



Kinetics and Mechanism of Pd(II) X→OH Anion Metathesis in the Suzuki-Miyaura Reaction

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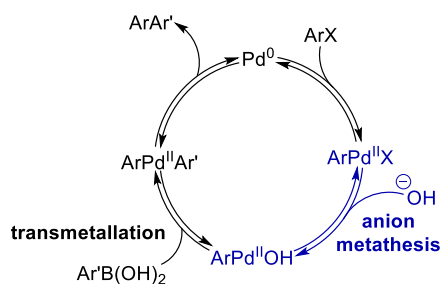
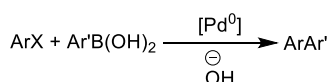
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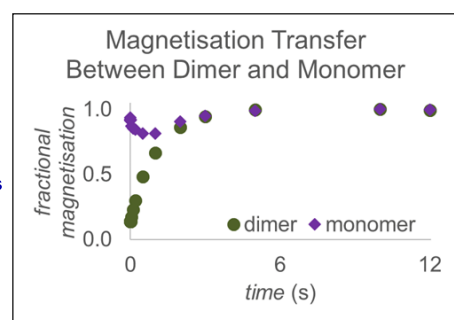
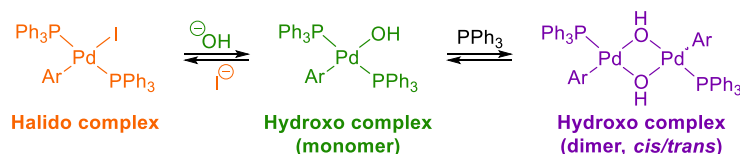
The Suzuki-Miyaura reaction is a transformation wherein organohalides react with boronic acids in the presence of a palladium(0) catalyst to form biaryls.¹ Being one of the most widely used processes in academia and industry, it has attracted a significant amount of research on the optimisation of the conditions, scope and mechanism. Within the catalytic cycle (Scheme 1a), the efficiency of transmetalation is key for the success of the overall process. In this context, previous works evidence the Suzuki-Miyaura reaction to occur *via* oxo-palladium(II) intermediates.²⁻⁴ However, the formation of these intermediates from the corresponding halidopalladium(II) complexes *via* X→OH anion metathesis is not yet well understood. In this regard, my research aims to study the mechanism of this critical event through comprehensive kinetic and thermodynamic analysis of the relevant intermediates, using NMR spectroscopy.

In my talk, I will introduce the NMR techniques used to study these equilibria and the results obtained thus far providing insight into the stability of the complexes and the influence of various parameters such as activity of water, temperature and added ligand on the reaction kinetics under Suzuki-Miyaura reaction conditions.

A) The Suzuki-Miyaura reaction



B) Our work: NMR mechanistic study on anion metathesis



- Stability of intermediates
- Effect of water and ligand
- Equilibrium constants
- Rate constants

Figure 1. a) The general scheme and mechanism of the Suzuki-Miyaura reaction. **b)** Our work: the mechanistic study on multiple equilibria between relevant palladium(II) complexes.

References:

- [1] N. Miyaura, K. Yamada, H. Sugimoto and A. Suzuki, *J. Am. Chem. Soc.*, 1985, **107**, 972–980.
- [2] B. P. Carrow and J. F. Hartwig, *J. Am. Chem. Soc.*, 2011, **133**, 2116–2119.
- [3] C. Amatore, G. Le Duc and A. Jutand, *Chem. Eur. J.*, 2013, **19**, 10082–10093.
- [4] A. F. Schmidt, A. A. Kurokhtina and E. V. Larina, *Russ. J. Gen. Chem.*, 2011, **81**, 1573.