

## Out-of-plane Trigonal Co-ordination in a Zerovalent Palladium Complex

Carlo A. Ghilardi, Stefano Midollini, Simonetta Moneti, and Annabella Orlandini

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via F. D. Guerrazzi, 27 50132 Firenze, Italy

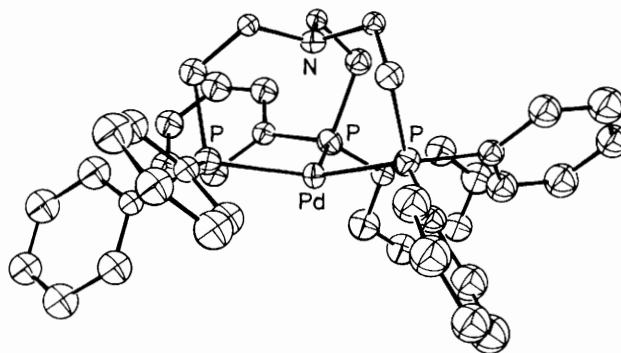
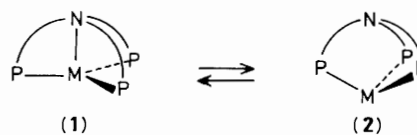
A complete structural determination has shown that the  $[\text{Pd}\{\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]$  complex displays an unusual out-of-plane trigonal co-ordination; the title compound undergoes oxidation with alkyl iodide to form five-co-ordinate methyl and ethyl palladium derivatives.

Multidentate ligands usually place strong restrictions on a metal's co-ordination number and geometry. In contrast the tripod-like phosphine,  $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ ,  $\text{np}_3$ , shows a noteworthy flexibility in terms of both unusual stereochemistry and the reactivity that it confers to its compounds.<sup>1</sup> This flexibility is essentially determined by the facile interconversion† between conformations (1) and (2) which is achieved by simple torsion of the C–C bond of the chains, the nature of the metal and of the coligand being of critical importance in determining the complex geometry.

The trigonal pyramidal geometry (1) has been established in the complex  $[\text{Ni}(\text{np}_3)]$  by an X-ray structural determination.<sup>2</sup> Now we report the molecular structure‡ of the complex  $[\text{Pd}(\text{np}_3)]^3$  which exhibits the unusual out-of-plane trigonal geometry (2). The three-co-ordinate palladium complexes have so far been attributed<sup>4</sup> planar trigonal co-ordination as in  $[\text{Pt}(\text{PPh}_3)_3]$ .<sup>5</sup>

The molecular structure of  $[\text{Pd}(\text{np}_3)]$  is shown in Figure 1. The palladium atom is co-ordinated by the three phosphorus atoms of the ligand in a trigonal distorted mode. The metal

atom, which lies together with the nitrogen atom on a crystallographic three-fold axis, is 0.42 Å out of the phosphorus plane in the opposite direction to the central nitrogen ligand. It follows that the metal–nitrogen separation reaches the value of 2.687(13) Å. This value together with the reduced tetrahedral character of the nitrogen atom [C–N–C = 113.4(19)°] is indicative of a palladium–nitrogen repulsion. Moreover the i.r. spectrum shows a band at 2820  $\text{cm}^{-1}$  of  $\text{CH}_2$  stretching frequencies, typical of  $\text{np}_3$  complexes with no metal–nitrogen bonding.<sup>6</sup>

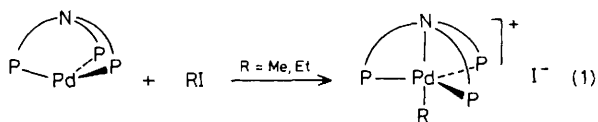


**Figure 1.** The molecular structure of  $[\text{Pd}(\text{np}_3)]$ . ORTEP drawing with 30% probability ellipsoids. Selected bond distances and angles: Pd···N 2.687(13), Pd–P 2.298(7) Å, N–Pd–P 79.4(5), P–Pd–P 116.7(2)°.

