Mor-Dalphos-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 $[(\kappa^2\text{-P,N-Mor-Dalphos})\text{Pd}(\text{Ar})\text{Cl}]$ 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-Dalphos 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-Dalphos-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-Dalphos-Pd(Ar)]-Cl precatalysts.

Keywords: palladium catalysis, monoarylation, chemical and physical interactions, quantum chemistry calculations.

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Graphical abstract

Bonding and Nonbonding Interactions in Mor-Dalphos-Pd(II) Complexes

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, 5, 6, 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 NH_3 a delicate substrate [8].

Recently, a new class of P,N-based ligand, named Mor-Dalphos, 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-Dalphos performance in ammonia arylation has been studied [11, 10]. An experimental study of Alsabeh and co-authors described a set of Mor-Dalphos-Pd (II) oxidative addition complexes, referred as $[(\kappa^2\text{-P,N-Mor-Dalphos})\text{Pd}(\text{Ar})\text{Cl}]$, as good precatalyst for the challenging NH_3 monoarylation reactions. Among them, an optimal precatalyst was identified and its coupling with NH_3 , 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 NH_3 -Pd bonding. Differently from the Pd-Mor-Dalphos 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 NH_3 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 NH_3 adducts. In addition, it is well known that metal-ligand and metal-substrate interactions are
40 key pieces to better understand reaction mechanisms [13, 14, 15, 16, 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
45 density 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
50 Grimme empirical correction [21] together with Becke-Johnson (BJ) damping function [22, 23, 24, 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 poten-
55 tial 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-
60 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 pro-
65 gram [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)]-NH₃ 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 [34, 35, 27, 28]. In the MP2 version of the Su-Li EDA scheme, the total interaction energy, ΔE_{MP2}^{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):

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

The Boys and Bernardi counterpoise (CP) method [36] is an option for the
70 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
75 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 NH₃ binding and those present in the [Mor-Dalphos-Pd(Ar)]-Cl interaction.

80 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,CH₂Cl₂)/def2-TZVP optimized structures of these systems, designated as **OAC1** (a), **OAC2**
 85 (b), **OAC3** (c), **OAC4** (d) are presented in Figure 1.

Figure 1: DF-RKS/PBED3(BJ)(COSMO,CH₂Cl₂)/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.

Among the **OAC** complexes, Alsabeh and co-authors identified the **OAC1** (see Figure 1a) system as the optimal precatalyst for coupling NH₃ with chlorobenzene at room temperature [10]. Under halide abstraction conditions, this complex yields a cationic ammine adduct as the one shown in Figure 2a, here referred
 90 as **ADD1**. Based on that, NH₃ derivatives of **OAC2**, **OAC3**, **OAC4**, named as **ADD2** (b), **ADD3** (c) and **ADD4** (d), respectively, were studied. The DF-RKS/PBED3(BJ)(COSMO,CH₂Cl₂)/def2-TZVP optimized geometries of these ammine adducts are seen in Figure 2.

The geometric parameters of the palladium complexes, obtained at the DF-
 95 RKS/PBED3(BJ)(COSMO,CH₂Cl₂)/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 2.390 (2.387), 2.389 (2.382) and 2.405 (2.376) Å for the complexes **OAC1**, **OAC2**, and **OAC4**, respectively. For the

Figure 2: DF-RKS/PBED3(BJ)(COSMO,CH₂Cl₂)/def2-TZVP optimized ammine derivatives: **ADD1** (a), **ADD2** (b), **ADD3** (c) and **ADD4** (d). For clarity, only selected hydrogen atoms are seen.

OAC3 complex, the crystallographic molecular parameters were not described.

