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Synthesis and Molecular Structure of *trans*-$PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O\text{-}(CH_2)_3\text{-}2\text{-}C_5H_4N\}$. The First Transition Metal Complex Containing *trans* Coordinating Bidentate Pyridyl-phosphine Ligand

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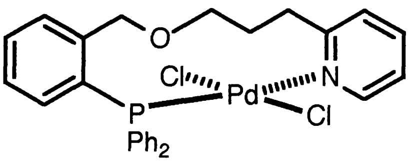
As the first example of a crystallographically confirmed transition metal complex with a bidentate hybrid ligand spanning *trans* positions, the square-planar palladium(II) complex containing the *trans* chelating pyridyl-phosphine bidentate hybrid ligand, bound through a pyridine and a phosphine, *trans*-$PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3\text{-}2\text{-}C_5H_4N\}$, is prepared and the crystal structure was determined.

Although there are a large number of square-planar complexes containing bidentate ligands, those with *trans* chelating ligands are rare.1) To our knowledge, only one example of such mononuclear complexes containing *trans* chelating bidentate hybrid ligands has been reported without confirmation of the structure by X-ray analysis.1g) Almost all of the reported examples of the transition metal complexes with *trans* chelating ligands lack the X-ray analysis. Mainly from the catalytic interest, several transition metal complexes with bidentate pyridyl-phosphine ligands have been prepared,2) but those with the *trans* spanning chelates have not been reported. Transition metal complexes containing *trans* chelating bidentate ligands are expected to show unique functions in catalysis. The preparation of new complexes containing *trans* chelating ligands and elucidation of their structures and properties, therefore, become a matter of interest. Here we describe the first example of palladium(II) complex with the *trans* chelating bidentate pyridyl-phosphine ligand and the results of its X-ray structural analysis.

Reaction of $o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3\text{-}2\text{-}C_5H_4N$ (**1**)3) and an equimolar amount of Na_2PdCl_4 in absolute ethanol or $PdCl_2(PhCN)_2$ in dichloromethane gave *trans*-[$PdCl_2$(**1**)] (**2**),4) mp 213-215 °C(dec), as orange crystals in about 40% yield. As the minor by-product the trinuclear complex of the molecular formula,



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$Pd_3Cl_6(\mathbf{1})_2$ (**3**)$^{5)}$ was obtained as yellow crystals, mp 196-197 °C(dec). Neither the *cis* chelating mononuclear complex nor the binuclear one with the bridging ligand was detected in the reaction mixture. Separation between these two products could be achieved by the solubility difference; **2** is more soluble than **3** in common organic solvents. Single crystals of **2** suitable for X-ray analysis could be obtained by recrystallization from dichloromethane-ether. When the ligand was employed in excess in the above reaction, **2** was always contaminated with $[PdCl_2(\mathbf{1})_2]$, where **1** acts as a monodentate phosphine ligand. Then the separation between these two complexes was difficult. ^1H NMR of **2** showed the signal of 6-H of the pyridine ring at 8.90 ppm, 0.41 ppm lower than that of the free ligand; the signal shape with a complex fine structure is very characteristic and indicative of the coupling with the *trans* phosphorus atom. We observed the Pd-Cl stretching frequency of the main band at 343 cm^{-1} accompanied by a shoulder at 350 cm^{-1}. This indicates that only one M-Cl stretching frequency for the *trans* square-planar complex $MCl_2L_2$$^{6)}$ is not a necessary condition for non-centrosymmetric complexes.$^{1g, 7)}$

The molecular structure of the *trans* complex **2** is illustrated in Fig. 1.$^{8)}$ It warrants a square-planar palladium(II) complex with the bidentate ligand spanning *trans* positions. Almost linear array of P-Pd-N and Cl-Pd-Cl with the planar structure is confirmed. The etheric oxygen in the ligand does not interact with the central metal atom; Pd-O separation is 4.032(4) Å. The pyridine ring is approximately perpendicular to the molecular

