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SYNTHESES AND REACTIONS OF THE σ-PYRIDYL NICKEL(II) AND PALLADIUM(II) COMPLEXES

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Tetrakis(triphenylphosphine)-nickel(0) and -palladium(0) react with 2-chloropyridine in toluene to afford the dinuclear complexes $[MCl(C_5H_4N\text{-}C^2)(PPh_3)]_2$ (1). The bridging chloride can be readily replaced by Br^-, I^-, N_3^-, NCO^-, NCS^-, and $NCSe^-$, preserving the dinuclear structure. The nickel(II) complex 1(M = Ni) was found to catalyze the cross-coupling reaction between 2-chloropyridine and MeMgBr in THF at room temperature and a mechanism is proposed for this catalysis.

In the case of nickel(II), the 3-pyridyl complex was less stable than the corresponding 2-pyridyl complex and the 4-pyridyl complex was not obtained. On the other hand all of the 2-, 3-, and 4-pyridyl complexes with palladium(II) have been isolated, and 3- and 4-pyridyl complexes, trans-$PdX(C_5H_4N\text{-}C^3$ or $-C^4)(PPh_3)_2$, were all mononuclear irrespective of the nature of X. Triethylphosphine reacted with complex 1(M = Pd) to substitute PPh_3 at first and then to split the bridge, resulting in the mononuclear complexes. In this way three linkage isomers, trans-PdBr(2-, 3-, and 4-pyridyl)$(PEt_3)_2$ were prepared and the ^{13}C chemical shifts of pyridine-ring carbons and the base strength were determined. It is worth noting that the 2-pyridyl complex is 3700 times more basic than uncoordinated pyridine. The CO insertion reactions into the Pd-pyridyl bonds and methanolysis of the acyl complexes are also reported.

Very stable 2-pyridylpalladium(II) complexes containing ClO_4^-, BF_4^-, and PF_6^- as the bridging ligand were obtained by the reactions of 1(M = Pd) with the silver salts of these anions. These dinuclear complexes are converted into mononuclear ones, $PdX(C_5H_4N\text{-}C^2)(py)(PPh3)$ (X = ClO_4, BF_4, and PF_6) by the bridge-splitting reactions with pyridine, which are much more stable than the salts $[Pd(C_5H_4N\text{-}C^2)(py)_2(PPh_3)]X$.

The rections of $Pd(PPh_3)_4$ with 2- and 3-chloromethylpyridines in toluene at 100°C afforded the picolyl complexes. $[PdCl(2\text{-picolyl})(PPh_3)]_2$ (2) is much more stable than the corresponding 3-picolyl complex and reacted with silver acetate and phenylacetic chloride to produce the corresponding ester and ketone, respectively. Complex 2 also reacts with CO in THF to yield PdCl(2-pyridylacetyl-N,O)(PPh_3).