

Insights into Ammonia Binding to Mor-Dalphos-Pd Oxidative Addition Complex: A Theoretical Study.

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Introduction

The use of Dalphos ligands, a P,N-based ligand class, in Pd-catalyzed Buchwald–Hartwig amination has improved the reaction conditions.¹ Recently, the Mor-Dalphos ligand was able to couple efficiently a variety of aryl halides to ammonia.² Although its performance in ammonia arylation has been studied in order to provide further understanding over the catalyst formation process,³ the structure and reactivity of derived intermediates along the catalytic cycle remain unclear. In this context, computational chemistry is able to give more details, at molecular level, including energetics and geometric parameters. Herein, preliminary theoretical results on ammonia binding to Mor-Dalphos-Pd oxidative addition complex (**morOAC**) are reported. This kind of study can help to rationalize what aspects of ligand structure favor the NH₃ coordination, and which ones take the Pd-amido complex to the reductive elimination, next step in the catalytic cycle.

Results and Discussion

All calculations were done using ORCA. Geometry optimizations were carried at PBE-D3(BJ)/def2-TZVP level of theory in combination with the resolution of identity (RI) approximation. For Pd atom, an effective core potential (ECP) named SD(28,MWB) was applied. Single-point energy (SPE) calculations were performed out using DLPNO-CCSD(T)/def2-TZVP approach. **Figure 1** shows the square-planar Pd(II) **morOAC** structure. There exists good overlap between experimental and theoretical structures. Next, binding modes of NH₃ to **morOAC** were explored. The relative energies were improved by SPE calculations taken at optimized PBE-D3(BJ) geometries. The mostly likely structure is **(A)**, **Figure 2**. It was observed that NH₃ properly binds to the metal only if a rotation of the square plane around the Pd is performed. Such reorientation allows a vacant site to NH₃ coordinates. Optimizations of two other modes, **(B)** and **(C)**, led to a dissociation of either the Cl or the NH₃ from metal center, because Pd(II) already has four ligands.

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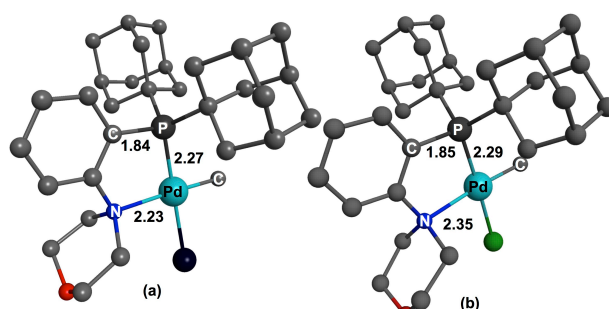


Figure 1. morOACs: (a) X-ray structure and (b) optimized structure. Only selected atoms are displayed. Key parameters are in ångström.

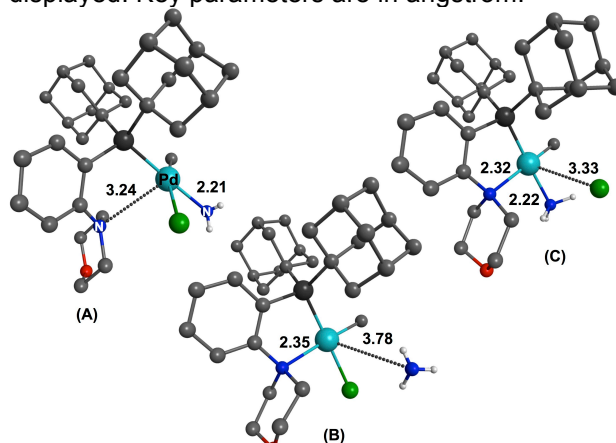


Figure 2. Some binding modes of NH₃ to morOAC. Only selected atoms are displayed. Key parameters are in ångström.

Conclusion

PBE-D3(BJ) method combined with DLPNO-CCSD(T) calculations showed that NH₃ is able to bind to Pd center only when a reorientation in the **morOAC** structure occurs.

Acknowledges

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