

### Preliminary communication

## PREPARATION AND PROPERTIES OF DINITROGEN COMPLEXES OF MOLYBDENUM AND TUNGSTEN WITH TRIMETHYLPHOSPHINE AS COLIGAND

### III\*. SYNTHESIS AND PROPERTIES OF *cis*-[W(N<sub>2</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>], *trans*-[W(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>] AND [M(N<sub>2</sub>)(PMe<sub>3</sub>)<sub>5</sub>] (M = Mo, W). THE CRYSTAL AND MOLECULAR STRUCTURE OF [Mo(N<sub>2</sub>)(PMe<sub>3</sub>)<sub>5</sub>]

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### Summary

The reduction of [WCl<sub>4</sub>(PMe<sub>3</sub>)<sub>3</sub>] with dispersed sodium, under dinitrogen, gives *cis*-[W(N<sub>2</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>], while under ethylene *trans*-[W(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>] is obtained. The ethylene complex can also be prepared by displacement of the dinitrogen molecules in *cis*-[W(N<sub>2</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>] by ethylene at room temperature and pressure. Interaction of *cis*-[M(N<sub>2</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>] complexes (M = Mo, W), with PMe<sub>3</sub>, under helium or argon, yields [M(N<sub>2</sub>)(PMe<sub>3</sub>)<sub>5</sub>]. The molybdenum complex crystallizes in the orthorhombic space group *Pnma*, with *a* 22.063(6), *b* 12.106(4), *c* 9.745(4) Å. The Mo—P distance *trans* to the dinitrogen ligand (2.483(7) Å) is slightly longer than the average of the other four Mo—P bonds (2.460(5) Å).

In a recent publication [1] we have described the synthesis and properties of some new dinitrogen and ethylene complexes of molybdenum of the types *cis*- and *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>] and *trans*-[Mo(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>]. We have now extended this work to the tungsten analogues, and prepared what seem to be the first examples of a new class of dinitrogen complexes of these metals, namely those of the type [M(N<sub>2</sub>)(PMe<sub>3</sub>)<sub>5</sub>] (M = Mo, W), which contain a

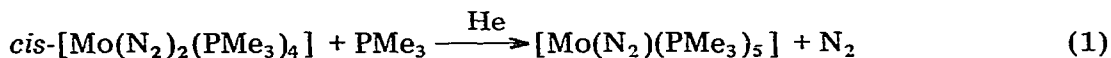
\*For part 2 see ref. 6.

single dinitrogen molecule and five tertiary phosphine ligands coordinated to the central atom. The molybdenum complex has been independently prepared from metal-atom synthesized  $[\text{Mo}(\text{PMe}_3)_6]$  and  $\text{N}_2$  [2].

When  $\text{WCl}_6$  and  $\text{PMe}_3$  are treated in toluene at  $120^\circ\text{C}$  in a sealed tube, the known complexes [3]  $[\text{WCl}_4(\text{PMe}_3)_2]$  or  $[\text{WCl}_4(\text{PMe}_3)_3]$  can be isolated in high yields depending on the  $\text{WCl}_6/\text{PMe}_3$  molar ratio. The reduction of  $[\text{WCl}_4(\text{PMe}_3)_3]$  with dispersed sodium, in tetrahydrofuran, under  $\text{N}_2$ , gives initially [3]  $[\text{WCl}_3(\text{PMe}_3)_3]$ . If the solution of this complex is further reduced, in the presence of 0.7–0.8 equiv of  $\text{PMe}_3$ , *cis*- $[\text{W}(\text{N}_2)_2(\text{PMe}_3)_4]$  (I), is formed in ca. 40–50% yield (total reaction time 4–6 h). Evaporation of the solvent in *vacuo*, extraction with petroleum ether and centrifugation, affords a yellow-orange solution from which yellow, very air and moisture sensitive crystals of I were isolated by partial removal of the solvent under vacuum and cooling at  $-30^\circ\text{C}$  (Anal. Found: C, 26.67, H, 6.62; N, 10.30; P, 22.80.  $\text{WC}_{12}\text{H}_{36}\text{N}_4\text{P}_4$  calcd.: C, 26.48; H, 6.65, N, 10.86; P, 21.86%. If the reduction of  $[\text{WCl}_4(\text{PMe}_3)_3]$  is carried out under an ethylene atmosphere, the bis(ethylene) complex *trans*- $[\text{W}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)_4]$  (II) is formed. (Anal. Found: C, 34.92; H, 8.01.  $\text{WC}_{16}\text{H}_{44}\text{P}_4$  calcd.: C, 35.30; H, 8.09%. Complex II can also be obtained by interaction of I with  $\text{C}_2\text{H}_4$ , in hexane, at ambient temperature and pressure, over a period of 8–10 h.

