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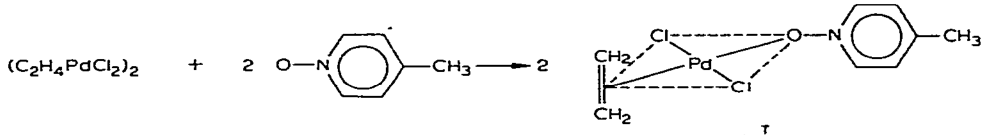
PRELIMINARY NOTE

Pyridine N-oxide–ethylenedichloropalladium(II) complexes

Although a large number of pyridine N-oxide–olefindichloroplatinum(II) complexes have been prepared[1], synthesis of the corresponding palladium complexes has not previously been reported. Palladium–monoolefin-π complexes are believed to be thermodynamically and kinetically less stable than platinum ones[2], and there is a paucity of such examples. The existence of palladium–olefin complexes as transient intermediates in a variety of industrial processes[3,4] and in palladium(II) catalyzed olefin isomerizations[5] has frequently been suggested, but actual isolation and identification of these olefin–metal intermediates has not been accomplished. To investigate these olefin–Pd^{II} reactions, we feel it necessary that some experimentation be with actual monoolefin–palladium(II), square-planar-π complexes as initial reactants. In conjunction with this study we found it desirous to prepare an original series of Pd^{II}–ethylene complexes, and we now wish to report a synthesis of 1,3-dichloro-2-ethylene-4 (*p*-Z-pyridine N-oxide)–palladium(II) complexes. (Z = nitro, methoxy or methyl)

After a great deal of trial-and-error experimentation the following procedure for the preparation of the complexes was developed—as described for *p*-picoline N-oxide. A mixture of slightly soluble ethylene palladium chloride[6], $(C_2H_4PdCl_2)_2$, (0.5 mmole) and dichloromethane (10 ml) was stirred under a blanket of ethylene (ice-water-bath cooling). The *p*-picoline N-oxide (1 mmole in 3 ml of CH_2Cl_2) was fed slowly (~5 min) from a syringe to the stirred mixture. As the N-oxide was added, the solid ethylene dimer dissolved, and near the endpoint of addition a clear, red-brown solution existed. After several more minutes of stirring, pentane (50 ml) was added, and a solid precipitated. The supernatant liquid was syringed off, and the solid residue was washed thoroughly with pentane (under ethylene). The solid was then blown dry with ethylene, yielding a golden brown powder, I.



I

Compound I (m.p. (dec.), 96–98°) was identified in the following manner: infrared analysis showed picoline N-oxide absorptions characteristic of bonded ligand rather than free N-oxide [compared with spectra of free N-oxide, mixture of N-oxide and ethylene dimer, and picoline N-oxide–ethylenedichloroplatinum(II)]. In fact, the IR spectrum was very similar to that of the platinum analog. Treatment of a solution of I in a gasometric apparatus with excess triphenylphosphine resulted in the liberation of ethylene (94% based on 1-to-1 ethylene-to-palladium). Reaction of I with water produced palladium and acetaldehyde (67% isolated as the 2,4-dinitrophenylhydrazone; identified by comparison with an authentic sample). Preparative procedure required one mole of picoline N-oxide per mole of palladium (Found:

Pd, 32.4; Cl, 22.7. $C_8H_{11}Cl_2NOPd$ calcd.: Pd, 33.9; Cl, 22.6). This information together with prior knowledge of the reaction of *p*-picoline N-oxide with ethyleneplatinum chloride[7] strongly suggests the proposed structure for compound I.

A molecular weight value of 350 (freezing point method in benzene; determination difficult due to low solubility and poor stability of product; calcd.; 315) eliminates species such as an adduct comprised of 2 moles of N-oxide and 1 mole of ethylenepalladium dimer. Treatment of a solution of I in CH_2Cl_2 with one equivalent of ligand (N-oxide) results in displacement of ethylene and the formation of a brown precipitate. The solid formed is identical to the product of the reaction of dibenzonitrile palladous chloride with excess *p*-picoline N-oxide in acetone [believed to be bis(*p*-picoline N-oxide)-dichloropalladium(II)].

Using the described preparative procedure the *p*-nitropyridine N-oxide (m.p. (dec.), 123–125°), *p*-methoxypyridine N-oxide (m.p. (dec.), 105–107°), and pyridine N-oxide (m.p. (dec.), 107–109°) complexes were also prepared. At present no purification procedure for these complexes has been developed. Difficulty with decomposition has been encountered in all attempts. The complexes are golden-brown, dissolve in CH_2Cl_2 or sparingly in benzene, and tend to decompose slowly on standing at room temperature, even under ethylene. Considerable decomposition is apparent after several days. The *p*-nitropyridine N-oxide complex appears to be the most stable.

Additional applications of this synthetic route are presently being investigated. We are also undertaking a study of the reactivity of these complexes to ascertain, for example, if higher olefin or carbon monoxide[8] will exchange with the ethylene.

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