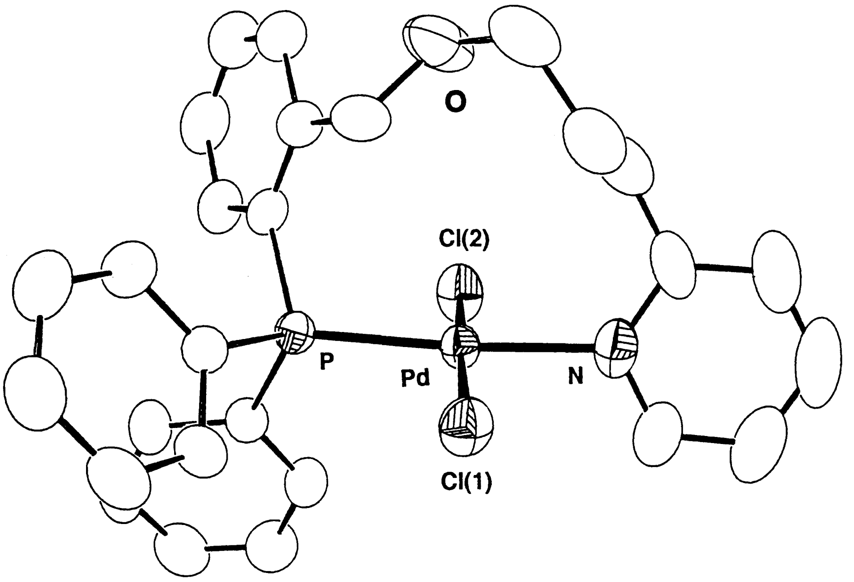

Fig. 1. An ORTEP drawing of complex **2**. Selected bond lengths (Å) and angles (°): Pd-P 2.259(1), Pd-N 2.104(4), Pd-Cl(1) 2.293(1), Pd-Cl(2) 2.307(1), P-Pd-N 175.8(1), Cl(1)-Pd-Cl(2) 174.85(5), Cl(1)-Pd-P 94.52(4), Cl(1)-Pd-N 88.0(1), Cl(2)-Pd-P 87.35(4), Cl(2)-Pd-N 90.5(1). The dihedral angle between the planes PPdCl(2) and NPdCl(1) is 6.07(8)°.

plane. There was no anomaly in the bond lengths and angles in the complex **2**; thus, special strain is not present in the chelate ring. As the corresponding *cis* chelating product could not be obtained, the ligand coordinating *cis* positions will produce much strain and the complex becomes labile.

The analogous hybrid ligand containing less methylene groups in the bridge, *o*-$Ph_2PC_6H_4CH_2OCH_2$-2-C_5H_4N, gave only the corresponding *cis* chelating palladium(II) complex in ca. 70% yield as an isolable product, although the molecular model indicates the *trans* chelation possible.

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3) The hybrid ligand **1** was prepared from the reaction of (2-bromomethyl)diphenylphosphine oxide,[9)] derived from *o*-diphenylphosphinobenzoic acid, with sodium 3-(2-pyridyl)propanolate and subsequent reduction with trichlorosilane and triethylamine as an air-sensitive colorless oil in 42% yield. HRMS(EI) m/e obsd 412.1830, Calcd for $C_{27}H_{27}NOP^+(MH^+)$ 412.1835. ^1H NMR ($CDCl_3$, 270 MHz): δ 1.88(2H, m, $C_5H_4NCH_2CH_2$), 2.75 (2H, t, $J = 7.70$ Hz, $C_5H_4NCH_2$), 3.44 (2H, t, $J = 6.35$ Hz, CH_2O), 4.69 (2H, d,

J_{PH} = 1.62 Hz, $OCH_2C_6H_4$), 6.87-7.56 (22H, m, arom.), 8.49 (1H, m, 6-H of pyridyl group). $^{31}P\{^1H\}$ NMR (5% $CDCl_3$, 109.25 MHz, external reference 85% H_3PO_4): δ -16.0 (s).

