

Reaction between Bis(benzyl)tetraisopropoxytungsten($W \equiv W$) and But-2-yne: $W_2(CH_2Ph)_2(OPri)_4(\eta^2-C_2Me_2)_2$ and $W_2(H)(OPri)_4(\mu-CPh)(\mu-C_4Me_4)$. A Terminal Metal Hydride with a 1H N.M.R. Resonance 20 p.p.m. Downfield of Me_4Si

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1,2- $W_2(CH_2Ph)_2(OPri)_4(W \equiv W)$ reacts in hydrocarbon solvents at ambient temperatures with $MeC \equiv CMe$ to give initially $(\eta^2-C_2Me_2)(PhCH_2)(PriO)W(\mu-OPri)_2W(OPri)(CH_2Ph)(\eta^2-C_2Me_2)$, which has a puckered central $W_2(\mu-OR)_2$ core, $W-W$ 2.67 Å, and eliminates one equivalent of toluene with the formation of the novel compound $W_2(H)(OPri)_4(\mu-C_4Me_4)(\mu-CPh)$ upon heating to +60 °C.

Previous studies have shown that ditungsten hexa-alkoxides and alkynes react to give a wide variety of products depending upon the nature of the alkoxide, the alkyne, and the reaction conditions.¹⁻⁸ These include products derived from C-C scission and C-C coupling. We describe here a reaction between 1,2- $W_2(CH_2Ph)_2(OPri)_4$ † and but-2-yne which reveals a totally different type of chemistry.

In hydrocarbon solvents, $W_2(CH_2Ph)_2(OPri)_4$ reacts with $MeC \equiv CMe$ to form a 2:1 adduct $W_2(CH_2Ph)_2(OPri)_4(\eta^2-C_2Me_2)_2$ ‡. This contrasts with the chemistry of the $W_2(OPri)_6$

molecule which has been shown to give $W_3(\mu_3-CMe)(OPri)_9$ ⁵ and $W_2(OPri)_6(\mu-C_4Me_4)(\eta^2-C_2Me_2)$.⁴ The molecular structure of the 2:1 alkyne adduct found in the solid state§ is shown in Figure 1 and is entirely consistent with solution n.m.r. data. At low temperatures rotation of the alkyne about the alkyne-tungsten vector is frozen out. The n.m.r. data are also consistent with a dimer based on the fusing of two trigonal bipyramidal units as depicted in structure (I), and it is not obvious why the latter geometry is not favoured. All previous examples⁹ of $M_2(\mu-OR)_2$ units involving five-co-ordinate metal atoms having M-M bonds of order in the range 2—0 have been seen to prefer structure (I).

The alkyne ligand, as in several recently characterized alkyne adducts of the early transition elements, e.g.^{10,11}

† This compound was prepared from the reaction between 1,2- $W_2(CH_2Ph)_2(NMe_2)_4$ and $PriOH$ (ca. 4.2 equiv.) in hexane at room temperature in a manner analogous to that described for 1,2- $Mo_2R_2(OR')$ compounds where $R = Me, CH_2CMe_3$, and CH_2SiMe_3 . See M. J. Chetcuti, M. H. Chisholm, K. Foltling, D. A. Haitko, J. C. Huffman, and J. Janos, *J. Am. Chem. Soc.*, 1983, **105**, 1163; M. H. Chisholm, J. C. Huffman, and R. J. Tatz, *ibid.*, 1983, **105**, 2075.

‡ Dry and oxygen-free solvents and atmospheres (N_2) were used at all times. Satisfactory elemental analyses were obtained. N.m.r. data: (a) $W_2(CH_2Ph)_2(OPri)_4(\eta^2-C_2Me_2)_2$: 1H n.m.r. ($C_6D_5CD_3$, -80 °C) δ 7.53 (d, 4H, J_{HH} 7.2 Hz, CH_2Ph), 7.20 (t, 4H, J_{HH} 7.6 Hz, CH_2Ph), 6.88 (t, 2H, J_{HH} 7.2 Hz), 4.72 (septet, 2H, J_{HH} 6.5 Hz, $OCHMe_2$), 4.06 (d, 2H, J_{HH} 10.1 Hz, CH_2Ph), 3.90 (d, 2H, J_{HH} 10.1 Hz, CH_2Ph), 3.25 (s, 6H, $MeCCMe$), 3.05 (s, 6H, $MeCCMe$), 2.82 (septet, 2H, J_{HH} 6.5 Hz, $OCHMe_2$), 1.25 (d, 6H, J_{HH} 6.5 Hz, $OCHMe_2$), 1.20 (d, 6H, J_{HH} 6.5 Hz, $OCHMe_2$), 0.51 (d, 6H, J_{HH} 6.5 Hz, $OCHMe_2$), and 0.418 (d, 6H, J_{HH} 6.5 Hz, $OCHMe_2$).

