

Synthesis and Molecular Structure of *trans*-PdCl₂{*o*-Ph₂PC₆H₄CH₂O-(CH₂)₃-2-C₅H₄N}. The First Transition Metal Complex Containing *trans* Coordinating Bidentate Pyridyl-phosphine Ligand

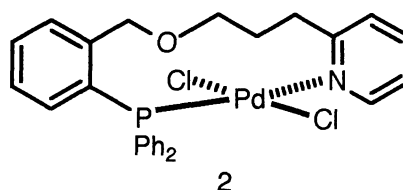
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As the first example of a crystallographically confirmed transition metal complex with a bidentate hybrid ligand spanning *trans* positions, the square-planar palladium(II) complex containing the *trans* chelating pyridyl-phosphine bidentate hybrid ligand, bound through a pyridine and a phosphine, *trans*-PdCl₂{*o*-Ph₂PC₆H₄CH₂O(CH₂)₃-2-C₅H₄N}, 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*-Ph₂PC₆H₄CH₂O(CH₂)₃-2-C₅H₄N (**1**)³⁾ and an equimolar amount of Na₂PdCl₄ in absolute ethanol or PdCl₂(PhCN)₂ in dichloromethane gave *trans*-[PdCl₂(**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,



$\text{Pd}_3\text{Cl}_6(\mathbf{1})_2$ ($\mathbf{3}$)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; $\mathbf{2}$ is more soluble than $\mathbf{3}$ in common organic solvents. Single crystals of $\mathbf{2}$ suitable for X-ray analysis could be obtained by recrystallization from dichloromethane-ether. When the ligand was employed in excess in the above reaction, $\mathbf{2}$ was always contaminated with $[\text{PdCl}_2(\mathbf{1})_2]$, where $\mathbf{1}$ acts as a monodentate phosphine ligand. Then the separation between these two complexes was difficult. ^1H NMR of $\mathbf{2}$ 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 $\mathbf{2}$ 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 $4.032(4)\text{ \AA}$. The pyridine ring is approximately perpendicular to the molecular

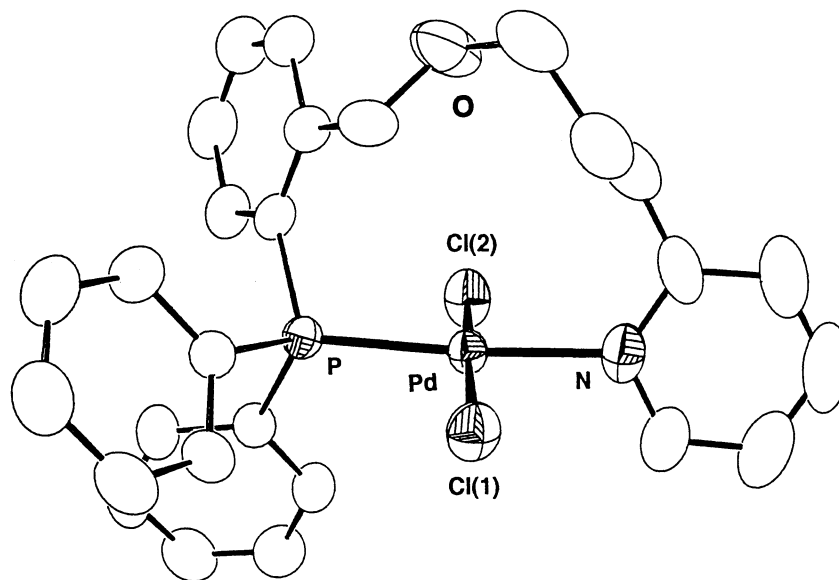


Fig. 1. An ORTEP drawing of complex $\mathbf{2}$. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Pd-P 2.259(1), Pd-N 2.104(4), Pd-Cl(1) 2.293(1), Pd-Cl(2) 2.307(1), P-Pd-N 175.8(1), Cl(1)-Pd-Cl(2) 174.85(5), Cl(1)-Pd-P 94.52(4), Cl(1)-Pd-N 88.0(1), Cl(2)-Pd-P 87.35(4), Cl(2)-Pd-N 90.5(1). The dihedral angle between the planes PPdCl(2) and NPdCl(1) is $6.07(8)^\circ$.

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*-Ph₂PC₆H₄CH₂OCH₂-2-C₅H₄N, 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.

This work was partly supported by a Grant-in-Aid for General Project Research (C) from the Japanese Ministry of Education, Science and Culture (Grant No. 03640519).

