

Intermolecular Insertion of Unactivated Alkenes into Palladium-Nitrogen Bonds

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We report a series of THF-coordinated palladium-diarylamido complexes ligated by a cyclometallated benzyl phosphine ligand. These complexes react with unactivated alkenes to form enamine products by a concerted migratory insertion into the palladium-amide bond. The reactions occur by reversible generation of a four coordinate amido-alkene complex by displacement of bound THF or direct coordination to a three-coordinate complex. The proposed mechanism is supported by a series of kinetic experiments that indicate a first-order dependence on the palladium-amide and alkene concentration, and an inverse first-order dependence on THF concentration. NMR spectroscopic evidence for an alkene-amido intermediate which reacted at $-40\text{ }^{\circ}\text{C}$ to generate enamine products was gained in part by the addition of $\text{H}_2\text{C}=\text{CH}_2$ at $-100\text{ }^{\circ}\text{C}$ to a three-coordinate THF-free amido complex. A *syn*-aminopalladation that would result from migratory insertion was revealed by the stereochemistry of the enamine products resulting from reaction with *cis*- D_2 -ethylene. Initial results determining the electronic effects of the ancillary ligand and the alkene are reported.

