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X-Ray Molecular Structure of a Picolyl-Bridged Dinuclear Palladium(II) Complex, *trans*(*P*,*N*)-[PdCl(μ-C_5H_4N-2-CH_2)PPh_3]$_2$

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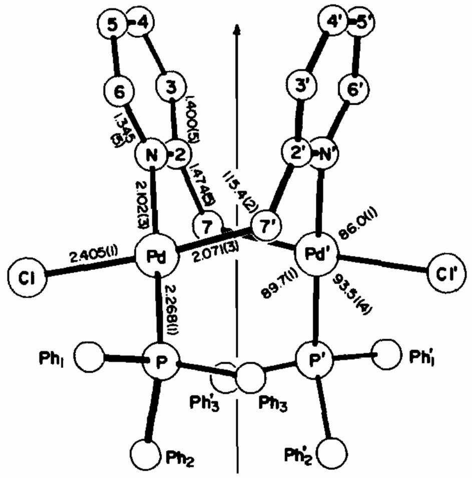

Fig. 1. Stereochemistry of *trans*(*P*,*N*)-[PdCl(μ-C_5H_4N-2-CH_2-*N*,*CH_2*)PPh_3]$_2$ (*I*) viewed perpendicular to the crystallographic two-fold axis, which is indicated by the arrow. The atoms with and without a prime are related to each other by C_2. Phenyl groups are not shown for clarity, except for the three carbon atoms bonded to each phosphorus atom. Important bond lengths (in Å) and angles (in °) are also shown with e.s.d.'s in parentheses. Other relevant length and angles are: C(2)–N 1.344(5) Å, N'–Pd'–C(7) 90.7(1), C(7)–Pd'–Cl' 174.6(1), N'–Pd'–P' 178.3(1), Pd'–N'–C(2') 121.5(2), N'–C(2')–C(7') 117.8(3)°.

In the course of our studies on the σ-pyridyl palladium(II) complexes, we elucidated a novel structure of pyridyl-bridged dinuclear palladium(II) complex [1]. These studies have been extended to the picolyl palladium(II) complexes, of which studies have been rather few. The oxidative addition of 2-chloromethylpyridine to tetrakis(triphenylphosphine)palladium(0) in toluene at 100 °C gave a stable, yellow dinuclear complex, PdCl(C_5H_4N-2-CH_2)-PPh_3]$_2$ (*1*) in a 73% yield, which was characterized by analytical, molecular-weight and IR data as well as ^1H, ^{13}C and ^{31}P NMR spectroscopy [2]. Finally the structure was determined by an X-ray analysis.

Single-crystal specimens of the complex were grown from a dichloromethane–methanol (1:5 by volume) solution.

Crystal Data

$C_{48}H_{42}Cl_2N_2P_2Pd_2$, M_r = 992.6; monoclinic, space group $C2/c$; a = 12.206(1), b = 33.487(4), c = 13.462(1) Å, β = 111.98(1)°; Z = 4; D_m = 1.51, D_x = 1.5132(3) g cm^{-3} (calculated with $2CH_2Cl_2$). The X-ray intensity data up to 2θ of 55° were collected on a computer-controlled diffractometer with the ω–2θ scan mode by use of graphite-monochromated MoKα radiation (λ = 0.71069 Å). The structure was solved by the heavy-atom technique and refined by the block-diagonal least-squares method on the basis of 3961 observed ($|F_o| > 3\sigma(F)$) reflections. A difference Fourier map showed on the two-fold axis a peak of 6.0 eÅ^{-3}, which was tentatively assigned to an oxygen atom of occluded water or disordered MeOH. The final residuals are: R = 0.035 and R_w = $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ = 0.037. The weighting scheme used was $1/w = \sigma^2(F) + 0.00035|F_o|^2$.

The crystal structure consists of discrete dinuclear complex molecules and solvent molecules of crystallization. No unusual intermolecular contact was found. The complex molecule, as shown in Fig. 1, lies on the crystallographic two-fold axis: thus the molecular symmetry is C_2. Hence the centrosymmetric structure proposed by Onishi *et al.* [3] appears to be improbable [4]. The picolyl ligands span the two Pd atoms to give a boat-form-like eight-membered ring. The Pd atom assumes a square-planar configuration: the P and N atoms are *trans* to each other as expected from analogy with the corresponding pyridyl complex [1]. The important dihedral angles are: 34° between the pyridine-ring planes, 63° between the coordination planes, and 85° between the pyridine-ring and the coordination plane.

The Pd–P and Pd–N lengths are almost equal to those found in *trans*(*P*,*N*)-[PdBr(μ-C_5H_4N-*C^2*,*N*)-PPh_3]$_2$ [1], and imply the *trans* influence of PPh_3 as discussed in [1]. The lengths of Pd–C(7) and Pd–Cl bonds are comparable to those of 2.405(3) Å and 2.086(11) Å, respectively, found in one of the complexes containing a *trans*-C(sp^3)Pd^{II}–Cl fragment [5], and are in the expected ranges for the Pd^{II}–C(sp^3) and Pd^{II}–Cl bond lengths.

As far as we know, the present complex is the first example of picolyl-bridged dinuclear complexes well characterized by X-ray crystallographic study.

The PPh_3 ligand in *1* is readily replaced by another more basic phosphine (L) such as PMe_2Ph and PEt_3 prior to the bridge-splitting reaction to give a mononuclear complex, *trans*-[PdCl(picolyl)L_2]. Complex *1* also reacts with carbon monoxide in THF at room temperature to afford a mononuclear insertion product, $[\overline{\mathrm{PdCO(2\text{-}CH_2)C_5H_4N}}\mathrm{(PPh_3)Cl}]$.

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