4) The complex **2** crystalizes with one molecule of dichloromethane. Found: C, 49.95; H, 4.29; N, 2.13; Cl, 20.74%. Calcd for $C_{27}H_{26}Cl_2NOPPd{\cdot}CH_2Cl_2$: C, 49.92; H, 4.19; N, 2.08; Cl, 21.05%. FD MS m/e 589 (M^+) and 554 [$(M\text{-}Cl)^+$]; ν_{max} 1603 (C=N), 1090 (COC), 343 cm^{-1} (PdCl); ^1H NMR ($CDCl_3$, 270 MHz): δ 2.59 (2H, dt, *J* = 16.5, 5.5 Hz, CH_2CH_2O), 3.53 (2H, t, *J* = 5.9 Hz, $C_5H_4NCH_2$), 3.98 (2H, t, *J* = 5.5 Hz, CH_2CH_2O), 5.59 (2H, s, $C_6H_4CH_2O$), 6.86-7.95(21H, m, arom.), 9.90 (1H, m, 6-H of pyridyl group); $^{31}P\{^1H\}$ NMR (5% $CDCl_3$, 109.25 MHz, external reference 85% H_3PO_4): δ 23.41 (s).

5) Found: C, 47.61; H, 3.89; N, 2.10; Cl, 15.15%. Calcd for $C_{54}H_{52}Cl_6N_2O_2P_2Pd_3$: C, 47.87; H, 3.87; N, 2.07; Cl, 15.70%. ν_{max} (nujol) 1603 (C=N), 1090 (CO C), 355, 265 cm^{-1} (PdCl); ^1H NMR ($CDCl_3$, 270 MHz): δ 2.30 (2H, dt, *J* = 16.9, 6.2 Hz, CH_2CH_2O), 3.96 (2H, t, *J* = 6.2 Hz, $CH_2C_5H_4N$), 4.04 (2H, t, *J* = 8.2 Hz, CH_2O), 5.60 (2H, s, $C_6H_4CH_2O$), 6.89-7.95 (23H, m, arom.), 9.04 (1H, ddd, *J* = 5.7, 1.5, 0.74 Hz, 6-H of pyridyl group); $^{31}P\{^1H\}$ NMR (5% $CDCl_3$, 109.25 MHz, external reference 85% H_3PO_4): δ 27.41 (s). A single crystal suitable for the X-ray analysis was not obtained.

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8) *Crystal data* for **2**: $C_{27}H_{26}Cl_2NOPPd{\cdot}CH_2Cl_2$, M = 673.8, triclinic, space group $P\bar{1}$, a = 10.135(1), b = 16.171(2), c = 9.023(1) Å, α = 99.98(1), β = 101.41(1), γ = 86.51(1)°, U = 1427.0(2) $Å^3$, Z = 2, D_{calcd} = 1.568 g cm^{-3}, D_{obsd} = 1.54(6) g cm^{-3}, $F(000)$ = 680, $\mu(Mo\text{-}K_\alpha)$ = 10.97 cm^{-1}, crystal size: 0.20 x 0.25 x 0.25 mm. 8600 reflections (8324 unique reflections, $R_{sym}(F_o)$ = 0.022) were collected on a Rigaku AFC-4R (8 kW) using graphite monochromated Mo–K_α (λ = 0.71069 Å) radiation with $2\theta/\omega$ scan of which 4789 were observed [$|F_o| > 6.0\sigma(|F_o|)$]. The structure was solved by SHELXS-86 (G. M. Sheldrick, University of Göttingen, 1986) and refined by full-matrix least-squares (ANYBLK, H. Imoto, The University of Tokyo, 1990) to R = 0.0338, R_w = 0.0401 ($\omega = 1/\sigma^2(F_o)$, parameters = 325, Δ/σ_{max} = 0.00). The reflection data collection and the all calculations were performed at the Research Center for Protein Engineering Institute for Protein Research Research, Osaka University.

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