The First Example of a d^3–d^3 Dinuclear Compound containing Four-co-ordinate Metal Atoms sharing a Pair of Bridging Ligands: $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$

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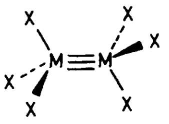
$(p\text{-Tolyl})(Bu^tO)_2W{\equiv}W(OBu^t)_2(p\text{-tolyl})$ and Ph_2PH (2 equiv.) react in hydrocarbon solvents to give toluene (2 equiv.) and $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$ which in the solid state contains a puckered W_2P_2 moiety, W–W 2.59 Å; in solution the $W_2(\mu\text{-}PPh_2)_2$ moiety is undergoing rapid inversion on the n.m.r. time-scale.

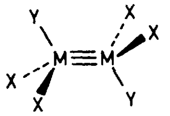
Since Wilkinson's[1] discovery of the unbridged compounds $M_2(CH_2SiMe_3)_6$, where M = Mo and W, numerous other examples of ethane-like molecules of formula $X_3M{\equiv}MX_3$, (I), or $X_2(Y)M{\equiv}M(Y)X_2$, (II), have been prepared and characterized and the chemistry of the M–M triple bond of configuration $\sigma^2\pi^4$ has been systematically developed.[2,3] Rather interestingly, not one example of the alternate structure (III), where the metal atoms are four-co-ordinate and share a pair of bridging ligands, has yet been reported. The structural type (III), is, of course, the more common in co-ordination chemistry where dimerization of two co-ordinatively unsaturated MX_3 groups occurs by bridge formation *e.g.* as in Al_2Cl_6.

The preference for structural types (I) and (II), for Mo and W, reflects the importance of M–M bonding. In (III), the fusing of two tetrahedra along a common edge can at best lead to a M–M bond of configuration $\sigma^2\pi^2\delta^2$ which, taken together with an increased M–M separation as a result of the μ-X groups, will result in a significant sacrifice of M–M bond strength. The situation is also influenced by the π-donor properties of the ligands X and Y. In (I) and (II), π-donation to the metal atoms can occur without weakening the M–M bond whereas in (III) π-donation from the terminal ligands will further weaken the M–M bond by interaction with metal d orbitals otherwise used for M–M bonding.

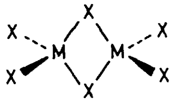
Formation of a d^3–d^3 dinuclear compound of type (III) requires the introduction of at least two ligands Y that have a high thermodynamic preference for bridging two metal atoms. They should also be significantly weaker π-donor ligands than the groups X. The compounds of formula $M_2(PR_2)_2X_4$ where M = Mo or W and X = OR or NMe_2 seemed likely to favour structural type (IIIb) over (II). A rational synthesis of such a



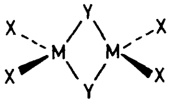
(I)



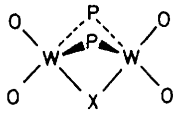
(II)



(IIIa)



(IIIb)



(IV)

compound involves the reaction between a $M_2R'_2(OR)_4$ compound,[4] which is co-ordinatively unsaturated, and a dialkyl or diarylphosphine R_2PH. We report here the first success of this synthetic strategy and our characterization of a compound of type (IIIb), namely $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$.

Hydrocarbon solutions of $(p\text{-tolyl})(Bu^tO)_2W{\equiv}W(OBu^t)_2(p\text{-tolyl})$ react with Ph_2PH (2 equiv.) according to equation (1) to yield dark orange solutions from which $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$ is obtained in *ca.* 60% yield as brown crystals. The new compound, like its precursor tungsten complex, is air-sensitive and must be handled in dry and deoxygenated solvents and atmospheres (N_2). N.m.r. spectroscopy ($[^2H_8]$toluene, 22 °C) shows only one type of Bu^tO and one type of PPh_2, having equivalent phenyl rings. The ^{31}P resonance possesses satellites due to coupling to two equivalent ^{183}W nuclei, and the *ipso*-carbon atoms of the phenyl rings show both one-bond (40 Hz) and three-bond (4 Hz) couplings to phosphorus. These data[†] support a time-averaged molecular structure (IIIb) for $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$, having C_{2v} symmetry.