(b) $W_2(H)(OPri)_4(\mu-CPh)(\mu-C_4Me_4)$: 1H n.m.r. ($C_6D_5CD_3$, -40 °C) δ 20.42 (s, 1H, J_{WH} 125 Hz, WH), 8.37 (d, 2H, J_{HH} 7.2 Hz, $\equiv CPh$), 7.53 (t, 2H, J_{HH} 7.6 Hz, $\equiv CPh$), 7.01 (t, 1H, J_{HH} 7.2 Hz, $\equiv CPh$), 5.34 (septet, 2H, J_{HH} 6.1 Hz, $OCHMe_2$), 4.53 (septet, 2H, J_{HH} 6.1 Hz, $OCHMe_2$), 2.18 (s, 6H, $\mu-C_4Me_4$), 1.69 (s, 6H, $\mu-C_4Me_4$), 1.40 (d, 6H, J_{HH} 6.1 Hz, $CHMe_2$), 1.29 (d, 6H, J_{HH} 6.1 Hz, $OCHMe_2$), 1.20 (d, 6H, J_{HH} 6.1 Hz, $OCHMe_2$), and 0.86 (d, 6H, J_{HH} 6.1 Hz, $OCHMe_2$).

§ Crystal data (i) for $W_2(OPri)_4(CH_2Ph)_2(\eta^2-C_2Me_2)_2$ at -159 °C: $a = 11.999(2)$, $b = 18.650(4)$, $c = 15.522(3)$ Å, $\beta = 97.84(1)^\circ$, $Z = 4$, $D_c = 1.727$ g cm⁻³, space group $P2_1/n$. Of 4511 unique reflections collected using $Mo-K_\alpha$ radiation, $6^\circ < 2\theta < 45^\circ$, the 3874 having $F > 3.00 \sigma(F)$ were used in the full-matrix least-squares refinement. All hydrogen atoms were located and refined isotropically and all non-hydrogen atoms were varied anisotropically. The final residuals are $R(F) = 0.025$ and $R_w(F) = 0.030$.

(ii) For $W_2(OPri)_4(H)(\mu-CPh)(\mu-C_4Me_4)$ at -159 °C: $a = 9.183(3)$, $b = 15.606(6)$, $c = 19.977(9)$ Å, $Z = 4$, $D_c = 1.862$ g cm⁻³. Of 3710 unique intensities collected using $Mo-K_\alpha$ radiation, $6^\circ < 2\theta < 45^\circ$, the 3204 having $F > 3\sigma(F)$ were used in the full-matrix least-squares refinements. H atoms were included on the Ph and OPri ligands in idealized positions during the final refinement. All non-hydrogen atoms were varied anisotropically. The final residuals are $R(F) = 0.066$ and $R_w(F) = 0.062$.

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.

