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A New Palladium(I) Dinuclear Complex Forming a Coplanar Structure for Two Coordination Planes

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Dinuclear Pd(I) and Pt(I) complexes bridged by (dimethylphosphinomethyl)dimethylamine (mm-pcn), $[M_2Cl_2\{\mu\text{-(mm-pcn)}\}_2]$, were prepared. X-Ray crystal structure analysis revealed that the Pd complex is a head-to-tail isomer in which the two coordination planes around Pd are coplanar.

While a number of dinuclear Pd(I) and Pt(I) complexes bridged by bidentate ligands with various donor groups have been reported,[1-3] no complex bridged by ligands with a phosphino donor group and an amino donor group has been known. In this letter we report preparation of dinuclear complexes bridged by (dimethylphosphinomethyl)dimethylamine (mm-pcn), *HT* (head-to-tail)-$[M_2Cl_2\{\mu\text{-(mm-pcn)}\}_2]$ (M = Pd, Pt), and the unusual coplanar structure for two coordination planes around metal found in the Pd complex by X-ray crystal structure analysis.

The mm-pcn ligand was prepared from $KP(CH_3)_2$ and $[(CH_3)_2N{=}CH_2]Cl$ by a reported method[4] and purified by distillation (4.0 kPa, bp 33 - 38 °C). Yield 18.4%. The Pd complex was prepared by reducing a mixture of $[PdCl_2(PhCN)_2]$ (1 mmol) and mm-pcn (2.2 mmol) with $[Pd_2(dba)_3]\cdot CHCl_3$ (0.5 mmol, dba = $(C_6H_5CH{=}CH)_2CO$) in CH_2Cl_2, and crystallized by adding diethyl ether to the reaction mixture. Yield 69%. The Pt complex was obtained similarly from $K_2[PtCl_4]$, mm-pcn, and $[Pt_2(dba)_3]\cdot CHCl_3$. Yield 18.5%. Elemental analysis and ^{31}P NMR spectra ($CDCl_3$; Pd complex: $\delta = -28.5$. Pt complex: $\delta = -35.7$, $^1J_{(Pt,P)} = 3931$, $^2J_{(Pt,P)} = 251.3$, $^3J_{(P,P)} = 11.1$ Hz) indicate *HT*-$[M_2Cl_2\{\mu\text{-(mm-pcn)}\}_2]$ for these complexes,[1] and the structure was confirmed in the Pd complex by X-ray structure analysis.

Crystal data and final R values are: $C_{10}H_{28}Cl_2N_2P_2Pd_2$, MW 522.04, monoclinic, $P2_1/a$, a = 14.7290(8), b = 10.5329(8), c = 11.5706(7) Å, $\beta = 102.392(5)°$, V = 1783.9(2) Å^3, Z = 4, $D_m = 1.87$, $D_x = 1.94$ Mg m^{-3}, and μ(Mo Kα) = 24.60 cm^{-1}, R = 0.042 and $R_w = 0.053$ for 4843 unique reflections.

The structure of the Pd complex in Fig. 1 has two features. One is the extremely short Pd-P lengths (2.164(2), 2.167(2) Å) compared with those of related complexes bridged by diphosphines such as $Me_2PCH_2PMe_2$ (2.275(3), 2.291(3) Å).[2] The difference in Pd-P length may be attributed to a large difference in trans influence between the $-CH_2NMe_2$ and $-CH_2PMe_2$ groups. The other feature is the coplanar structure of two coordination planes around Pd, the dihedral angle between the two planes being only 1.92 (3)°. Two coordination planes in the structurally known related Pd(I) and Pt(I) complexes are always twisted with the dihedral angle of 37 - 51°.[2,3,5] The twisted structure would be more favourable than the coplanar one from both steric and electronic factors.[2] The coplanar structure in the present complex might be enforced by the short nonbonded P···N distance of bridging mm-pcn (2.682(5), 2.691(5) Å). The distance is nearly the same as that of the Pd-Pd bond (2.621(1) Å), and is short to bridge two Pd atoms in a twisted structure.

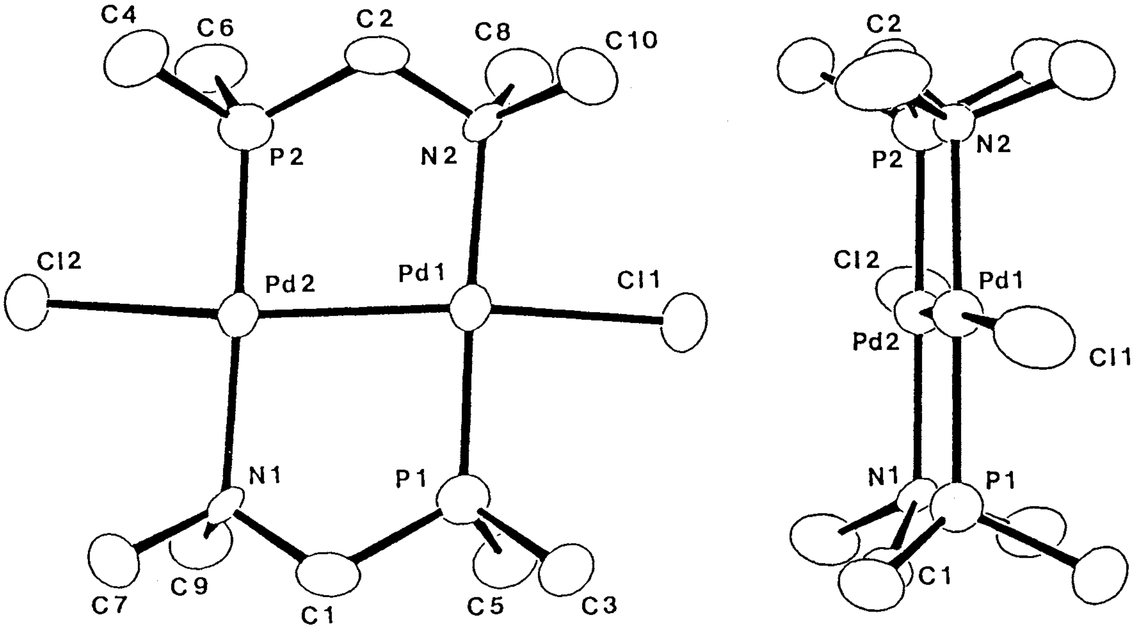

Fig. 1. *ORTEP* drawings of *HT*-$[Pd_2Cl_2\{\mu\text{-(mm-pcn)}\}_2]$.

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