100 The Pd-C_{aryl} bond distance, on the other hand, are only slightly greater than the experimental values, respectively, 2.021 (2.001), 2.023 (2.000) and 2.002 (1.990) Å for the complexes, **OAC1**, **OAC2** and **OAC4**. There is also a good agreement between experimental and theoretical values for the two ligand-Pd bond distances, Pd-P and Pd-N. The experimental values for the Pd-P bond distance are practically the same among these complexes, 2.256 (**OAC1**), 2.257 (**OAC2**) and 2.259 Å (**OAC4**); our DFT results are, 2.265, 2.263 and 2.260 Å, respectively, for the complexes **OAC1**, **OAC2** and **OAC4**. The experimental values for the Pd-N bond, on the other hand, range from 2.214 to 2.253 Å. For the **OAC1** and **OAC2** complexes, our calculated bond distances are 2.352 and 2.353 Å, respectively, while for the **OAC4** system, the Pd-N bond is predicted to be 2.322 Å. For the sake of completeness, the optimized Cartesian coordinates are provided inside the Supplementary material. The available experimental data is seen in ref [10].

Using the described DFT approach, our attention is given to the analysis of

the ligand-Pd and substrate-Pd bonding by a novel approach, the IBO method. The investigation that follows should provide a better understanding of the nature of the Pd-Cl and Pd-NH₃ bonding and the main interactions that drive it. As mentioned, we can use this approach to assign the electrons in a doubly occupied IBO to individual atoms and, therefore, it allow us to investigate the contributions of each atom atoms to a bonding. The IBO study is in agreement with the structural characterization (see optimized structures in Figures 1 and 2), four intrinsic bond orbitals were found for each one of all the square planar Pd^{II} complexes and their ammine derivatives. These IBOs represent the Pd bonding interactions and they are depicted in Figure 3 and 4, respectively, for the **OAC** complexes and the ammine adducts.

Figure 3: The four IBOs (a, b, c and d) present in the Pd coordination sphere of each **OAC** complex. The numbers in parenthesis are the fraction of electrons assigned to individual atoms of each IBO. Note that the fraction of electrons indicated in the figure adds up to two. For clarity, only selected atoms are displayed.

The first IBO to be analyzed is the phosphorous σ lone pair coordinated to the metal, which appears in all complexes as it is seen in Figure 3a and 4a. This IBO has contributions from the Pd, P and C_{aryl}; this holds true for all **OAC**

Figure 4: The four IBOs (a, b, c and d) present in the Pd coordination sphere of each **ADD** complex. The numbers in parenthesis are the fraction of electrons assigned to individual atoms of each IBO. Note that the fraction of electrons indicated in the figure adds up to two. For clarity, only selected atoms are displayed.

and **ADD** complexes. The contributions from the Pd atom to this bond are greater in the ammine adducts. A similar bonding between the N_{dalphos} and Pd is also identified, they are shown in Figure 3b and 4b. However, one sees that in **OAC1**, **OAC2** and **OAC3** complexes there are contributions from C_{aryl}, C₁, Pd and N_{dalphos}. For the remaining complexes, **OAC4** and the **ADD** systems, the C₁ atoms is not contributing to this interaction.

The other two IBOs represent a picture of the palladium bonding with the substrates, NH₃ and Cl⁻. For the **OAC** complexes, the Pd-aryl and Pd-Cl bonds are associated to the IBOs in Figure 3c and Figure 3d, respectively. The Pd-aryl and Pd-NH₃ interactions in the **ADD** adducts are related to the IBOs in Figures 4c and 4d, respectively. Focusing on the Pd-aryl bond, which is related to the IBOs in Figure 3c and 4c, in the **OAC** systems, the C_{aryl} atoms hold the major fraction of the electrons, about 1.1 electrons, while the Pd metallic center has about 0.9 of the electrons in this bonding. For the Pd-aryl bond in

the **ADD** systems, a similar trend is observed.

