Cyanide Formation During the Reaction of Diacetatopalladium(II) and Nitrate Ion

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Summary The reaction of $Pd(OAc)_2$ and nitrate ion in acetic acid resulted in the formation of cyanide ion which was detected by the isolation of the novel compound acetatocyanopalladium(II).

When a solution of diacetatopalladium(II) (0·1 M) and lithium nitrate trihydrate (1·0 M) in acetic acid was heated under reflux, nitrous fumes were evolved and an orange precipitate slowly separated. Palladium analysis showed that, after a 3 hr. reflux period, 30% of the original palladium could be accounted for in the form of the orange compound. In the i.r. region the compound had ν_{max} 2217(sh) and 2211 (which was assigned to cyanide), and 1582, 1440, 700 cm.$^{-1}$ assigned to acetate ion. The material was completely insoluble in dilute mineral acids and in non-basic organic solvents, thus ruling out the possibility of free palladous acetate being present. (A recently encountered pale purple form of palladous acetate which is insoluble in acetic acid has ν_{max} 1500 and 1430 cm.$^{-1}$). With ammonia solution dismutation of the compound occurred and the known[1] dicyanodiamminepalladium(II) was isolated. Similarly, with pyridine (equation 1) a mixture of dicyanodipyridinepalladium(II) and diacetatodipyridinepalladium(II)[2] was obtained.

$$\mathrm{Pd(CN)OAc]}_n + 2n\mathrm{C_5H_5N} \rightarrow n/2\,\mathrm{(C_5H_5N)_2Pd(CN)_2} + n/2\,\mathrm{(C_5H_5N)_2Pd(OAc)_2} \qquad (1)$$

Elemental analysis confirmed the orange precipitate to be acetatocyanopalladium(II) and its extreme insolubility coupled with the closeness of ν_{CN} to that of dicyanopalladium(II) [1a] makes it likely that this compound has a macromolecular layer structure containing single bridging anions between metal atoms and with like anions *trans* to each other. Such linear bridging of cyanide is well known[3] and bridging of metal atoms by a single carboxylate group is exemplified in the case of diformatocopper(II).[4]

The cyano-complex was also formed when sodium or potassium nitrate was used instead of lithium nitrate, but not when the reaction was attempted using nitric acid which should remove acetate ion from the solution. The reaction therefore proceeds by the oxidation of acetate ion by nitrate probably through the intermediacy of a quadrivalent palladium species such as $Pd(NO_3)_2(OAc)_2$; *cf.* the formation of $Pd(NO_3)_2(OH)_2$ when palladium metal is dissolved in nitric acid.[5] The oxidation of acetate leads to the formation of methyl radicals which can then combine (2) with nitric oxide;[6]

$$\mathrm{CH_3^{\bullet}} + \mathrm{NO} \rightarrow \mathrm{CH_3NO} \rightleftharpoons \mathrm{CH_2{=}NOH} \qquad (2)$$

Just as fulminate [7] is produced when *aci*-nitromethane is treated with mercuric chloride so the formation of formaldoximato-ions (equation 2) in the present reaction could lead to the cyano-compound.

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