CHEMISTRY LETTERS, pp. 1947 - 1948, 1984. © The Chemical Society of Japan 1984

DOUBLY-CHELATED CYCLOPALLADATED COMPLEXES OF 1,3-BIS(2-PYRIDYL)PROPANE[1]

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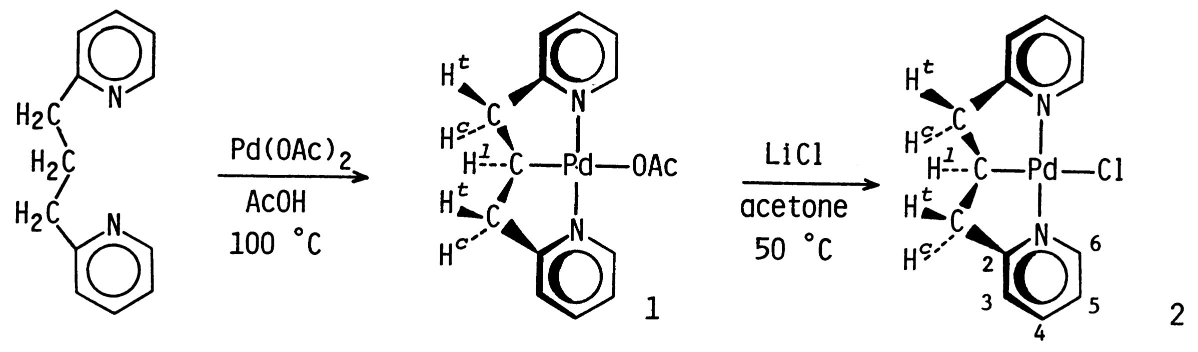
1,3-Bis(2-pyridyl)propane reacted with palladium(II) acetate in acetic acid at 100 °C, resulting in the formation of a brown oil. The oil was treated with lithium chloride to give a doubly-chelated cyclopalladated complex, $[Pd\{(C_5H_4N)CH_2CHCH_2(C_5H_4N)\}Cl]$.

Shaw and his coworkers reported that pentamethylene-1,5-bis(di-*tertiary*-butylphosphine) reacted with $[PdCl_2(NCPh)_2]$,[2] $[PtCl_2(NCR)_2]$,[2,3] $RhCl_3 \cdot 3H_2O$,[4,5] and hydrated iridium(III) chloride[5] to give binuclear 16-membered complexes and mononuclear doubly-chelated cyclometallated ones. When a hexamethylene homologue of the diphosphine was treated with $[PtCl_2(NCPh)_2]$, an addition complex and the corresponding cyclometallated one were formed.[6] However, no reaction of an oligomethylene-α,ω-di(nitrogen base) with a transition metal compound has ever been reported, producing a doubly-chelated cyclometallated complex. [2,6-Bis(*N*,*N*-dimethylaminomethyl)phenyl-*N*,C^1, *N'*]bromopalladium(II) or -platinum(II) was obtained from the reaction among lithium, 1-bromo-2,6-bis(*N*,*N*-dimethylaminomethyl)benzene and $[PdBr_2(c\text{-}1,5\text{-}C_8H_{12})]$ or $[PtCl_2(SEt_2)_2]$, respectively.[7] Here, we wish to present the direct metallation of methylene carbon of 1,3-bis(2-pyridyl)propane by use of palladium(II) acetate, resulting in the formation of a new type of the doubly-chelated cyclopalladated complex.

1,3-Bis(2-pyridyl)propane was treated with palladium(II) acetate in acetic acid at 100 °C for 8 h. After the reaction mixture was vigorously shaken with water and dichloromethane, the lower layer was separated and evaporated at reduced pressure to give a brown oil (1). The oil, 1 was treated with lithium chloride in acetone at 50 °C for 5 h to afford a khaki solid, $[Pd\{(C_5H_4N)CH_2CHCH_2(C_5H_4N)\}Cl]$ (2) in 45% yield based on palladium(II) acetate.[8]

The IR spectrum of 2 showed a sharp band at 1605 cm^{-1} characteristic of pyridine ring, whereas the far infrared spectrum did a band at 331 cm^{-1} ascribable to



