Intermolecular Insertion of Unactivated Alkenes into Palladium-Nitrogen Bonds

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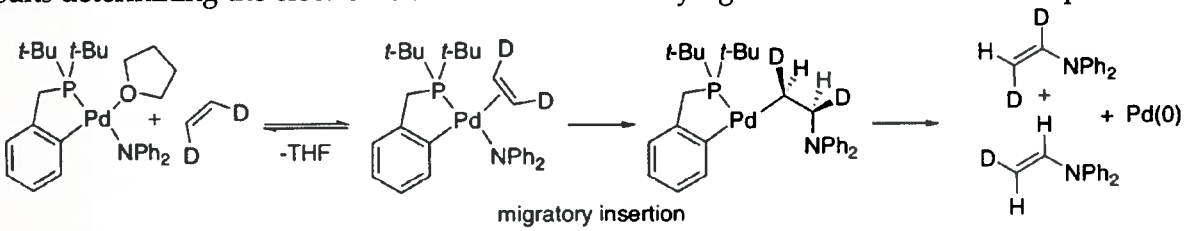
We report a series of THF-coordinated palladium-diarylamido complexes ligated by a cyclometallated benzyl phosphine ligand. These complexes react with unactivated alkenes to form enamine products by a concerted migratory insertion into the palladium-amide bond. The reactions occur by reversible generation 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 °C to generate enamine products was gained in part by the addition of $H_2C{=}CH_2$ at -100 °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.



Supramolecular Coupling Agents for Adhesion Promotion at Interfaces

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Fiber-reinforced composites are widely used as structural materials where high strength and low weight are required. Thermoplastic polymer composites offer complimentary properties to thermoset polymer composites, however, poor adhesion at the interface of the non-polar polymer matrix and polar reinforcement can limit the performance of such materials. To overcome these problems, a number of coupling agents have been designed relying on covalent bonds or intermolecular interactions for promotion of interfacial adhesion. We have initiated study of supramolecular coupling agents based on the stable ($K_{assoc} \sim 10^8\ M^{-1}$ in $CHCl_3$), complementary, quadruple hydrogen-bonding interaction between 2,7-diamido-naphthyridine (DAN) and 7-deazaguanine urea (DeUG). Surface functionalization of the adherend has been accomplished via derivatization of (aminopropyl)triethoxysilane-treated surfaces. Surface analysis is consistent with the expected functionality. Polymeric adhesives have been prepared via C–H activation of commercially available thermoplastics. Mechanical tests and spectroscopic measurements have been used to probe interfacial adhesion in this model system. Mechanical test data are consistent with specific H-bonding interactions playing some role in adhesion.