δ-Bonded 2-Phenylpyridine Palladium Complex

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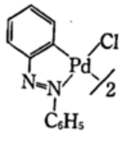
In general, heterocyclic amines such as pyridine react with palladium(II) dichloride to give a square-planar complex such as Pd(pyridine)$_2$Cl$_2$. However, the observation[1] that azobenzenes and *N,N*-dimethylbenzylamine react with palladium(II) halides and platinum(II) halides in alcoholic solutions to give complexes (1) and (2) with carbon-metal σ-bonds has led to an examination of a similar reaction between palladium(II) dichloride and heterocyclic amines. We have found that, in alcoholic media, 2-phenylpyridine undergoes a similar unusual reaction with sodium chloropalladate.

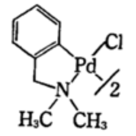
2-Phenylpyridine and sodium chloropalladate were dissolved in alcohol and allowed to stand at room temperature for two days. A pale yellow material believed to have the structure (3) was isolated in about a 70% yield. The compound (3) is insoluble in all common organic solvents and does not melt before decomposition, which occurs at about 270°C. The structure of the complex (3) was established by the results of the elementary analysis (Found: C, 44.38; H, 2.56; N, 4.57%. Calcd for $C_{22}H_{16}N_2Pd_2Cl_2$: C, 44.82; H, 2.72; N, 4.14%) and the following data.

In the infrared spectrum of the compound (3), the characteristic C–H out-of-plane deformation modes of a mono-substituted benzene at 770—730 and 690 cm^{-1} are absent and are replaced by one at 737 cm^{-1}, which can be assigned to a C–H deformation mode of an ortho-disubstituted benzene.[2] The lithium aluminum hydride reduction of the compound (3) gave 2-phenylpyridine (4a), whose mass spectrum, picrate, and hydrochloride were identical with those of an authentic sample. On the other hand, the lithium aluminum deuteride reduction of the compound (3) gave 2-phenylpyridine-d$_1$ (4b). The position of the deuterium and, therefore, the site of the carbon-to-palladium σ-bond, were established by a comparison of the mass spectrum of (4b) with that of the undeuterated (4a). The compound (4a) gave peaks at *m/e* 155 (100%, parent ion), 128 (12%, loss of HCN), and 52 (21%, loss of PhCN). The mass spectrum of the compound (4b) showed peaks at *m*/e 156 (100%, parent ion), 129 (13%, loss of HCN), and 52 (21%, loss of PhCN-d$_1$).

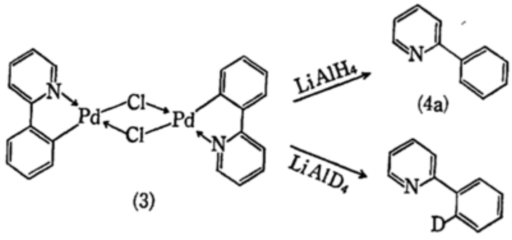
2-Phenylquinoline also reacted with sodium chloropalladate in alcohol to give a yellow compound believed to have the structure (5) (dec. p. 270°C; Found: C, 51.72 H, 2.68; N, 3.87%. Calcd for $C_{30}H_{20}N_2Pd_2Cl_2$: C, 52.05; H, 2.91; N, 4.04%). In the infrared spectrum of the compound (5), the characteristic C–H deformation mode of a mono-substituted benzene is absent, but an intense band at 738 cm^{-1} can be assigned to the C–H deformation mode of an ortho-disubstituted benzene. This behavior is analogous to that of the spectra of the 2-phenylpyridine palladium complex (3). The presence of a bond between the metal atom and a carbon atom of the phenyl group in the 2-phenylquinoline molecule was also established by mass spectrometric analysis. The compound (5) was reduced with lithium aluminum hydride to 2-phenylquinoline (6a), whereas with lithium aluminum deuteride it was reduced to 2-phenylquinoline-d$_1$ (6b). The mass spectrum of the compound (6a) gave peaks at *m/e* 205 (100%, parent ion) and 102 (13%, loss of Ph-CN). The mass spectrum of 6b showed peaks at *m/e* 206 (100%, parent ion) and 102 (12%, loss of PhCN-d$_1$).



(1)



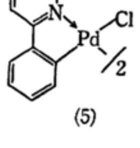
(2)



(3)

(4a)

(4b)



(5)

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[1] A. C. Cope and R. W. Sieman, *J. Am. Chem. Soc.*, **87**, 3272 (1965); A. C. Cope, J. M. Kliegman and E. C. Friedrich, *ibid.*, **89**, 287 (1967).

[2] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., Methuen, London (1958), p. 77.