Preparation and Crystal Structure of $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$

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The complex $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$ has been prepared and structurally characterised by *X*-ray analysis.

Although the conversion of terminal dinitrogen into ammonia in mononuclear complexes of tungsten has been studied in detail and related to the function of nitrogenase,[1-3] there has been no similar study of bridging dinitrogen, because no dimeric tungsten complex containing bridging dinitrogen has hitherto been reported. Moreover, complexes with both bridging and terminal dinitrogen groups are confined to the group 4 metals, *i.e.* $[\{M(C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$ (M = Ti or Zr).[1,4]

Here we report the preparation and structure of a tungsten complex containing both terminal and bridging dinitrogen ligands, $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$ (**1**).

Compound (**1**) is isolated in rather low yields (10—15%) from the reduction with magnesium (with PEt_2Ph) of WCl_6 or *trans*-$[WCl_4(PEt_2Ph)_2]$ in tetrahydrofuran (THF) under dinitrogen at 20 °C. The purification is complicated by the formation of other dinitrogen complexes, *e.g.* $[W(N_2)_2(PEt_2Ph)_4]$ in the reaction mixture; these are difficult to separate. Complex (**1**) forms bright red plates which analyse as $W(N)_5(PEt_2Ph)_3$ and has N_2 stretching bands in its i.r. spectrum (Nujol) at 1890 and 1895 cm^{-1}. Its ^{31}P n.m.r. spectrum [THF; rel. to $P(OMe)_3$] has resonances at δ −134.7 (t) and −138.6 p.p.m. (d), a pattern typical of a meridional arrangement of phosphines.

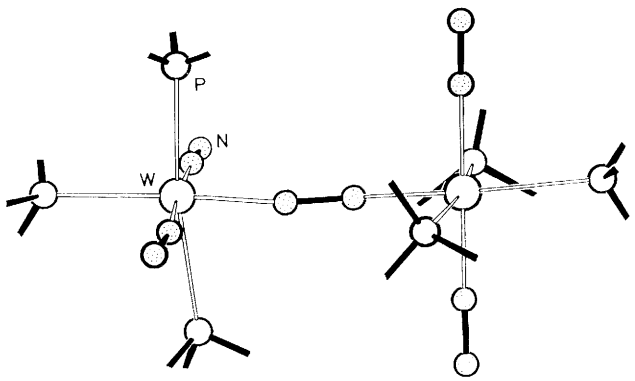

Figure 1. The core of the structure of $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$, (**1**).

These data are consistent with the preliminary *X*-ray structure (Figure 1) which shows that (**1**) has two $W(N_2)_2(PEt_2Ph)_3$ units linked by a bridging dinitrogen ligand.

Crystal data: $C_{60}H_{90}N_{10}P_6W_2$, M = 1505.0, monoclinic, a = 19.08(1), b = 14.79(2), c = 25.32(2) Å, β = 110.1(7)°, U =

6711 Å^3, space group $P2_1/c$, $D_c = 1.49$ g cm^{-3}, $Z = 4$, $F(000) = 3032$, μ(Mo-K_α) = 36.8 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.†

The crystals are fragile, extremely fine plates and are air-sensitive. A selected crystal was coated in epoxy-resin to arrest deterioration, and photographed to confirm acceptability. Data collection by diffractometer was difficult, and of 2567 independent reflections with $\theta \leqslant 15°$, only 1029 were considered observed with $I > 2\sigma(I)$. The current state of refinement of the structure ($R = 0.15$) does not allow discussion of bond distances. Nevertheless, the structure of the complex is unequivocally established as shown in Figure 1 (the phosphine substituent groups have been omitted for clarity).

Each tungsten is octahedrally co-ordinated with a *mer*-arrangement of phosphine ligands, two *trans* terminal dinitrogen ligands, and the bridging N_2 ligand. The co-ordination octahedra of the pair of tungsten atoms are rotated about the W–W axis by *ca.* 90°, so that, in every case, a terminal N_2 ligand on one W-atom is eclipsed by a W–P bond on the other.

Complex (**1**) reacts with HCl (THF, 20 °C) to give hydrazine and this and other reactions will be described at a later date. Possibly the bulky PEt_2Ph ligand hinders approach of a fourth phosphine to the metal, thus allowing entry of the bridging dinitrogen ligand. It is also possible that analogues of (**1**), or dinitrogen complexes of low co-ordination number, will exist for other bulky phosphine co-ligands.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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