

Crystal and Molecular Structure of $[W(NPh)(\mu-O)Me_2(PMe_3)]_3$; a Trimeric Oxo-bridged Imido Complex of Tungsten(VI)

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Summary Reaction of phenylimidotungsten tetrachloride with dimethylmagnesium in the presence of trimethylphosphine gives a yellow crystalline product, shown to be the title compound by *X*-ray structure determination.

MUCH interest has been shown recently in the preparation and properties of transition metal complexes containing the organo-imido group $M=N-R$. To date, such complexes of several transition metals have been prepared¹ although the only examples of complexes additionally containing metal-alkyl bonds are the dimeric amido-bridged complexes of molybdenum and tungsten.² As part of studies to explore the chemical properties of imido-containing complexes, we

have examined the reactions of phenylimidotungsten tetrachloride with alkylating agents, and report here the preparation and structure of a novel trimeric complex of tungsten(VI) containing alkyl, oxo, and phosphine ligands in addition to the phenylimido-group.

Reaction of phenyl isocyanate with tungsten tetrachloride oxide gives phenylimidotungsten tetrachloride³ which, on further reaction with dimethylmagnesium in the presence of trimethylphosphine and subsequent work-up, gives a yellow solid consisting of several products. Extraction with *n*-pentane and crystallisation at -25°C gives a yellow crystalline product, the structure of which has been determined by a single-crystal *X*-ray study.

Crystal data: $[\text{W}_3(\mu\text{-O})_3\text{Me}_6(\text{NPh})_3(\text{PMe}_3)_3]$, $\text{C}_{33}\text{H}_{60}\text{N}_3\text{O}_3\text{-P}_3\text{W}_3$, $M = 1191.32$, monoclinic, $a = 16.825(3)$, $b = 16.241(2)$, $c = 17.675(4)$ Å, $\beta = 114.22(2)^\circ$, $U = 4404.6$ Å³, space group $P2_1/c$, $Z = 4$, $D_c = 1.796$ g cm⁻³, $F(000) = 2280$, $\mu(\text{Mo-K}\alpha) = 76.2$ cm⁻¹, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å.

Intensity data were recorded on a Nonius CAD4 diffractometer with Mo-K α radiation, and corrected for

Lorentz, polarisation, and absorption effects. The structure was solved from Patterson and electron density syntheses, and refined by full-matrix least-squares (all non-hydrogen atoms anisotropic) to an R -value of 0.037 for 4576 reflections with $F_o > 4\sigma(F_o)$. Hydrogen atoms were not located.†

The structure (Figure) contains an equilateral triangle of tungsten atoms bridged by three oxo atoms; each metal atom is also bonded to one NPh, one PMe₃ (*trans* to the oxo ligand) and two *trans* Me groups.

The bridging oxygen atoms are almost coplanar with the W₃ triangle (maximum deviation 0.05 Å) and the W–O distances in each bridge are significantly different, with one short [1.776–1.803(7) Å] and one long [2.102–2.114(8) Å], the latter being *trans* to the N–Ph group.

Bearing in mind that W^{VI} is a d⁰ system and that ligand → metal π -bonding is required to attain an 18-electron configuration, the structure of this compound suggests a partial triple bond (W≡N) structure in the phenylimido-tungsten moiety and localized π -donation to only one tungsten atom by the bridging oxygen atoms. Thus, the oxygen atoms preferentially π -bond to the metal when they are *trans* to the π -acceptor phosphorus donor atom but are repelled by the *trans*-imido nitrogen owing to competition for the same metal d π orbital. This explains the unsymmetrical oxo-bridge and the wide angle (*ca.* 153°) at oxygen.

The origin of the oxygen is subject to conjecture since the reactions were carried out under strictly anaerobic conditions; the solvents used (diethyl ether, dioxan) seem the most likely source.

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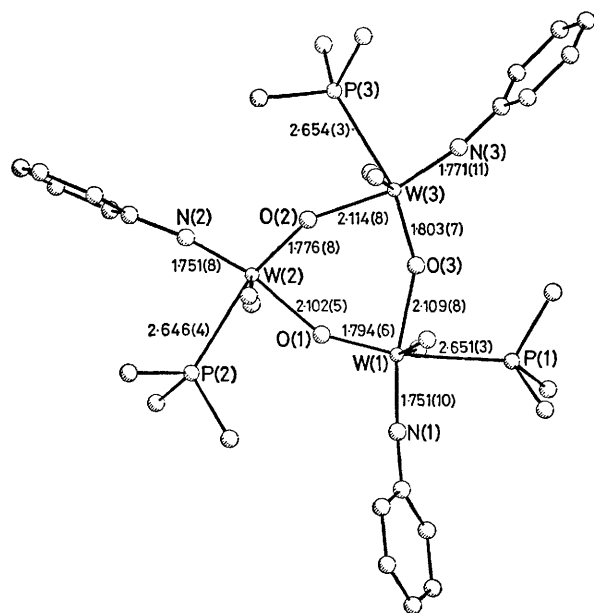


FIGURE. Molecular structure of $[\text{W}_3(\mu\text{-O})_3\text{Me}_6(\text{NPh})_3(\text{PMe}_3)_3]$ showing the approximate 3-fold axis and some important bond lengths (Å).

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

¹ W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123.

² W. A. Nugent and R. L. Harlow, *J. Am. Chem. Soc.*, 1980, **102**, 1759.

³ D. C. Bradley and A. J. Nielson, unpublished results.

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