

Mor-Dalpos-Pd (II) oxidative addition complexes and related NH₃ adducts: Insights into bonding and nonbonding interactions



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ABSTRACT

The stabilizing effects and bonding properties of the Pd metallic center in $[(\kappa^2\text{-P,N-Mor-Dalpos})\text{Pd}(\text{Ar})\text{Cl}]$ complexes and related NH₃ adducts were investigated by density functional theory (DFT), the intrinsic bond orbital (IBO) approach and the Su–Li energy decomposition method (Su–Li EDA). The IBO analysis showed that the P atom from the P,N-Mor-Dalpos structure has stabilizing contributions in all Pd–Cl and Pd–NH₃ bonds in the complexes. According to the Su–Li energy decomposition analysis, the main energy that drives the interaction between the [Mor-Dalpos-Pd(Ar)] moiety and Cl[−] is the electrostatic term, therefore, the electrostatic energy interaction between them might be an important factor for taking into account when designing other [Mor-Dalpos-Pd(Ar)]-Cl precatalysts.

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1. Introduction

Palladium-catalyzed C–N and C–C bond-forming reactions have a crucial role in chemical synthesis [1,2]. In this context, the Buchwald–Hartwig Amination (BHA) is an important method for coupling amines with aryl halides [3]. Besides the great effort of many groups [4–7], the direct synthesis of nitrogen-containing molecules using ammonia as N source remains a notable challenge in BHA protocols. This difficulty is mainly attributed to the strong N–H bonds, moderate basicity and, low acidity that make NH₃ a delicate substrate [8].

Recently, a new class of P,N-based ligand, named Mor-Dalpos, was used in palladium catalyzed protocols and it efficiently coupled ammonia with a variety of aryl halides at mild temperatures [7,9,10]. In order to provide a further understanding over the formation of the active catalyst and others intermediates present in the reaction mechanism, the Pd-Mor-Dalpos performance in ammonia arylation has been studied [10,11]. An experimental study of Alsabeh and co-authors described a set of Mor-Dalpos-Pd (II) oxidative addition complexes, referred as $[(\kappa^2\text{-P,N-Mor-Dalpos})\text{Pd}(\text{Ar})\text{Cl}]$, as good precatalyst for the challenging NH₃ monoarylation reactions. Among them, an optimal precatalyst was

identified and its coupling with NH₃, under halide abstraction conditions, yielded an ammine adduct [10], i.e., in these tests, ammonia coordinates to the metallic center after chlorine was released.

Although optimized reactions conditions are important parameters in chemical synthesis, the understanding of chemical and physical properties, at molecular level, of the systems is a first step towards the rationalization of feasible mechanistic cycles. For instance, an interesting point in these systems regards the main processes that governs the chemical behavior of the NH₃-Pd bonding. Differently from the Pd-Mor-Dalpos catalyst, the vast majority of well established Pd catalytic systems did not show the same activity in ammonia monoarylations [12]. Consequently, the determination of what aspect(s) of the ligand effectively affect the metallic center, thus changing its bonding with NH₃ become an important task. However, to the best of our knowledge, there are no studies focusing on the chemical and physical origin of the Pd bonding within $[(\kappa^2\text{-P,N-Mor-Dalpos})\text{Pd}(\text{Ar})\text{Cl}]$ complexes and related NH₃ adducts. In addition, it is well known that metal-ligand and metal-substrate interactions are key pieces to better understand reaction mechanisms [13–17].

In this context, the present work investigates stabilizing effects and bonding properties involving the palladium metallic center in Mor-Dalpos complexes. Toward this end, selected Mor-Dalpos-Pd (II) oxidative addition (OAC) complexes and related ammine derivatives (ADD) are studied by using Kohn–Sham density

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functional theory (DFT), the intrinsic bond orbital (IBO) approach [18] and the Su–Li [19] energy decomposition analysis (Su–Li EDA).

2. Computational details

Geometry optimizations of selected structures were carried out using the PBE [20] density functional. Dispersion contributions were included via the D3 Grimme empirical correction [21] together with Becke–Johnson (BJ) damping function [22–25]. The resolution of identity (RI) approximation [26] was adopted during all calculations. The def2-TZVP basis set [27,28] and corresponding auxiliary basis set, which is used along with the RI approximation, were applied for all atoms. For the palladium atom, the effective core potential SD(28,MWB) [29] with the corresponding orbital and auxiliary basis sets was used throughout this work. To better simulate the reaction conditions, the conductor-like screening model (COSMO) [30] was used to incorporate solvation effects of CH_2Cl_2 ($\epsilon = 9.08$), an usual solvent for this class of reaction. In this work, this approach is referred as DF-RKS/PBED3(BJ)(COSMO, CH_2Cl_2)/def2-TZVP. This level of theory was chosen because it produced structural parameters in good agreement with the available experimental ones. All calculations were performed using the ORCA [31] package program. The optimized structures were confirmed as true minima by the vibrational analysis.

The intrinsic bond orbitals (IBOs) were obtained with the IboView program [18], using the DFT approach described above. The IBOs are a non-empirical form of localized molecular orbitals that provide quantitative interpretation of bonding by assigning the electrons in a doubly occupied IBO to individual atoms [32].

