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Oxidative addition to palladium(0) Diphosphine complexes: Observations of mechanistic complexity with iodobenzene as reactant

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Abstract

Using a combination of electrochemical and NMR techniques, the oxidative addition of PhX to three closely related bis-diphosphine P2Pd 0 complexes, where the steric bulk of just one substituent was varied, has been analysed quantitatively. For the complex derived from MetBu2P, a rapid reaction ensued with PhI following an associative mechanism, and data was also obtained by cyclic voltammetry for PhOTs, PhBr and PhCl, revealing distinct relative reactivities from the related (PCx 3)2Pd complex (Cx=cyclohexyl) previously studied. The corresponding EttBu2P complex reacted more slowly with PhI and was studied by NMR spectroscopy. The reaction course indicated a mixture of pathways, with contribution from a component that was [PhI] independent. For the CxtBu2P complex, reaction was again monitored by NMR spectroscopy, and was even slower. At high PhI concentrations reaction was predominantly linear in [PhI], but at lower concentrations the [PhI] independent pathway was again observed, and an accelerating influence of the reaction product was observed over the concentration range. The NMR spectra of the EttBu2P and CxtBu2P complexes conducted in C6D6 shows some line broadening that was augmented on addition of PhI. NMR experiments carried out in parallel show that there is rapid ligand exchange between free phosphine and the Pd2Pd complex and also a slow ligand crossover between different P2Pd complexes. DFT calculations were carried out to further test the feasibility of C6D6 involvement in the oxidative addition process, and located Van der Waals complexes for association of the P2Pd0 complexes with either PhI or benzene. PhI or solvent-assisted pathways for ligand loss are both lower in energy than direct ligand dissociation. Taken all together, these results provide a consistent explanation for the surprising complexity of an apparently simple reaction step. The clear dividing line between reactions that give a di- or monophosphine palladium complex after oxidative addition clarifies the participation of the ligand in coupling catalysis. Copyright © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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Keywords

electrochemistry, NMR spectroscopy, oxidative addition, palladium, reaction mechanisms