

GAUSSIAN 98 [11] was used to fully optimize all the structures reported in this paper at the B3LYP [12] level of density functional theory. The effective core potentials of Hay and Wadt with double- $\zeta$  valance basis sets (LanL2DZ) [13] were chosen to describe Pd, P, Br and Cl. The 6-31G basis set was used for other atoms [14]. Polarization functions were also added for C ( $\zeta_d = 0.6$ ), Cl ( $\zeta_d = 0.514$ ), Br ( $\zeta_d = 0.389$ ) and P ( $\zeta_d = 0.340$ ) [15]. Frequency calculations at the same level of theory have also been performed to identify all of the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency), and to compute free energies in the gas phase at 298.15 K and 1 atm, which include entropic contributions by taking into account the vibrational, rotational, and translational motions of the species under consideration. Chemically more interesting  $\Delta G$  values were used in the discussion, and corresponding  $\Delta E$  values were given in parentheses. Partial atomic charges were calculated on the basis of the natural bond orbital (NBO) analyses [16].

To test the accuracy of the medium-size basis set (BS1) used, we carried out single point energy calculations for several selected structures by using a larger basis set: SDDALL for Pd and 6-311G\*\* for all other atoms. We also added an f polarization function of 1.472 [17] to SDDALL [18] for Pd. This basis set will be referred to as BS2. These additional calculations show that the basis set dependence is small. For example, using the smaller basis set (BS1), the

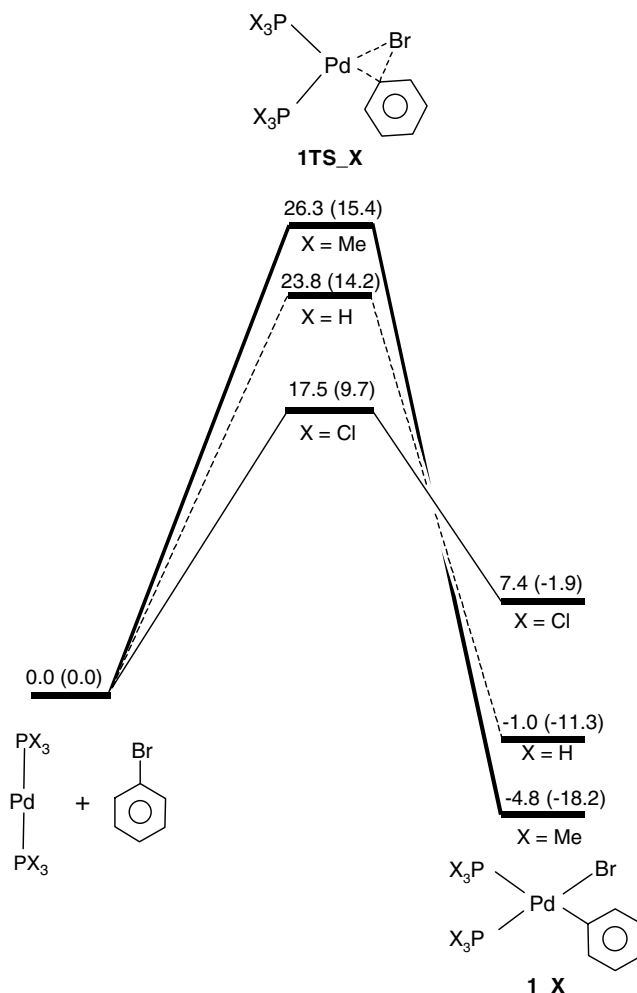


Fig. 1. Potential energy profiles calculated for the oxidative addition of PhBr to  $Pd(PX_3)_2$  ( $X = Me, H, Cl$ ). Gibbs free energies at 1 atm, 298.15 K and electronic energies (in parentheses) relative to the  $Pd(PX_3)_2$  and PhBr fragments are given in kcal/mol.

relative energies of **1TS\_Me**, **1TS\_H**, and **1TS\_Cl** (Fig. 1) are 15.4, 14.2, and 9.7 kcal/mol, respectively. Using the larger basis set (BS2), the relative energies are 17.0, 15.1, and 9.8 kcal/mol, respectively. Using the smaller basis set (BS1), the relative energies of **2TS\_Me**, **2TS\_H**, and **2TS\_Cl** (Fig. 5) are  $-0.3$ ,  $1.2$ , and  $6.2$  kcal/mol, respectively. Using the larger basis set (BS2), the relative energies are  $-1.1$ ,  $0.8$ , and  $4.1$  kcal/mol, respectively.

Charge decomposition analyses (CDA) were calculated on optimized geometries at the same level of theory for structural optimization [19]. In the CDA [20] scheme, the orbital contributions to the charge distributions of the complex and the two fragments that define the bond of interest are divided into four parts: (i) the donation from occupied donor fragment orbitals to vacant orbitals on the acceptor fragment (d) (ii) the back-donation from occupied orbitals on the acceptor fragment to vacant orbitals on the donor fragment (b), (iii) the repulsive polarization of occupied orbitals on both the fragments (r) and (iv) the residual term (s) which should be approximately zero for true donor–acceptor complexes.

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