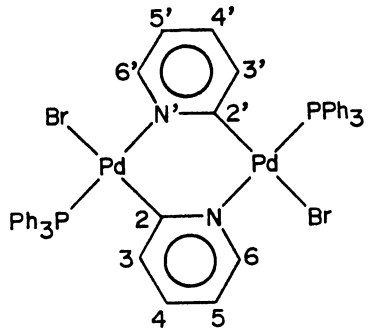
CHEMISTRY LETTERS, pp. 913-914, 1980. 

# X-RAY MOLECULAR STRUCTURE OF A PYRIDYL-BRIDGED DINUCLEAR PALLADIUM COMPLEX, trans(P,N)-[PdBr(μ-$C_5H_4N$-$C^2$,N)($PPh_3$)]$_2$

Kazumi NAKATSU,* Kenji KINOSHITA,* Hitoshi KANDA,* Kiyoshi ISOBE,**
Yukio NAKAMURA,** and Shinichi KAWAGUCHI**
*Department of Chemistry, Faculty of Science, Kwansei Gakuin University, Uegahara, Nishinomiya, Hyogo 662
**Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558

The structure of the dinuclear complex obtained from the reaction of $Pd(PPh_3)_4$ and 2-bromopyridine was determined by X-ray analysis to be trans(P,N)-bis-[bromo(μ-pyridyl-$C^2$,N)(triphenylphosphine)palladium(II)], having an approximate symmetry of $C_2$.

2-Bromopyridine reacted with tetrakis(triphenylphosphine)palladium(0) in toluene at 90 °C to give a stable dinuclear complex, [PdBr($C_5H_4N$)($PPh_3$)]$_2$, (1), whereas 3- and 4-bromopyridines afforded mononuclear complexes, trans-[PdBr($C_5H_4N$-$C^2$ and $C^4$)($PPh_3$)$_2$].[1] X-Ray analysis of (1) revealed that, contrary to our expectation, the bridging ligands are not bromines but pyridyls. Thus (1) is written as trans(P,N)-bis[bromo(μ-pyridyl-$C^2$,N)(triphenylphosphine)palladium(II)]. Figure shows the novel molecular structure of (1).



(1)

Single crystal specimens were grown from a dichloromethane—methanol solution. Crystal Data: $C_{46}H_{38}Br_2N_2P_2Pd_2$, $M_r$ = 1053.2; triclinic, space group $P\bar{1}$; a = 13.134(2), b = 18.122(3), c = 10.588(4) Å, α = 101.56(2), β = 108.62(1), γ = 79.25(1)°; Z = 2; $D_x$ = 1.5804(7) g cm$^{-3}$. Intensities of the reflections currently up to 2θ of 45° were measured by an automatic diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by the heavy-atom technique and refined by the least-squares method to a current conventional R value of 6.4% for the 5079 observed reflections, anisotropic thermal vibrations being assumed for the non-hydrogen atoms. The hydrogen atoms were not included in the refinement. The $C^2$ and N atoms were identified from the distribution of the residual electron densities on difference Fourier maps around those atoms, and from their reasonable temperature factors.[2] The longer bond lengths of $C^2$-$C^3$ than those of N-$C^6$ support the present identification.

Each Pd atom assumes a square-planar configuration: the Br and $C^2$ atoms are trans to each other about the Pd atom as expected from similar oxidative addition reactions so far studied. Unusually, the Pd—($C_5H_4N$)$_2$—Pd part is folded along the Pd...Pd line to give a six-membered boat-form ring. The dihedral angle between the pyridyl planes is 82°; that between the coordination