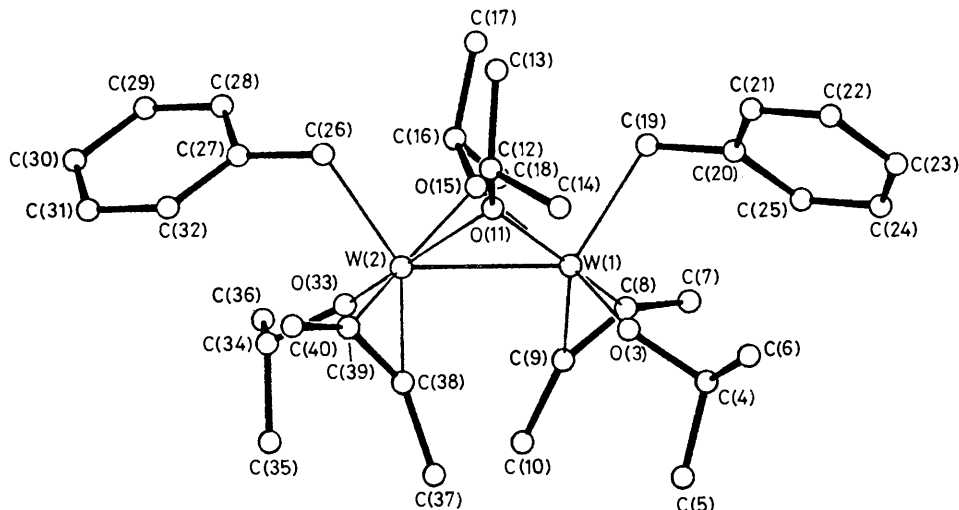


Figure 1. A ball and stick drawing of the $W_2(OPri)_4(CH_2Ph)_2(\eta^2-MeCCMe)_2$ molecule. Selected bond distances (Å) and angles ($^\circ$), averaged where appropriate: W-W 2.6684(6), W-O(terminal) 1.85(1), W-O(μ -OR) 2.15(1), W-C(benzyl) 2.21(1), W-C(η^2 -alkyne) 2.05(1), C-C(η^2 -alkyne) 1.31(1), C-C-C(alkyne) 136(2).

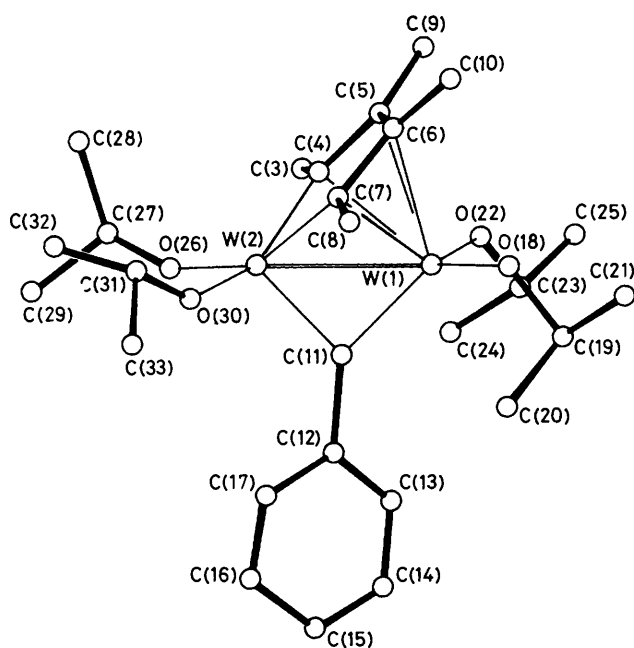
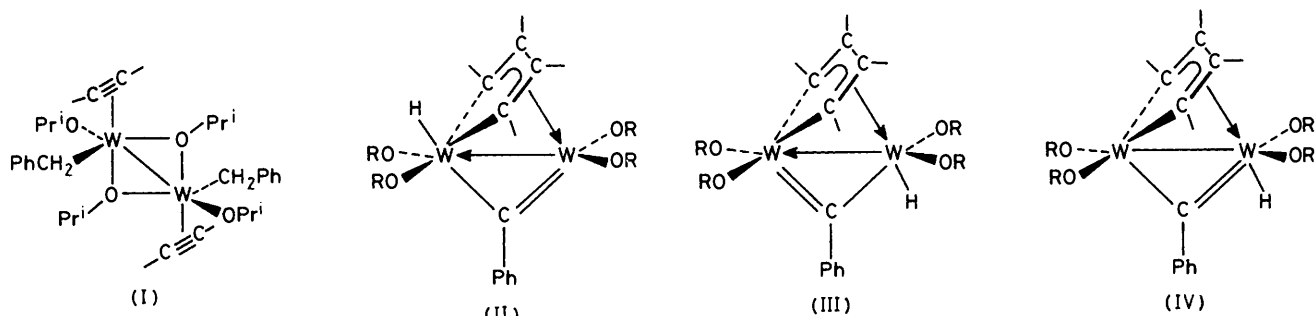


Figure 2. A ball and stick drawing of the $W_2(OPri)_4(\mu-CPh)(\mu-C_4Me_4)(H)$ molecule. Selected distances (Å) and bond angles ($^\circ$), averaged where appropriate: W-W 2.755(2), W(1)-O 1.90(2), W(2)-O 1.89(2), W(2)-C(4) 2.10(2), W(2)-C(7) 2.08(3), W(2)-C(11) 1.95(2), W(1)-C(11) 1.97(3), W(1)- η^4 -carbons 2.44(4); W(1)-C(11)-C(12) 140(2), W(2)-C(11)-C(12) 131(2), W(1)-C(11)-W(2) 89(1).