Next, the Pd-Cl and Pd-NH₃ bonds are the focus. In the **OAC** complexes, there are contributions from the Pd, Cl, P and C_{aryl} atoms for the Pd-Cl bonding; the chlorine atom has the largest fraction of the electron in the Pd-Cl bond in all complexes (see Figure 3d), followed by the Pd atom. Small contributions come from the P and C_{aryl} atoms. In the **ADD** complexes, contributions for the Pd-NH₃ bonding comes from the Pd, N_{NH3}, P and C_{aryl} atoms for all systems, with the exception of the **ADD2**, which doesn't show contribution from the C_{aryl} atom. Although with small contributions, one notes that the P atom in the Mor-Dalphos ligand structure plays an important role in the stabilization of the Pd-Cl and Pd-NH₃ interactions. This could be an additional way of evidencing the ligand *trans* effects [38] present in many metal complexes. The N atom from the ligand, however, does not show any contribution to these two kind of bonds.

3.2. The Su-Li EDA analysis

Next, the Su-Li EDA method is applied for interaction analysis between the [Mor-Dalphos-Pd(Ar)] moiety and its interacting species, Cl⁻/NH₃. The main point here is to quantify the energetic terms that contributes to the [Mor-Dalphos-Pd(Ar)] and Cl⁻ bonding on the **OAC** complexes and those that drives the [Mor-Dalphos-Pd(Ar)]-NH₃ interaction in the ammine derivatives. The Su-Li EDA results are shown in Table 1. It is worth to mention that the total interaction energy, ΔE_{MP2}^{int} , is defined as the instantaneous interaction energy between two or more monomers. Consequently, ΔE_{MP2}^{int} differs from the dissociation energy, D_e , because ΔE_{MP2}^{int} uses the fragments at their bonded geometries as reference for the dissociated supermolecule, *i.e.*, geometry relaxation is ignored [19].

In Table 1, one sees that the total interaction energy between the [Mor-Dalphos-Pd(Ar)] and Cl⁻ is higher than the total interaction between the [Mor-Dalphos-Pd(Ar)] and NH₃. Complexes featuring the 4-trifluoromethylphenyl group, **OAC4** and **ADD4**, have the largest ΔE_{MP2}^{int} values, respectively, -120.5

Table 1: Bond interaction analysis (kcal mol^{-1}) results for Mor-Dalphos-Pd (II) complexes computed at the MP2/def2-TZVP level of theory. The components are: total interaction energy (ΔE_{MP2}^{int}), electrostatic energy (ΔE_{ele}), exchange energy (ΔE_{ex}), repulsion energy (ΔE_{rep}), polarization energy (ΔE_{pol}), and dispersion energy (ΔE_{disp}).

[Mor-Dalphos-Pd(Ar)]-Cl	ΔE_{ele}	ΔE_{ex}	ΔE_{rep}	ΔE_{pol}	ΔE_{disp}	ΔE_{MP2}^{int}
OAC1	-136.6	-120.1	209.1	-57.7	-11.4	-116.8
OAC2	-135.7	-120.8	210.2	-58.1	-11.0	-115.4
OAC3	-137.4	-120.0	208.7	-58.2	-12.0	-118.9
OAC4	-141.2	-120.5	209.5	-57.9	-10.4	-120.5
[Mor-Dalphos-Pd(Ar)]-NH ₃						
ADD1	-60.0	-81.3	147.7	-28.4	-6.2	-28.2
ADD2	-59.1	-75.6	137.7	-29.1	-13.4	-39.4
ADD3	-59.2	-75.2	137.0	-29.4	-14.2	-40.9
ADD4	-59.3	-69.4	126.6	-28.6	-12.9	-41.7

and $-41.7 \text{ kcal mol}^{-1}$, among their related halide and ammine complexes.

