Introduction to DyadPalladate™ Precatalysts and Insights Into Their Activation Mechanism

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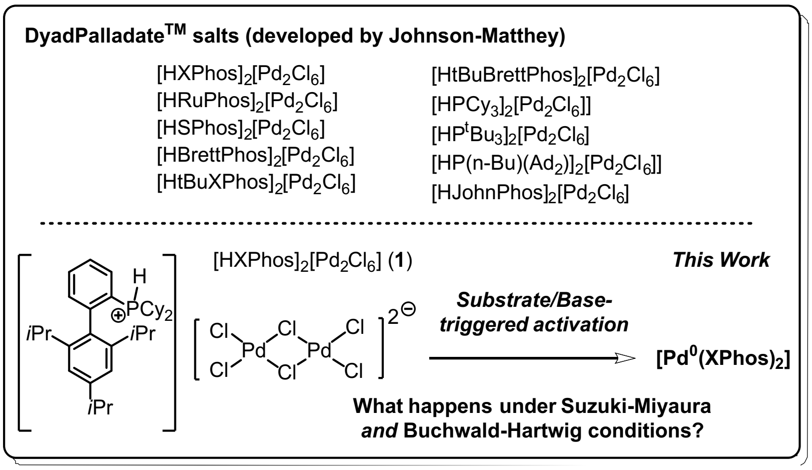
DyadPalladate™ precatalysts are a recently developed class of air- and moisture-stable bis phosphonium palladium complexes that show a unique close coordination of the acidified phosphine ligand and palladium. Unlike the analogous mixture of $PdCl_2$ with acidified ligand, these have been found to be effective catalysts for Suzuki–Miyaura (SMCC) reaction and Buchwald–Hartwig aminations (BHA) cross-coupling reactions with similar activity to industry leading Pd π-ally and Buchwald Palladacycle complexes. Through a more suscinct synthetic path, these precatalysts offer a more cost-effective and sustainable (calculated through PMI and E Factor) alternative to the advanced cross-coupling pre-catalysts while preserving their high catalytic performance.[1]

The unique form of these precatalysts brought into question the active complex generated and how the precatalyst arrives at this form in relation to the standard Pd(0)-Pd(II) catalytic cycle. We found it important to understand this pathway; thus, we examined the activation behaviour of $[HXPhos]_2[Pd_2Cl_6]$ as a model system for the many variants of this class of complexes in the two most widely employed cross-coupling reaction classes: SMCC and BHA reactions.

It was found that under BHA and SMCC reaction conditions, the valorized Pd^0 active catalyst was reached as $[Pd^0(XPhos)_2]$ under milder conditions compared to the presumed $Pd(XPhos)_2Cl_2$ intermediate.[2] The active catalytic species was generated efficiently through a reductive activation step involving a dual base/nucleophile chemical trigger. However, the mechanistic path of each was dictated by the selected nucleophile. The mechanism of activation was further investigated under catalytically relevant conditions, providing valuable insight into future catalyst design and targeting optimal efficiency in specific reactions.



[1] R. Kahan, M. Pitak, C. Seechurn, WO 2020/229848 A1, **2020**.

[2] N. W. Scott, P. G. Chirila, C. S. Horbaczewskyj, E. D. Slack, A. C. Whitwood, I. J. Fairlamb, Organometallics, **2025**, *44*, 5, 654–664