† Recent MO calculations<sup>1b</sup> have shown that for  $d^{10}$  metals this interconversion is symmetry allowed and requires an activation energy of a few kilocalories per mole.

‡ Crystal data for  $[\text{Pd}(\text{np}_3)] \cdot 0.5\text{Me}_2\text{CO}$ :  $M = 789.1$ , trigonal, space group  $R\bar{3}$ ,  $a = 10.827(8)$  Å,  $\alpha = 108.82(9)^\circ$ ,  $U = 999.9$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.31$  g  $\text{cm}^{-3}$ , monochromatic Mo- $K_\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu(\text{Mo-}K_\alpha) = 6.05$   $\text{cm}^{-1}$ . The intensity data were collected within  $2\theta \leq 40^\circ$  on a Philips PW 1100 diffractometer using  $\omega$ - $2\theta$  scan technique at 295 K. The structure was solved by the heavy atom method and refined by full-matrix least-squares procedure. The phenyl rings were treated as rigid groups and the hydrogens were included in their calculated positions but not refined. Final  $R$  and  $R_w$  values 0.054 and 0.051 for 574 observed [ $I > 3\sigma(I)$ ] reflections.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.



Both electronic and steric factors have been generally invoked to justify low co-ordination numbers for  $d^{10}$  metal complexes.<sup>7</sup> The comparison of the geometries of  $[\text{Ni}(\text{np}_3)]$  and  $[\text{Pd}(\text{np}_3)]$  shows the fundamental role of the electronic factors. As a matter of fact in the title compound, notwithstanding the availability of the fourth donor atom, the tripod ligand is forced to distort itself in order to allow the metal a  $16 e^-$  configuration.

The versatility of the  $\text{np}_3$  ligand is further illustrated by the oxidative addition of alkyl halides to the title complex.  $[\text{Pd}(\text{np}_3)]$  reacts, at room temperature, in tetrahydrofuran solution with  $\text{RI}$  ( $\text{R} = \text{Me}, \text{Et}$ ) to form crystalline products of formula  $[(\text{np}_3)\text{PdR}]\text{I}$ , equation (1).

The complexes, which are stable under a nitrogen atmosphere, behave as 1 : 1 electrolytes in 1,2-dichloroethane. The  $^{31}\text{P}$   $\{^1\text{H}\}$  n.m.r. spectra of the complexes ( $\text{CD}_2\text{Cl}_2$ ), showing only a singlet [ $\delta$  9.6 ( $\text{R} = \text{Me}$ ), 8.95 ( $\text{R} = \text{Et}$ )], indicate the symmetrical co-ordination of the three  $\text{np}_3$  phosphorus atoms. The  $^1\text{H}$  n.m.r. spectrum of  $[(\text{np}_3)\text{Pd}(\text{CH}_3)]\text{I}$  ( $\text{CD}_2\text{Cl}_2$ ) shows besides the ligand signals [ $\delta$  7.25 (m, 30H, aromatic CH), 3.0 (m, 6H, N- $\text{CH}_2$ ), 2.65 (m, 6H,  $\text{CH}_2\text{-P}$ )] a quartet (3H,  $^3J_{\text{P-H}}$  8 Hz) at  $\delta$  1.6 which must be attributed to the  $\text{CH}_3$  group linked to the metal. The  $^1\text{H}$  spectrum of the ethyl derivative is closely related, with the signal due to the  $\text{CH}_2\text{-Pd}$  group at  $\delta$  1.1 (complicated multiplet, 2H) and the  $\text{CH}_3$  (ethyl) signal

superimposed on the  $\text{CH}_2\text{-CH}_2$  phosphine absorptions. On the other hand the i.r. spectra are indicative of the nitrogen atom's co-ordination. These data are consistent with a trigonal bipyramidal geometry which is quite unusual for alkyl palladium derivatives.

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