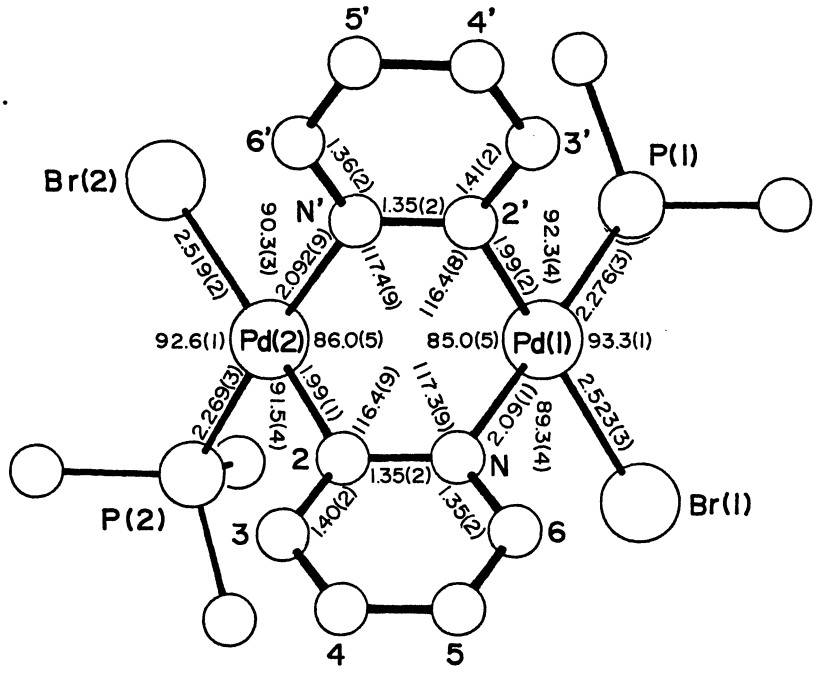



Figure. Stereochemistry of trans(P,N)-[PdBr(μ-$C_5H_4N$-$C^2$,N)($PPh_3$)]$_2$, (1), viewed perpendicular to the plane containing C(2), N, C(2'), and N'. Phenyl groups are not shown for clarity, except for the three carbon atoms bonded to each phosphorus atom. Important bond lengths(in Å) and angles(in °) are also given with e.s.d.'s in parentheses.

| | |
|---|---|
| Pd(1)-N-C(6) | 122.6(9)° |
| Pd(2)-N'-C(6') | 121.7(9) |
| Pd(1)-C(2')-C(3') | 124.1(12) |
| Pd(2)-C(2)-C(3) | 123.7(11) |
| Br(1)-Pd(1)-C(2') | 172.1(4) |
| Br(2)-Pd(2)-C(2) | 172.8(4) |
| P(1)-Pd(1)-N | 177.4(4) |
| P(2)-Pd(2)-N' | 174.8(4) |

planes is 79°. Thus the approximate symmetry of the molecule is $C_2$. The long Pd...Pd distance of 3.194(2) Å implies no bonding interaction between the metal atoms.

The distances of Pd-C(av 1.99 Å) and Pd-N(av 2.09 Å) are in the range of 1.98-2.03 Å observed for $Pd^{II}$-C($sp^2$) with trans-Br and 2.02-2.09 Å for $Pd^{II}$-N(py and bpy), respectively. The Pd-Br lengths(av 2.521 Å) agree with the reported values(2.490-2.562 Å) for those with the trans ligand atom of C($sp^2$), while the Pd-P lengths(av 2.273 Å) are slightly shorter than those so far found (2.306-2.350 Å).

Compound (1) did not react with a large excess of pyridine, but reacted with excess triethylphosphine to result in trans-[PdBr($C_5H_4N$-$C^2$)($PEt_3$)$_2$], which gave a value of 8.04 as $pK_a$ of its conjugate acid in dioxane-water(1:1 by volume).[1] Such an astonishingly increased basicity of the pyridine coordinated to palladium via $C^2$ may be the origin of stability of the pyridyl-bridged structure of (1).

As far as we know, the present complex is the first example of pyridyl-$C^2$,N-bridged dinuclear complex fully characterized by X-rays, although a similarly bridged trinuclear structure was presumed for 2-pyridylgold(I).[3]

References and Note

1) K. Isobe, E. Kai, Y. Nakamura, K. Nishimoto, T. Miwa, S. Kawaguchi, K. Kinoshita, and K. Nakatsu, J. Am. Chem. Soc., 102, 2475(1980).
2) The isotropic temperature factors equivalent to the anisotropic ones were 2.7 $Å^2$ for all the N and $C^2$ atoms.
3) L. G. Vaughan, J. Am. Chem. Soc., 92, 731(1970).

(Received May 31, 1980)