The physical nature of the [Mor-Dalphos-Pd(Ar)]- NH_3 and [Mor-Dalphos-Pd(Ar)]-Cl chemical interactions was further explored by the Su–Li EDA analysis. This approach allows the partition of the electronic energy in physically meaningful terms, for bonding and nonbonding interactions. The Su–Li EDA was performed with GAMESS [33] at the MP2/def2-SVP level of theory [27,28,34,35]. In the MP2 version of the Su–Li EDA scheme, the total interaction energy, $\Delta E_{\text{MP2}}^{\text{int}}$, is decomposed into five terms: electrostatic (ΔE_{ele}), exchange (ΔE_{ex}), repulsion (ΔE_{rep}), polarization (ΔE_{pol}), and dispersion (ΔE_{disp}), as described in Equation (1):

$$\Delta E_{\text{MP2}}^{\text{int}} = \Delta E_{\text{ele}} + \Delta E_{\text{ex}} + \Delta E_{\text{rep}} + \Delta E_{\text{pol}} + \Delta E_{\text{disp}} \quad (1)$$

The Boys and Bernardi counterpoise (CP) method [36] is an option for the calculations and it is adopted to account for the basis set superposition error (BSSE). MacMolPlt [37] and IboView were used to visualize structures and IBOs, respectively.

3. Results and discussion

In order to analyze bonding and nonbonding interactions on **OAC** systems and their cationic ammine derivatives, the discussion is organized as follows. First, the IBO analysis results are presented for **OAC** and **ADD** complexes. In the next section, the Su–Li EDA approach is applied to these complexes in order to understand the chemical and physical effects that govern the NH_3 binding and those present in the [Mor-Dalphos-Pd(Ar)]-Cl interaction.

3.1. The IBO analysis

Of the various Mor-Dalphos-Pd (II) oxidative addition complexes identified and characterized in the original papers [10,7], four of them were chosen to be explored in the current paper. The DF-RKS/PBED3(BJ)(COSMO, CH_2Cl_2)/def2-TZVP optimized structures of these systems, designated as **OAC1** (a), **OAC2** (b), **OAC3** (c), **OAC4** (d) are presented in Fig. 1.

Among the **OAC** complexes, Alsabeh and co-authors identified the **OAC1** (see Fig. 1a) system as the optimal precatalyst for coupling NH_3 with chlorobenzene at room temperature [10]. Under halide abstraction conditions, this complex yields a cationic ammine adduct as the one shown in Fig. 2a, here referred as **ADD1**. Based on that, NH_3 derivatives of **OAC2**, **OAC3**, **OAC4**, named as **ADD2** (b), **ADD3** (c) and **ADD4** (d), respectively, were studied. The DF-RKS/PBED3(BJ)(COSMO, CH_2Cl_2)/def2-TZVP optimized geometries of these ammine adducts are seen in Fig. 2.

The geometric parameters of the palladium complexes, obtained at the DF-RKS/PBED3(BJ)(COSMO, CH_2Cl_2)/def2-TZVP, are in good agreement with the available experimental data. Starting with the Pd–Cl bond distance, the corresponding DFT (X-Ray) values are

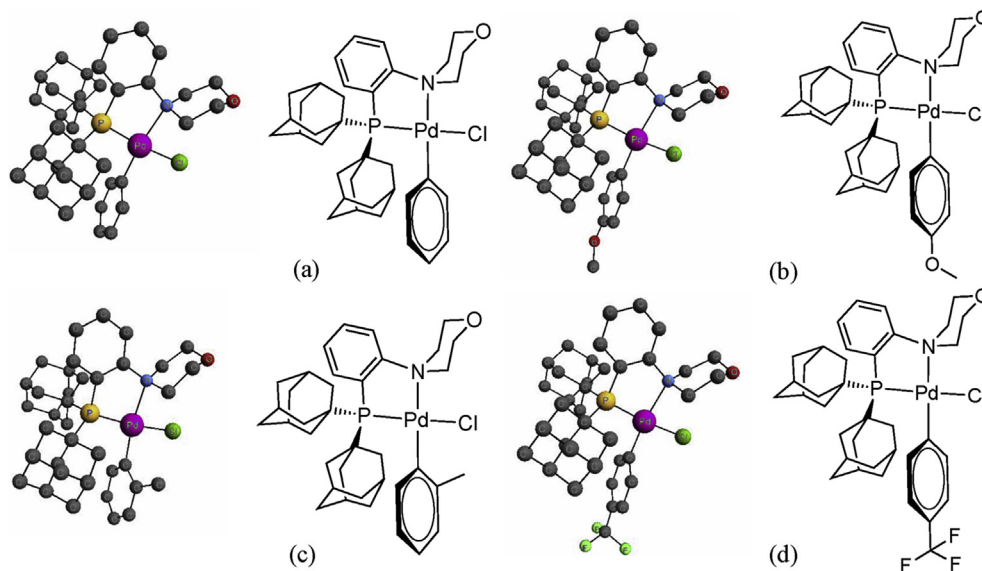


Fig. 1. DF-RKS/PBED3(BJ)(COSMO, CH_2Cl_2)/def2-TZVP optimized Mor-Dalphos-Pd (II) oxidative addition complexes: **OAC1** (a), **OAC2** (b), **OAC3** (c) and **OAC4** (d). For clarity, hydrogen atoms were omitted.

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