Interestingly, according to the experiments that evaluated the performance of Mor-Dalphos-Pd (II) oxidative addition complexes in the monoarylation of ammonia, the **OAC4** system, which features an electron-withdrawing aryl group (4-trifluoromethylphenyl) coordinated to the Pd atom, is an inferior precatalyst [10] when compared to **OAC1**. Looking to the electrostatic energy ΔE_{ele} term, which is the term with the largest disparity among the **OAC** complexes, one sees that **OAC4** has the largest value. Since the monoarylation process takes place after the Cl^- release, such result suggests that the electrostatic interaction between [Mor-Dalphos-Pd(Ar)]-Cl might be an important factor for taking into account when designing other [Mor-Dalphos-Pd(Ar)]-Cl precatalysts. In other words, it appears that reductions in its Coulombic attraction by the Cl^- species might facilitate the chlorine release and allow the NH_3 coordination during the mechanism. For all the neutral complexes, the electrostatic energy ΔE_{ele} is the term that dominates the interaction, while for the ammine adducts, the interaction is dominated by the exchange term, ΔE_{ex} . For the

OAC complexes, these observations reflect that the [Mor-Dalphos-Pd(Ar)]-Cl
 190 interaction is mainly stabilized by the Coulomb energy between Cl^- and the
 [Mor-Dalphos-Pd(Ar)] moiety. In the ammine complexes, the exchange energy
 between [Mor-Dalphos-Pd(Ar)] and NH_3 is the driving term.

The dispersion term, ΔE_{disp} , has the lowest contributions. However, they
 are not negligible and for the ammine adducts, the ΔE_{disp} term ranges from
 195 $-6.2 \text{ kcal mol}^{-1}$ for **ADD1** to $-14.2 \text{ kcal mol}^{-1}$ for **ADD3**. The polarization
 energy, ΔE_{pol} , in the formation of the Pd-Cl bond is about twice the ΔE_{pol}
 value observed for the Pd- NH_3 bond, which suggests that the orbitals undergo
 more pronounced changes in the former case. Taking back the IBO analysis to
 complement the EDA results, one notes that the difference in the fraction of
 200 the electrons between Cl^- and Pd in the Pd-Cl bonding are greater than those
 between the N_3 and Pd in the Pd- NH_3 bonding. As the **OAC** systems have
 higher values of ΔE_{pol} , *i.e.*, more orbital overlap on the Pd-Cl bond than on the
 Pd- NH_3 bond, the repulsion energy becomes greater in **OAC** systems, compare
 the ΔE_{rep} values between the **OAC** and **ADD** complexes in Table 1.

205 Conclusions

The stabilizing effects and bonding properties involving the palladium center
 in Mor-Dalphos complexes were investigated for the first time. The interaction
 between the [Mor-Dalphos-Pd(Ar)] moiety and the Cl^-/NH_3 species in different
 Mor-Dalphos-Pd (II) oxidative addition complexes (**OAC**) and related ammine
 210 derivatives (**ADD**) were explored by density functional theory, the intrinsic
 bond orbital (IBO) approach and the Su-Li EDA method.

In all complexes, four intrinsic bond orbitals were found around the Pd metal
 center, which is consistent with the structural characterization of these systems.
 In addition, the IBO analysis showed that for all Pd-Cl and Pd- NH_3 bonds, the
 215 P atom from the ligand structure has stabilizing contributions.

According to the Su-Li EDA analysis, the main energetic term that drives
 the interaction between [Mor-Dalphos-Pd(Ar)] and Cl^- in the **OAC** complexes

is the electrostatic energy between them, while for the **ADD** systems, the interaction between [Mor-Dalphos-Pd(Ar)] and NH₃ is modulated, mainly, for the exchange energy. These results suggest that the electrostatic interaction between [Mor-Dalphos-Pd(Ar)]-Cl could be an important factor for taking into account when designing other [Mor-Dalphos-Pd(Ar)]-Cl precatalysts. A following step involving these systems will explore the possible mechanistic pathway for the reaction.

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References

- [1] Negishi, E.-I. *Angew. Chem. Int. Ed.* **2011**, *50*, 6738–6764.
- [2] Johansson Seechurn, C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem. Int. Ed.* **2012**, *51*, 5062–5085.
- [3] Bariwal, J.; Van der Eycken, E. *Chem. Soc. Rev.* **2013**, *42*, 9283–9303.
- [4] Vo, G. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 11049–11061.
- [5] Cheung, C. W.; Surry, D. S.; Buchwald, S. L. *Org. Lett.* **2013**, *15*, 3734–3737.
- [6] Schulz, T.; Torborg, C.; Enthaler, S.; Schäffner, B.; Dumrath, A.; Spannenberg, A.; Neumann, H.; Börner, A.; Beller, M. *Chem. Eur. J.* **2009**, *15*, 4528–4533.
- [7] Lundgren, R. J.; Peters, B. D.; Alsabeh, P. G.; Stradiotto, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 4071–4074.

