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$(\eta^3\text{-}P_3)W(OCH_2Bu^t)_3(HNMe_2)$ Formed by Cleavage of the W≡W Bond in the Reaction Between $W_2(OCH_2Bu^t)_6(HNMe_2)_2$ and P_4

MALCOLM H. CHISHOLM*, JOHN C. HUFFMAN
and JAMES W. PASTERCZYK

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Ind. 47405, U.S.A.

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Recent work has resulted in the synthesis and structural characterization of compounds of empirical formula $(RO)_3M{\equiv}X$ where M = Mo, R = Bu^t, Pr^i, CH_2Bu^t and Et and X = N [1], or M = W, R = Bu^t, and X = N or CR′ where R′ = alkyl or aryl [2]. These findings led us to examine the reactivity of P_4 towards $W_2(OR)_6$ compounds [3] in an attempt to prepare a related $(RO)_3W{\equiv}P$ compound. We describe here our discovery of the first η^3-P_3 metal complex supported by π-donor ligands, namely alkoxides, which is formed in the reaction between $W_2(OCH_2Bu^t)_6(HNMe_2)_2$ [3] and P_4.

The reaction between $W_2(OR)_6$ compounds and P_4 (purified by sublimation) in dry and deoxygenated hydrocarbon solvents (N_2 atmospheres) is sensitive to the steric requirements of R. Reactions employing $W_2(OCH_2Bu^t)_6(HNMe_2)_2$, which acts as a source of the coordinatively unsaturated compound $W_2(OCH_2Bu^t)_6$, and P_4 gave a mixture of two products. One, a brown compound which crystallizes from CH_2Cl_2 solutions, displays an ambiguously simple ^1H NMR spectrum (two CMe_3 singlets in the integral ratio of 2:1 and an AB quartet and singlet for their respective methylene protons) but contains no detectable phosphorus by either ^{31}P NMR or elemental analysis. Efforts to characterize this product by single crystal X-ray diffraction have as yet been unsuccessful due to problems associated with twinning, high symmetry space groups, and no diffraction beyond $2\theta = 15°$. The other compound, which is more soluble and can subsequently be crystallized from hexanes as yellow prisms, is reliably formulated as $(\eta^3\text{-}P_3)W(OCH_2Bu^t)_3(HNMe_2)$**. The yield of this latter compound (as determined by ^1H NMR) is *ca.* 30% based on tungsten.

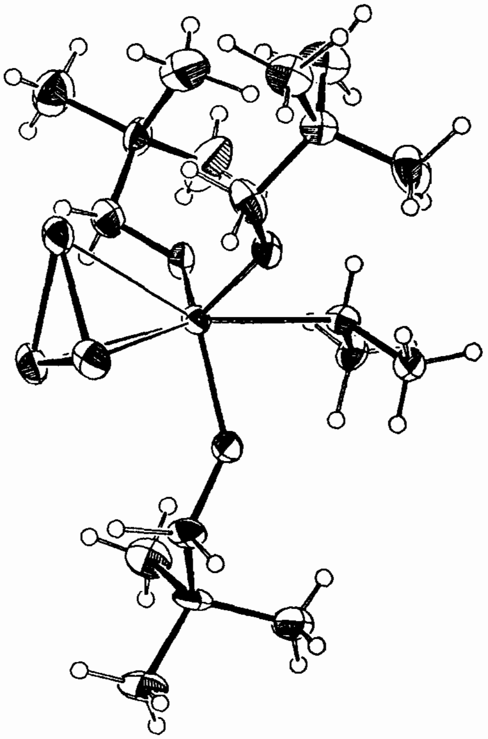

Fig. 1. ORTEP diagram of $(\eta^3\text{-}P_3)W(OCH_2Bu^t)_3(HNMe_2)$. Bond lengths (Å) and angles (°) (averaged where appropriate) are: W–P, 2.4930(25); W–O, 1.908(5); W–N, 2.315(7); P–P, 2.155(4); P–W–P, 51.23(9); P–W–O (proximal), 88.34(17); P–W–O (distal), 134.15(17); W–O–C, 136.6(5); P–W–N, 150.03(18); O–W–O, 114.17(24); O–W–N, 75.80(24); W–P–P, 64.39(9).

An ORTEP diagram of the molecule is given in Fig. 1. If the η^3-P_3 ligand is counted as occupying a single coordination site X, then the WO_3XN moiety can be viewed as a trigonal bipyramid with X and N occupying the axial sites. The tungsten atom is displaced 0.47 Å from the O_3 plane toward the P_3 ring. The phosphorus atoms of the η^3-P_3 ligand are nearly perfectly staggered with respect to the three W–O bonds in the equatorial plane. The P–P distance of 2.155(4) Å is slightly shorter than that found in P_4 but at the upper end of the range seen for η^3-P_3 compounds containing only σ-donor ancillary ligands [4].

The ^1H and ^{31}P NMR spectra of the new compound are simple and consistent with expectations based on the solid-state molecular structure. There is

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*Author to whom correspondence should be addressed.

**Crystal data for $(\eta^3\text{-}P_3)W(OCH_2Bu^t)_3(HNMe_2)$ at −155 °C: $a = 10.444(3)$, $b = 17.171(8)$, $c = 14.619(6)$ Å, $\beta = 105.02(2)°$, $Z = 4$, $D_c = 1.530$ gm cm^{-3}, space group $P2_1/n$. Of the 4422 unique intensities collected using Mo Kα radiation ($6° \leq 2\theta \leq 45°$), the 2716 having $F > 3\sigma(F)$ were used in a full matrix least-squares refinement. The hydrogen atoms were located and refined and no absorption or extinction corrections were used. Final residual values are $R = 0.0335$ and $R_w = 0.0340$.

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one type of neopentoxide ligand and one type of amine [^{1}H NMR, benzene-d_6, 22°, δ 0.85 (s, 27 H), 2.41 (s, br, 6 H), 3.00 (s, 1 H), 4.52 (s, 6H)] which requires rapid rotation about the W–N σ bond. In the ^{31}P(^{1}H) spectrum the η^3-P_3 ligand resonates at δ −205.2 ppm (relative to 85% H_3PO_4) with a small coupling to ^{183}W (I = 1/2, 14.5% natural abundance): $^1J(^{183}W-^{31}P)$ = 16 Hz. The small value for $^1J(^{183}W-^{31}P)$ is understandable in terms of the small degree of phosphorus 3s orbital contribution to the η^3-P_3-to-W bond. A Fenske–Hall molecular orbital calculation indicates that the molecular orbitals of a and e symmetry for the η^3-P_3-to-W moiety are composed of phosphorus 3p and tungsten $5d_{z^2}$, d_{xz} and d_{yz} orbitals while the phosphorus 3s orbitals are used predominantly to form P–P bonds. Similarly small values of $^1J(M-^{31}P)$ for η^3-P_3 complexes of platinum and rhodium have been noted [4a].

Further studies are in progress.

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