Oxidation of Metallic Palladium by Nitrosyl Tetrafluoroborate

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DESPITE continued experimental and theoretical interest in square planar d^8 Pd^{II} complexes, there are only very limited data available for cationic complexes of this type. During our investigations of non-aqueous solvent co-ordination of second transition series metal ions, a convenient method was developed for the preparation of square-planar cationic Pd^{II} complexes. Hathaway, Holah, and Underhill[1] have reported that many first transition series metals can be oxidized by nitrosyl tetrafluoroborate [NO^+; BF_4^-] (I) in acetonitrile to produce the bivalent cations and evolve nitric oxide. This report describes the oxidation of metallic palladium by (I) in acetonitrile, which has several features of interest: (i) oxidation occurs in a non-hydroxyllic media, and (ii) the "non-co-ordinating" tetrafluoroborate anion is introduced thus allowing Pd^{II} to fulfil its co-ordination sites with neutral ligands.

Sponge palladium was added under nitrogen to a solution of (I) in acetonitrile. Care was taken to exclude oxygen from the reaction vessel in order to prevent formation of nitrate anions.[2] Nitric oxide was slowly evolved at the palladium–solution interface and was removed periodically by application of light vacuum. The reaction was complete in 10 hr. and the resulting yellow solution was filtered under nitrogen and a yellow compound precipitated by slow addition of anhydrous ether. The isolated complex analyzed for $[Pd(MeCN)_4](BF_4)_2$, (II). No palladium(IV) was found in the complex, even when the reaction was carried out in the presence of an excess of oxidizing agent. The complex is diamagnetic. This is consistent with square-planar four co-ordination commonly found for Pd^{II} complexes. A broad intense band centred at 1050 cm.$^{-1}$ and a very weak band at 760 cm.$^{-1}$ in the Nujol mull i.r. spectrum indicate ionic tetrafluoroborate anion[1]. A prominent band at 2347 cm.$^{-1}$ is associated with the co-ordinated nitrile

C≡N stretching frequency. The shift of 80—93 cm.$^{-1}$ to higher frequency relative to the free ligand frequency (ν_{CNl} = 2254, ν_{CNg} = 2267) is consistent with normal nitrogen co-ordination.[3,4]

The oxidation of Pd probably proceeds *via* an intermediate nitrosyl complex which subsequently loses nitric oxide to form the cationic Pd^{II} complex with acetonitrile. Although no direct evidence for this intermediate has been obtained in acetonitrile, preliminary investigations of this reaction in ethyl acetate have yielded complexes with an i.r. band at 1830 cm.$^{-1}$ suggesting co-ordinated nitrosyl. Further work on this reaction is in progress.

The reaction of metallic palladium with (I) in acetonitrile leads to the selective oxidation of Pd to Pd^{II}. This reaction offers a convenient route to Pd^{II} with the very weakly co-ordinating tetrafluoroborate anion. The resulting acetonitrile complex, (II), can be readily converted by metathesis reactions into other cationic Pd^{II} complexes with ligands such as amides, sulphoxides, and amines.

A study of the reactions of heavy metals with the related oxidizing agents nitrosonium tetrafluoroborate [NO_2^+; BF_4^-] (III) and dinitrogen tetroxide, N_2O_4, (IV), has also been initiated. Palladium readily reacts with (III) to yield the unexpected complex (II) in high yield. A nitrite or nitrate complex was expected. The expected product $Pd(CH_3CN)_2(NO_3)_2$ results from reaction of (IV) with Pd.

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