- [8] Klinkenberg, J. L.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2011**, *50*, 86–95.
- [9] Alsabeh, P. G.; McDonald, R.; Stradiotto, M. *Organometallics* **2012**, *31*,
245 1049–1054.
- [10] Alsabeh, P. G.; Lundgren, R. J.; McDonald, R.; Seechurn, C. C. C. J.;
Colacot, T. J.; Stradiotto, M. *Chem. Eur. J.* **2013**, *19*, 2131–2141.
- [11] Lundgren, R. J.; Stradiotto, M. *Chem. Eur. J.* **2012**, *18*, 9758–9769.
- [12] Alsabeh, P. G.; Stradiotto, M.; Neumann, H.; Beller, M. *Adv. Synth. Catal.*
250 **2012**, *354*, 3065–3070.
- [13] Moncho, S.; Ujaque, G.; Espinet, P.; Maseras, F.; Lledós, A. *Theor. Chem.*
Acc. **2009**, *123*, 75–84.
- [14] Beletskaya, I. P.; Cheprakov, A. V. *Organometallics* **2012**, *31*, 7753–7808.
- [15] Xia, Y.; Miao, Z.; Wang, F.; Yao, H.; Cui, M.; Ma, Y.; Qi, Z.; Sun, Y. *J.*
255 *Organomet. Chem.* **2015**, *779*, 81 – 85.
- [16] Khusnutdinova, J. R.; Milstein, D. *Angew. Chem. Int. Ed.* **2015**, *54*, 12236–
12273.
- [17] Guest, D.; da Silva, V. H. M.; de Lima Batista, A. P.; Roe, S. M.; Braga, A.
A. C.; Navarro, O. *Organometallics* **2015**, *34*, 2463–2470.
- 260 [18] Knizia, G. *J. Chem. Theory Comput.* **2013**, *9*, 4834–4843.
- [19] Su, P.; Li, H. *J. Chem. Phys.* **2009**, *131*, 014102.
- [20] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–
3868.
- [21] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*,
265 154104.
- [22] Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456–
1465.

- [23] Johnson, E. R.; Becke, A. D. *J. Chem. Phys.* **2006**, *124*.
- [24] Johnson, E. R.; Becke, A. D. *J. Chem. Phys.* **2005**, *123*.
- 270 [25] Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2005**, *123*.
- [26] Neese, F. *J. Comput. Chem.* **2003**, *24*, 1740–1747.
- [27] Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.
- [28] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- [29] Andrae, D.; Hfermann, U.; Dolg, M.; Stoll, H.; Preu, H. *Theor. Chim.*
275 *Acta* **1990**, *77*, 123–141.
- [30] Klamt, A.; Schuurmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799–805.
- [31] Neese, F. *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78.
- [32] Comprido, L. N. S.; Klein, J. E. M. N.; Knizia, G.; Kastner, J.; Hashmi, A. S. K. *Angew. Chem. Int. Ed.* **2015**, *54*, 10336–10340.
- 280 [33] Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem* **1993**, *14*, 1347–1363.
- [34] Mller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- 285 [35] Fletcher, G. D.; Rendell, A. P.; Sherwood, P. *Mol. Phys.* **1997**, *91*, 431–438.
- [36] Boys, S.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553–566.
- [37] Bode, B.; Gordon, M. S. *J. Mol. Graphics Mod.* **1998**, *16*, 133–138.
- [38] Carina Bcktorp and Per-Ola Norrby, *J. Mol. Catal. A: Chem.* **2010**, *328*, 108 – 113.