$$1,2\text{-}W_2(p\text{-tolyl})_2(OBu^t)_4 + 2Ph_2PH \xrightarrow[\text{Hexane}]{22\,°C} [(Bu^tO)_2W(\mu\text{-}PPh_2)]_2 + 2\ \text{Toluene} \qquad (1)$$

A ball-and-stick drawing of the structure found in the solid state[‡] is shown in Figure 1. While the general prediction of terminal alkoxides and bridging phosphido ligands is confirmed, the molecular structure is significantly distorted from (IIIb). The co-ordination about the tungsten atoms is grossly distorted from tetrahedral. The central $W_2(\mu\text{-}P)_2$ core is puckered, not planar, and the terminal Bu^tO ligands are of two types, those with short W–O distances, 1.85 Å and large W–O–C angles, 158°, and the others with long W–O distances, 1.96 Å and smaller W–O–C angles, 128°. The local co-ordination at each metal atom may be described as a trigonal bipyramidal (tbp) fragment, WO_2P_2X, where X represents a missing axial vertex. The central $W_2O_4P_2$ unit represents two cofacial tbp WO_2P_2X units sharing a common pair of equatorial ligands, PPh_2, and a common missing axial site X. In this way O(5) and O(20), which have the long W–O distances, occupy the axial sites *trans* to the missing vertex. Diagrammatically, this is depicted by (IV).

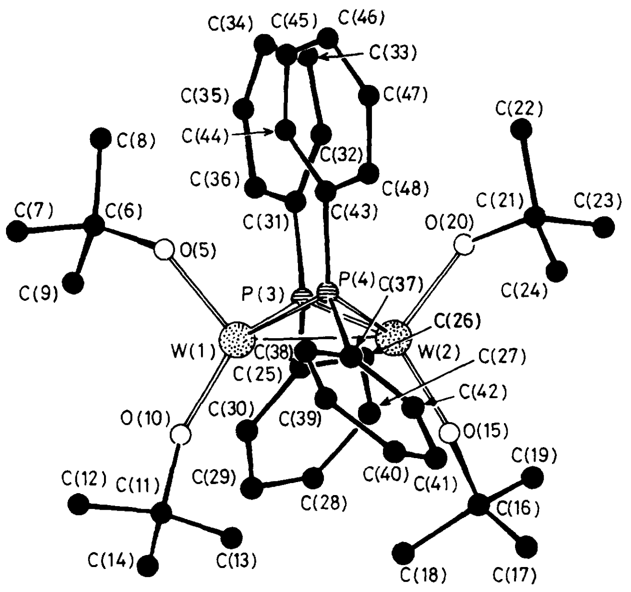


Figure 1. A ball-and-stick diagram of the $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$ molecule viewed nearly perpendicular to the virtual O_4W_2 plane showing the puckered central W_2P_2 moiety: the dihedral angle between the P(3)–W(1)–W(2) and P(4)–W(1)–W(2) planes is 136.4°. Pertinent bond distances (Å) and angles (°) are W–W 2.591(2); W(1)–P(3), W(1)–P(4), W(2)–P(4) 2.36(1); W(2)–P(3) 2.33(1); W(1)–O(5) 1.95(1); W(1)–O(10) 1.86(2); W(2)–O(15) 1.84(2); W(2)–O(20) 1.95(2); P(3)–W(1)–P(4) 101.2(2); P(3)–W(1)–O(5) 99.7(4); P(3)–W(1)–O(10) 126.2(5); P(4)–W(1)–O(5) 92.1(4); P(4)–W(1)–O(10) 120.4(5); O(5)–W(1)–O(10) 110.4(7); P(3)–W(2)–P(4) 102.1(2); P(3)–W(2)–O(15) 119.8(5); P(3)–W(2)–O(20) 89.8(5); P(4)–W(2)–O(15) 125.0(5); P(4)–W(2)–O(20) 99.2(5); O(15)–W(2)–O(20) 113.9(7); W(1)–P(3)–W(2) 67.0(2); W(1)–P(4)–W(2) 66.6(2).