As expected the IR spectrum of I shows two absorption bands at 2000 and  $1940\text{ cm}^{-1}$  (Nujol), both NN stretches being very intense, while the  $^1\text{H}$  NMR consists of two resonances of equal intensity ( $\text{C}_6\text{H}_6$ ,  $35^\circ\text{C}$ ) at  $\delta$  1.5 and 1.3 ppm, resembling respectively a virtually coupled triplet and a filled-in doublet. For II no bands due to the stretching of the C–C double bonds could be found in the IR spectrum, but the presence of coordinated ethylene is indicated by a weak absorption at ca.  $3020\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of the ethylene complex is not very informative consisting of a rather broad singlet centered at  $\delta$  1.3 ppm with resonances due to the ethylene ligands superimposed on the higher field side. Complex II is isostructural with its molybdenum analogue [1,4], and has the ethylene molecules staggered with respect to one another and eclipsing the *trans*-P–W–P bonds. Both ethylene molecules are symmetrically bound to the W atom, the mean distance for the W–C bonds being  $2.26(1)\text{ \AA}$ .

When *cis*- $[\text{Mo}(\text{N}_2)_2(\text{PMe}_3)_4]$  [1] is dissolved in petroleum ether under helium, in the presence of 2–3 equivalents of  $\text{PMe}_3$ ,  $[\text{Mo}(\text{N}_2)(\text{PMe}_3)_5]$  (III), is formed according to eq. 1:



The course of this reaction can be followed by IR spectroscopy. After stirring at room temperature for ca. 8 h the two characteristic solution bands of *cis*- $[\text{Mo}(\text{N}_2)_2(\text{PMe}_3)_4]$ , at  $2020$  and  $1965\text{ cm}^{-1}$ , disappear while a new strong absorption appears at  $1950\text{ cm}^{-1}$ . From the resulting solution, III can be crystallized in very high yields (90–95%), by evaporation of the solvent to dryness, extraction with petroleum ether, centrifugation, partial removal of the solvent in *vacuo* and cooling at  $-20^\circ\text{C}$  (Anal. Found C, 35.80; H, 8.90; N, 5.47.  $\text{MoC}_{15}\text{H}_{45}\text{N}_2\text{P}_5$  calcd.: C, 35.72; H, 8.93; N, 5.55%. The tungsten

complex I behaves similarly, although its reaction with  $\text{PMe}_3$  is slower and needs stirring at  $40\text{--}50^\circ\text{C}$ , under helium, for 24 h for completion.  $[\text{W}(\text{N}_2)(\text{PMe}_3)_5]$  (IV), can be isolated as yellow, very air and moisture sensitive crystals from petroleum ether solutions, also in very high yields. (Anal. Found: C, 29.36; H, 7.53; N, 4.55.  $\text{WC}_{15}\text{H}_{45}\text{N}_2\text{P}_5$  calcd.: C, 30.40; H, 7.60, N, 4.72%. The  $^1\text{H}$  NMR spectra of complexes III and IV are very similar, consisting of a rather broad singlet and a doublet (36H: 9H) in the region  $\delta$  1.7–1.3 ppm. While the conversion of the *cis*- $[\text{M}(\text{N}_2)_2(\text{PMe}_3)_4]$  complexes to the mono-dinitrogen derivatives  $[\text{M}(\text{N}_2)(\text{PMe}_3)_5]$  ( $\text{M} = \text{Mo}, \text{W}$ ) is essentially complete under the conditions mentioned, the reverse reactions do not occur so readily and, as an example, complex IV is recovered, together with some decomposition products, after being heated at  $50^\circ\text{C}$  under dinitrogen for 18 h.