ν(Pd-Cl). Its ^{1}H-NMR spectrum in CDCl$_3$ exhibited two double doublets at δ 2.53[9] (2H, $\underline{H}^cCH^t$) and 3.50[9] (2H, $H^c\underline{CH}^t$) and seven lines centered at δ 3.97 in an intensity ratio of 1:2:3:4:3:2:1[9] (1H, PdC$\underline{H}^l$). In the ^{13}C{^{1}H}-NMR spectrum in CDCl$_3$, two singlets at δ 46.6 and 45.1 were assigned to methylene carbons and methine one, respectively.[10] This assignment is reasonable, in consideration of the chemical shift of methine carbon (δ 40.96) in the ^{13}C-NMR data of [Pt(Bu$^t{}_2$PCH$_2$CH$_2$CHCH$_2$CH$_2$P-Bu$^t{}_2$)Cl].[2] The ^{1}H- and ^{13}C{^{1}H}-NMR data of 2, mentioned above, confirm that the central carbon of bis(2-picolyl)methyl moiety in 2 is σ-bonded to palladium and that two methylene protons of each 2-picolyl group are nonequivalent. The greater $^3J(H^tH^l)$ value is associated with the coupling constant between the methine proton and one of the methylene ones, situated *trans* to the methine proton. On the basis of these discussions, 2 was assigned to [bis(2-picolyl)methyl-*N*,*C*,*N*']chloropalladium(II). It is the first example to our knowledge that the relatively inactive methylene carbon of the oligomethylene-α,ω-di(nitrogen base) was metallated directly by the transition metal compound to form the doubly-chelated cyclometallated complex.

The IR spectrum of the oil, 1 showed a strong band at 1570 cm^{-1} and a medium one at 1415 cm^{-1} for carboxylato group. The ^{1}H-NMR pattern of 1 was very similar to that of 2.[11] Although 1 might not be in a pure state, 1 was believed to consist of acetato[bis(2-picolyl)methyl-*N*,*C*,*N*']palladium(II) virtually.

Support of this research by a Grant-in-Aid for Scientific Research from the Ministry of Education (Project No. 58550572) is gratefully acknowledged.

References

1) Metallation of Aliphatic Carbon Atoms. 3.
2) N. A. Al-Salem, H. D. Empsall, R. Markham, B. L. Shaw, and B. Weeks, J. Chem. Soc., Dalton Trans., 1979, 1972.
3) J. R. Briggs, A. G. Constable, W. S. McDonald, and B. L. Shaw, J. Chem. Soc., Dalton Trans., 1982, 1225.
4) C. Crocker, R. J. Errington, R. Markham, C. J. Moulton, K. J. Odell, and B. L. Shaw, J. Am. Chem. Soc., 102, 4373 (1980).
5) C. Crocker, H. D. Empsall, R. J. Erringron, E. M. Hyde, W. S. McDonald, R. Markham, M. C. Norton, and B. L. Shaw, J. Chem. Soc., Dalton Trans., 1982, 1217.
6) N. A. Al-Salem, W. S. McDonald, R. Markham, M. C. Norton, and B. L. Shaw, J. Chem. Soc., Dalton Trans., 1980, 59.
7) D. M. Grove, G. van Koten, J. N. Louwen, J. G. Noltes, A. L. Spek, and H. J. C. Ubbels, J. Am. Chem. Soc., 104, 6609 (1982).

8) The elementary analysis of 2 is satisfactory. Mp 238 °C.

9) $^2J(H^cH^t)$=17 Hz, $^3J(H^cH^l)$=5 Hz, and $^3J(H^tH^l)$=10 Hz.

10) The pyridyl carbon resonances are as follows; δ 121.1 (5-C), 122.0 (3-C), 137.7 (4-C), 151.6 (6-C), and 170.3 (2-C).

11) The ^{1}H NMR of 1 (CDCl$_3$); δ 2.44 [dd, $^2J(H^cH^t)$=17 Hz, $^3J(H^cH^l)$=5.5 Hz, 2H, $\underline{H}^cCH^t$], 3.55 [dd, $^2J(H^cH^t)$=17 Hz, $^3J(H^tH^l)$=11 Hz, 2H, $H^c\underline{CH}^t$], 3.80 (7 lines, 1H, PdC$\underline{H}^l$), and 2.09 (s, 3H, C$\underline{H}_3$CO$_2$).

(Received September 10, 1984)