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Deprotonated 2-Benzylpyridine as a Bridging Ligand. Synthesis and Structure of the Binuclear Palladium(II) Complex *trans*(N,N)-[Pd(μ-pyCHPh-N,CH)(γ-picoline)Cl]$_2$·CH_2Cl_2

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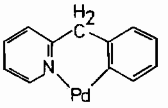
The initial report [1] that 2-benzylpyridine is readily orthometallated by palladium(II) acetate to give [Pd(pyCH$_2$(C$_6$H$_4$)-N,C^1)(μ-O$_2$CMe)]$_2$, with deprotonated 2-benzylpyridine bonded to palladium(II) as in (1), has led to extensive development of the organopalladium(II) chemistry of orthometallated 2-benzylpyridine [1–3].



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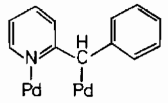

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As part of a study of the chemistry of anions of 2-pyridylmethanes [4], we have obtained a complex containing the moiety (2) on reaction of PdCl$_2$(γ-picoline)$_2$ with 2-benzylpyridine deprotonated by n-butyllithium. As this represents a new binding mode for deprotonated 2-benzylpyridine, we report here the synthesis and structure of *trans*(N,N)-[Pd(μ-pyCHPh-N,CH)(γ-picoline)Cl]$_2$·CH$_2$Cl$_2$ prior to investigation of its reactivity.

In a typical synthesis, lithiated 2-benzylpyridine in tetrahydrofuran was added to an equimolar quantity of PdCl$_2$(γ-picoline)$_2$ in diethyl ether at −80 °C under nitrogen. Benzene was added at ambient temperature, and on warming at 60 °C for 1 h, hydrolysis gave an orange solid from the organic phase. Extraction with hexane gave a small quantity (*ca.* 4% yield) of (pyCHPh)$_2$, which has been obtained previously in 80% yield from reaction of lithiated 2-benzylpyridine with mercury(II) iodide [4]. Recrystallization of the remaining orange residue from dichloromethane/acetone gave orange-red crystals of the title compound in *ca.* 30% yield, containing traces of recrystallization solvents.

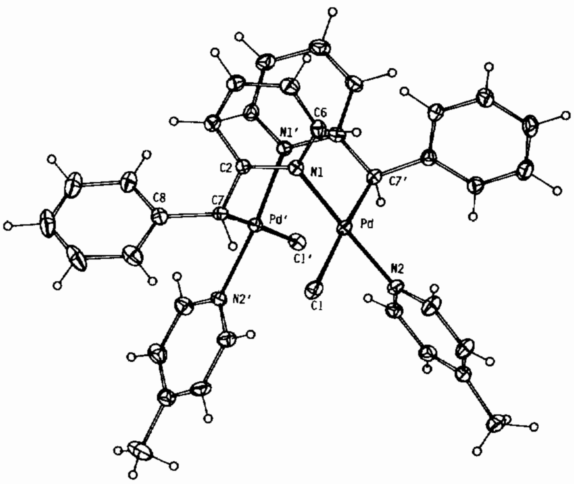

Fig. 1. ORTEP drawing of *trans*(N,N)-[Pd(μ-pyCHPh-N,CH)-(γ-picoline)Cl]$_2$ with selected atom numbering, bond distances (Å) and angles (deg) for the coordination plane of Pd [with corresponding values for Pd' in parentheses], and for the nitrogen and carbon atoms of pyCHPh$^-$ bonded to palladium: Pd–C7, 2.070(6) [2.079(5)]; Pd–N1, 2.046(4) [2.029(5)]; Pd–N2, 2.049(4) [2.041(5)]; Pd–Cl, 2.430(2) [2.446(2)]; C7'–Pd–N1, 91.7(2) [94.0(2)]; C7'–Pd–N2, 89.5(2) [88.6(2)]; N1–Pd–Cl, 91.1(1) [87.7(1)]; N2–Pd–Cl, 87.6(1) [89.9(1)]; C2–N1–Pd, 121.4(4) [124.0(4)]; C6–N1–Pd, 118.8(4) [119.7(5)]; C2'–C7'–Pd, 117.3(4) [112.9(4)]; C8'–C7'–Pd, 106.3(4) [112.1(4)]; C2–C7–C8, 115.5(4) [116.6(5)].

A single crystal X-ray study allowed unambiguous stereochemical assignment as the title compound (Fig. 1). Crystal data for $C_{37}H_{36}N_4Cl_2Pd_2$: monoclinic, space group $P2_1/c$ with a = 13.967(2), b = 13.996(3), c = 18.886(2) Å; β = 98.74(1) deg; V = 3649(1) Å^3; Z = 4 (two dimers/cell); ρ_{calc} = 1.623 g cm^{-3}; F(000) = 1784 electrons; μ(Mo–K$_\alpha$) = 12.9 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.3 × 0.3 × 0.1 mm, within the limit $2\theta_{max}$ = 50° using a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode; 6446 independent reflections were collected, 4930 with $I > 3\sigma(I)$ being considered 'observed' and used in the 9 × 9 block diagonal least squares refinement after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; hydrogen atoms were included at calculated positions (x, y, z, U_{iso}) and constrained. Residuals (F) at convergence were 0.037, 0.032 (R,R'), reflections weights being $(\sigma^2(F_o) + 0.0005(F_o)^2)^{-1}$. Neutral complex scattering factors were used [5]; computation used the XTAL 83 program system [6] implemented by Dr. S. R. Hall on a Perkin-Elmer 3240 computer.

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The complex has minor differences in coordination geometry for the two palladium atoms (Fig. 1). Two 2-benzylpyridine ligands link the palladium atoms as shown schematically in (**2**), with the square-planar coordination of palladium based on a *trans*-arrangement of nitrogen donors, '*trans*-PdN_2CCl'. Bond angles for the palladium atoms range from 87.7(1)–94.0(2)°, with maximum deviation from the mean planes 'PdN_2CCl' observed for N2 [0.057(6) Å]. The palladium atoms Pd and Pd′ are 3.0620(7) Å apart, and the structure of the complex is similar to that reported for the α-picolyl complex *trans*(P,N)-$[Pd(\mu\text{-}pyCH_2\text{-}N,CH)(PPh_3)Cl]_2$, obtained by oxidative addition of $pyCH_2Cl$ to $Pd(PPh_3)_4$ [7].

The complex $Pd(PyCH_2(C_6H_4)\text{-}N,C^1)(3,5\text{-}lutidine)Cl \cdot 0.2\,CH_2Cl_2$ [1] may be compared directly with *trans*(N,N)-$[Pd(\mu\text{-}pyCHPh\text{-}N,CH)(\gamma\text{-}picoline)Cl]_2 \cdot CH_2Cl_2$, as both complexes have a '*trans*-PdN_2CCl' coordination geometry, but with deprotonated 2-benzylpyridine present as (**1**) and (**2**), respectively. Work is in progress on a comparison of the reactivity of the different coordination forms of deprotonated 2-benzylpyridine.

Acknowledgements

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