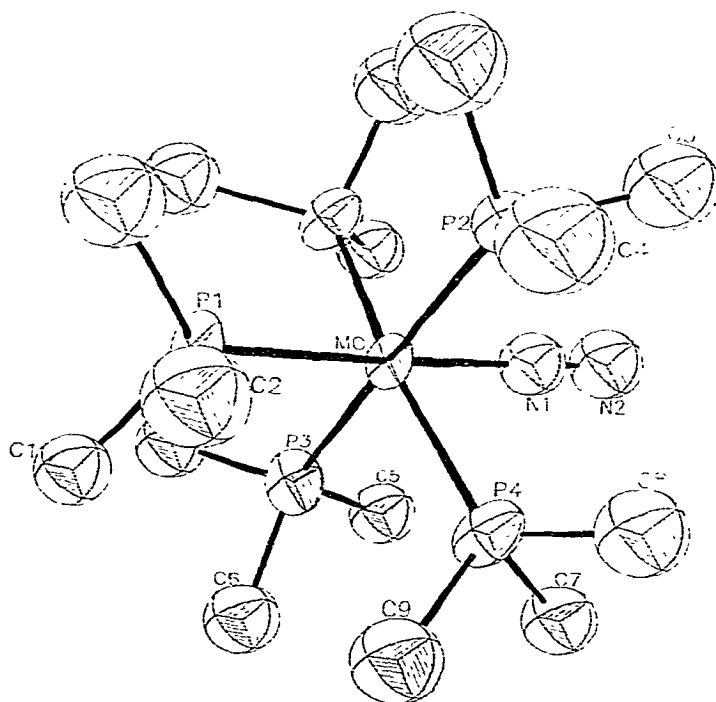


Fig. 1. The molecular structure of  $[\text{Mo}(\text{N}_2)(\text{PMe}_3)_5]$  with the atoms represented by their 50% probability ellipsoids for thermal motion.

The structure of  $[\text{Mo}(\text{N}_2)(\text{PMe}_3)_5]$  (III) is shown in Fig. 1 [5]. The molecule is essentially octahedral and resides on a crystallographic mirror plane containing Mo, P(1), P(2), P(3), N(1), N(2), C(1), and C(3). The dinitrogen moiety is bonded to the Mo atom with Mo–N 2.02(3) and N–N 1.12(3) Å. The Mo–P distance *trans* to the dinitrogen ligand is slightly longer at 2.483(7) Å than the average of the other four Mo–P bond lengths (2.460(5) Å).

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- 3 P.R. Sharp and R.R. Schrock, *J. Am. Chem. Soc.*, **102** (1978) 1430.
- 4 II crystallizes in the monoclinic space group  $P2_1/n$ , with  $a$  10.130(3),  $b$  13.699(4),  $c$  17.029(5) Å,  $\beta$  98.84(2) $^\circ$ ,  $U$  2335.1 Å $^3$ ,  $D_c$  1.53 g cm $^{-3}$ , and  $Z = 4$ .
- 5 III crystallizes in the orthorhombic space group  $Pnma$ , with  $a$  22.063(6),  $b$  12.106(4),  $c$  9.745(4) Å 730 independent observed reflections collected on an Enraf-Nonius CAD-4 diffractometer led to a final  $R$  value of 0.074. Only the molybdenum and phosphorus atoms were refined anisotropically.
- 6 E. Carmona, J.M. Marin, M.L. Poveda, J.L. Atwood, R.D. Rogers and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, submitted.