$[NbCl_3(C_2Ph_2)]_4$, $[WCl_4(C_2Ph_2)]_x$, and $W(OBu^t)_4(C_2Ph_2)$, can be considered as a 2-ligand. Formally the present molecule is a d^1-d^1 dimer with a bent W-W bond.¹² The structure is rather similar to the well known $(CO)_3Co(\mu-CO)_2Co(CO)_3$ structure.^{12,13}

In hydrocarbon solutions at temperatures above 60 $^\circ C$, $W_2(OPri)_4(CH_2Ph)_2(\eta^2-C_2Me_2)_2$ reacts to give $W_2H(OPri)_4(\mu-C_4Me_4)(\mu-CPh)$ with the release of one mole of toluene. The molecular structure of this ditungsten compound is shown in Figure 2 and is in agreement with 1H and ^{13}C n.m.r. data obtained in solution. The 1H n.m.r. spectrum reveals the presence of the W-H moiety, δ 20.42. We are confident of our assignment of a hydride ligand in this molecule and discount an agostic M-H-C interaction¹⁴ with the $\mu-CPh$ group on the following grounds. The coupling $J(^{183}W-H)$ is 125 Hz and in the ^{13}C n.m.r. spectrum the signal at δ 369, which we assign to the $\mu-CPh$ carbon, shows no detectable coupling to a hydrogen in the proton-coupled spectrum. The intensities of the satellites due to coupling to ^{183}W , $I = 1/2$, natural abundance 14.5%, are consistent with the hydride ligand being bound to only one tungsten atom.

Because the hydride ligand could not be detected crystallographically, one can only speculate on its location. There is room for a hydride ligand at either tungsten atom. If the hydride ligand is placed on W(2) *trans* to the $\mu-CPh$ ligand, then W(2) attains octahedral co-ordination and is W(6+) as shown in the valence bond description (II).

Alternatively if the hydride ligand is positioned *trans* to the $\eta^4-C_4Me_4$ ligand on W(1), W(1) attains a pseudo-trigonal bipyramidal co-ordination counting the $\eta^4-C_4Me_4$ ligand to occupy an axial position. The formal oxidation state of W(1)

may be either +4 or +5 depending upon how the μ -CPh ligand is assigned as shown in the valence bond descriptions (III) and (IV). It is thus possible to view the molecule as a d^0 - d^2 dimer (II, III) or a d^1 - d^1 dimer (IV); cf. $W_2(OPr^i)_6(\mu-C_4Me_4)(\eta^2-C_2Me_2)$.⁴

It is our opinion that the hydride ligand is on W(1) *trans* to the η^4 -C₄Me₄ ligand. This most readily explains the equivalent W-C distances to the μ -CPh ligand. Placing the hydride on W(2) would be expected to lead to a longer W(2)- μ -CPh bond distance on the grounds of both the valence bond description (II) and the well documented high *trans*-influence of hydride ligands;¹⁵ e.g. in $W_4(H)_2(OPr^i)_{14}$.¹⁶ Placing the H ligand on W(1) *trans* to the η^4 -C₄Me₄ ligand could also provide the cause for the observed twisting of the phenyl blade and the asymmetry of the W-C-C angles associated with the W₂(μ -CPh) moiety. At present we do not know what factor or factors are responsible for the anomalous chemical shift of the hydride ligand.¹⁷

Reactions involving related compounds of formula $W_2R_2(OR')_4$ and alkynes are currently under investigation.

We thank the Department of Energy, Office of Basic Research, Chemical Sciences Division, and the Wrubel Computing Center for support.

Received, 2nd January 1985; Com. 001

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