References

- 1) a) K. Issleib and G. Hohlfield, *Z. Anorg. Allg. Chem.*, **312**, 170 (1961); b) N. J. DeStefano, D. K. Johnson, and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, **13**, 133 (1974); c) N. J. DeStefano, D. K. Johnson, and L. M. Venanzi, *Helv. Chim. Acta*, **59**, 2683 (1976); d) D. K. Johnson, P. S. Pregosin, and L. M. Venanzi, *ibid.*, **59**, 2691 (1976); e) A. J. Pryde, B. L. Shaw, and B. Weeks, *J. Chem. Soc., Chem. Commun.*, **1973**, 947; f) A. J. Pryde, B. L. Shaw, and B. Weeks, *J. Chem. Soc., Dalton*, **1976**, 322; g) J. C. Chottard, E. Mulliez, J. P. Girault, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, **1974**, 780; h) N. W. Alcock, J. M. Brown, and J. C. Jeffery, *ibid.*, **1974**, 829; i) N. W. Alcock, J. M. Brown, and J. C. Jeffery, *J. Chem. Soc., Dalton*, **1977**, 888; j) I. Mochida, J. A. Mattern, and J. C. Bailar, *J. Am. Chem. Soc.*, **97**, 3021 (1975); k) H-B. Bürgi, J. Murray-Rust, M. Camalli, F. Caruso, and L. M. Venanzi, *Helv. Chim. Acta*, **72**, 1293 (1989); l) M. Sawamura, H. Hamashima, and Y. Ito, *Tetrahedron Asymmetry*, **2**, 593 (1991); m) A. L. Balch, F. Neve, and M. M. Olmstead, *Inorg. Chem.*, **30**, 3395 (1991).
- 2) M. P. Anderson, B. M. Mattson, and L. H. Pignolet, *Inorg. Chem.*, **22**, 2644 (1983); M. P. Anderson, A. L. Casalnuovo, B. J. Johnson, B. M. Mattson, A. M. Mueting, and L. H. Pignolet, *ibid.*, **27**, 1649 (1988); E. Rotondo, G. Bruno, F. Nicoló, S. L. Schiavo, and P. Piraino, *ibid.*, **30**, 1195 (1991); T. Yoshida, K. Tani, T. Yamagata, Y. Tatsuno, and T. Saito, *J. Chem. Soc., Chem. Commun.*, **1990**, 292; T. Tsuda, S. Morikawa, and T. Saegusa, *ibid.*, **1989**, 9.
- 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 C₂₇H₂₇NOP⁺(MH⁺) 412.1835. ¹H NMR (CDCl₃, 270 MHz): δ 1.88(2H, m, C₅H₄NCH₂CH₂), 2.75 (2H, t, *J* = 7.70 Hz, C₅H₄NCH₂), 3.44 (2H, t, *J* = 6.35 Hz, CH₂O), 4.69 (2H, d,

- $J_{\text{PH}} = 1.62$ Hz, $\text{OCH}_2\text{C}_6\text{H}_4$), 6.87-7.56 (22H, m, arom.), 8.49 (1H, m, 6-H of pyridyl group). $^{31}\text{P}\{^1\text{H}\}$ 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 $\text{C}_{27}\text{H}_{26}\text{Cl}_2\text{NOPPd}\cdot\text{CH}_2\text{Cl}_2$: C, 49.92; H, 4.19; N, 2.08; Cl, 21.05%. FD MS m/e 589 (M^+) and 554 [$(\text{M}-\text{Cl})^+$]; 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, $\text{CH}_2\text{CH}_2\text{O}$), 3.53 (2H, t, $J = 5.9$ Hz, $\text{C}_5\text{H}_4\text{NCH}_2$), 3.98 (2H, t, $J = 5.5$ Hz, $\text{CH}_2\text{CH}_2\text{O}$), 5.59 (2H, s, $\text{C}_6\text{H}_4\text{CH}_2\text{O}$), 6.86-7.95 (21H, m, arom.), 9.90 (1H, m, 6-H of pyridyl group); $^{31}\text{P}\{^1\text{H}\}$ 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 $\text{C}_{54}\text{H}_{52}\text{Cl}_6\text{N}_2\text{O}_2\text{P}_2\text{Pd}_3$: 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, $\text{CH}_2\text{CH}_2\text{O}$), 3.96 (2H, t, $J = 6.2$ Hz, $\text{CH}_2\text{C}_5\text{H}_4\text{N}$), 4.04 (2H, t, $J = 8.2$ Hz, CH_2O), 5.60 (2H, s, $\text{C}_6\text{H}_4\text{CH}_2\text{O}$), 6.89-7.95 (23H, m, arom.), 9.04 (1H, ddd, $J = 5.7, 1.5, 0.74$ Hz, 6-H of pyridyl group); $^{31}\text{P}\{^1\text{H}\}$ 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.
- 6) A, D. Allen and T. Theophaides, *Can. J. Chem.*, **42**, 1551 (1964); T. Weil, L. Spaulding, and M. Orchin, *J. Coord. Chem.*, **1**, 25 (1971); K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 4th ed, Wiley-Interscience, New York (1986), pp.191-201.
- 7) H. P. Fritz and D. Sellmann, *J. Organomet. Chem.*, **6**, 558 (1966).
- 8) Crystal data for **2**: $\text{C}_{27}\text{H}_{26}\text{Cl}_2\text{NOPPd}\cdot\text{CH}_2\text{Cl}_2$, $M = 673.8$, triclinic, space group $P\bar{1}$, $a = 10.135(1)$, $b = 16.171(2)$, $c = 9.023(1)$ Å, $\alpha = 99.98(1)$, $\beta = 101.41(1)$, $\gamma = 86.51(1)^\circ$, $U = 1427.0(2)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.568$ g cm⁻³, $D_{\text{obsd}} = 1.54(6)$ g cm⁻³, $F(000) = 680$, $\mu(\text{Mo}-K_\alpha) = 10.97$ cm⁻¹, crystal size: 0.20 x 0.25 x 0.25 mm. 8600 reflections (8324 unique reflections, $R_{\text{sym}}(F_o) = 0.022$) were collected on a Rigaku AFC-4R (8 kW) using graphite monochromated Mo- K_α ($\lambda = 0.71069$ 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 $R = 0.0338$, $R_w = 0.0401$ ($w = 1/\sigma^2(F_o)$, parameters = 325, $\Delta/\sigma_{\text{max}} = 0.00$). The reflection data collection and the all calculations were performed at the Research Center for Protein Engineering Institute for Protein Research Research, Osaka University.
- 9) G. Märkl, *Z. Naturforsch., B*, **18**, 84 (1963).

(Received November 11, 1992)