

Abstract

Palladium catalyzed reactions represent an important field in organic chemistry. Our research group have previously reported a mesoionic palladium NHC complex $[\text{Pd}(\text{Py-tzNHC})_2]^{2+} 2(\text{BF}_4^-)$ that has been employed in cross-coupling catalysis for C–C bond formation. Our purpose was to extend the scope of catalysis of palladium complex to the formation of carbon-heteroatom bonds, specifically, for the formation of carbon-nitrogen (C–N) and carbon-fluorine (C–F) bonds. In the present work, we investigated two reactions, namely palladium-catalyzed intermolecular hydroamination, which results in the formation of a new C–N bond, and palladium-catalyzed electrophilic aromatic fluorination, where C–F bond formation occurs.

The area of palladium catalyzed hydroamination has not yet been investigated in detail. There are only few reports on the use of palladium NHC complexes for catalytic intermolecular hydroamination of terminal acetylenes with primary anilines. In most cases, the reactions were carried out under harsh reaction conditions, i.e. elevated temperatures and additions of acid or base. In addition, none of the mechanistic proposals for described reaction has been confirmed so far. By employing different experimental and theoretical methods, we got an insight into the reaction mechanism of the intermolecular hydroamination reaction catalyzed by the palladium $[\text{Pd}(\text{Py-tzNHC})_2]^{2+} 2(\text{BF}_4^-)$ complex. We have shown that in addition to the stabilizing and activating role, pyridine wingtip of the Py-tzNHC ligand can also take on the role of an internal base. Namely, dissociation of pyridine wingtip from palladium allows substrate an access to the metal center, besides that uncoordinated pyridine can take the role of an internal base and is able of intermolecular proton transfer during catalysis. This demonstrated the unique role of the ligand in the catalysis for this type of reaction. Insight into the reaction mechanism allowed us to optimize reaction conditions. We have developed a synthetic procedure for palladium-catalyzed intermolecular hydroamination of terminal acetylenes with primary anilines, which meets the requirements regarding the availability of starting reagents, atomic economy, selectivity and is simple to perform. The reaction takes place at room temperature in the absence of any additive and with a low loading of palladium catalyst (1 mol%), producing imine products in high yields.

Fluorinated compounds play important role in pharmaceutical and agrochemical industry. By introducing fluorine atom, we can alter the hydrophobicity of the molecule, prevent

possible oxidation, etc. Because of that a lot of effort has recently been focused on the development of synthetic methodologies for introduction of fluorine atom under mild reaction conditions. Recently, a method for palladium-catalyzed electrophilic aromatic fluorination has been reported, which is a unique example of this type of reaction. We found that additional coordination of $[\text{Pd}(\text{Py-}t\text{zNHC})_2]^{2+} 2(\text{BF}_4^-)$ with phenanthroline, by which the square-planar coordination sphere of palladium is completely occupied and $[\text{Pd}(\text{Py-}t\text{zNHC})_2(\text{Phen})]^{2+} 2(\text{BF}_4^-)$ is formed, allows the palladium complex to react with the electrophilic fluorinating reagent. In this way, a reactive palladium (IV)-fluoro complex is formed that can fluorinate electronically poor aromatic systems. After optimization of the reaction conditions, the reaction was demonstrated on various aromatic compounds.

The doctoral thesis involves the development of new methods for the formation of carbon-heteroatom bonds, more specifically carbon-nitrogen and carbon-fluorine bonds. The development of processes was directed in such a way as to enable the preparation of hitherto inaccessible organic compounds and at the same time meet the requirements regarding the availability of materials, atomic economy, selectivity and the implementation of the synthesis itself. In this way, we achieved an improvement in synthetic methods compared to those known in the literature. At the same time, we investigated the mechanisms of reactions with experimental studies, which was of key importance in the rational planning and optimization of reaction conditions, and opened new way at the research work.

Keywords palladium, catalysis, C–N bond, C–F bond, hydroamination, fluorination