The W–W distance of 2.59 Å is *ca.* 0.3 Å longer than those in unbridged d^3–d^3 ditungsten compounds and a simple M–M bonding description in the new phosphido-bridged compound is not viable since there must be extensive mixing of orbitals involved in M–M and M–ligand bonding. Nevertheless there must exist at least a M–M σ bond, which in terms of the fusing together of two tbp WO_2P_2X units would involve a bent M–M bond formed from overlap of $d_z{}^2$ orbitals at the μ-X site. It seems likely that M–M bonding is responsible for the puckering of the central M_2P_2 unit. The present W–W distance of 2.59 Å is similar to that reported for the d^4–d^4 anion $W_2(\mu\text{-}Pcy_2)_3(Pcy_2)_2{}^-$ (cy = cyclohexyl), 2.55 Å.[6]

In related work, we have been studying the metathetical reaction shown in equation (2). For reactions involving

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[†] Selected n.m.r. data for $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$: $^{31}P\{^1H\}$ (p.p.m., C_6D_6, 22 °C) 212.8 [s, $J(^{31}P\text{–}^{183}W)$ 349 Hz, satellites of 25% integral intensity], ^1H (δ, C_6D_6, 22 °C) 1.27 (s, Bu^tO); $[(NMe_2)_2W(\mu\text{-}Pcy_2)]_2$: $^{31}P\{^1H\}$(p.p.m, $[^2H_8]$toluene, 22 °C) 228.5 [s, $J(^{31}P\text{–}^{183}W)$ 305 Hz, satellites of 26% integral intensity]; ^1H (δ, $[^2H_8]$toluene, 22 °C) 3.41 (s, NMe_2).

[‡] *Crystal data* for $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$ at −157 °C: a = 11.062(4), b = 19.185(8), c = 21.969(2) Å, β = 114.51(2)°, Z = 4, D_c = 1.614 g cm^{-3} and space group $P2_1/c$. Of the 6465 reflections collected using Mo-K_α (λ 0.71069 Å) with $6 \leqslant 2\theta \leqslant 45°$ only those 2904 having $F > 3\sigma(F)$ were used in the full least-squares refinement. The W,O, and P atoms were refined anisotropically and the carbon atoms isotropically. H atoms were included at idealized fixed positions. Final residuals were $R(F)$ = 0.0529 and $R_w(F)$ = 0.0522. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$$anti\text{-}1,2\text{-}W_2Cl_2(NMe_2)_4 + 2\ LiPR_2 \xrightarrow[\text{Tetrahydrofuran}]{-78\text{—}0\,°C} 1,2\text{-}W_2(PR_2)_2(NMe_2)_4 \quad (2)$$

$LiPBu^t_2$, we have now characterized both *anti* and *gauche* rotamers of the compound $W_2(PBu_2^t)_2(NMe_2)_4$.[7] The terminal phosphido ligands contain non-planar W–PC_2 units with W–P bond distances longer than those expected for W–P $\sigma + \pi$ double bonds. We now find that reactions employing $LiPcy_2$ lead, at low temperatures (<0 °C), to an orange crystalline compound whose n.m.r. spectroscopic properties are consistent with a structure of type (II). However, at room temperature there is a relatively slow (t_∞ *ca.* 4 h) and irreversible reaction leading to a new brown crystalline compound for which the n.m.r. spectroscopic data† are consistent with a time-averaged symmetrically-bridged structure $[(Me_2N)_2W(\mu\text{-}Pcy_2)]_2$. Thus it seems likely that a fairly extensive class of these new d^3–d^3 bridged compounds may be accessible for tungsten.

We thank the National Science Foundation and the Wrubel Computing Center for support. B. W. E. is the 1986/87 Indiana University SOHIO Graduate Fellow.

Received, 20th January 1987; Com. 074

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