# Exocylic Co-ordination of Phosphonitriles: The Crystal and Molecular Structure of $N_4P_4(NMe_2)_8$, $W(CO)_4$

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Summary In the compound $N_4P_4(NMe_2)_8$,$W(CO)_4$, the phosphonitrile acts as a bidentate σ-ligand, through one ring nitrogen atom and one exocyclic group.

Phosphonitrile derivatives form complexes with transition metal ions, and, where the geometry has been established crystallographically,[1-3] co-ordination occurs through the ring nitrogen atoms. They also react with metal carbonyls,[4] but hitherto no structures have been determined. The structure of the title compound is unusual in that the metal is co-ordinated to both a ring nitrogen atom and an exocyclic dimethylamido-group. The yellow crystals are monoclinic, $a = 18\cdot274$, $b = 18\cdot594$, $c = 10\cdot533$ Å, $\beta = 90\cdot39°$, $Z = 4$, space group $P2_1/n$. The structure was determined with Mo-K_α diffractometer data from Patterson and electron density maps, and was refined by full-matrix least squares methods to $R = 0\cdot071$ for 2545 observed reflections. Some of the more immediately important bond lengths $[\sigma(P-N) = 0\cdot02$ Å$]$ are shown in the Figure. The four atoms N(1)WN(8)P(2) are nearly coplanar, the co-ordination direction at N(1) being reasonably near the conventional lone pair direction, as it is when co-ordinated to protons[3,5,6] and transition metal ions.[1-3] In the unco-ordinated ligand,[7] substantial delocalisation of the lone
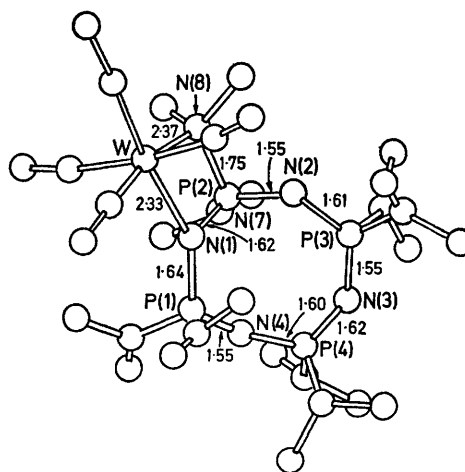
pairs on the dimethylamido-groups into the ring shortens the exocyclic P–N bonds from the single bond length[8] of 1·77 Å to 1·68 Å, the mean sum of the angles round the nitrogen atoms being 353°. In the complex, the tungsten atom is a competitive acceptor; P(2)N(8) is increased to 1·75 Å, and the co-ordination of N(8) is tetrahedral, dona-

tion from this atom to phosphorus being minimal. The compound appears to be a simple *cis-σ*-complex, an interpretation supported by a comparison of its carbonyl stretching frequencies (2000, 1870, 1849, 1809 cm⁻¹) with those[9] of enW(CO)$_4$ (2006, 1867, 1852, 1809 cm⁻¹). Coordination has further effects on the geometry of the ligand. The ring is formed from two nearly planar segments N(4)P(1)N(1)P(2) and P(2)N(2)P(3)N(3)P(4)N(4), making a dihedral angle of 53·7°, the former set being nearly coplanar with N(1)WN(8)P(2).

Three bonds, P(2)N(2), P(3)N(3), and N(4)P(1) are significantly shorter than the other five; a first order perturbation treatment accounts for these differences satisfactorily.[10] We thank the National Research Council of Canada for financial support.

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