The Remarkable Role of Steric Factors in the Reactions of Alkynes (HC≡CH and MeC≡CMe) with Ditungsten Hexa-alkoxides: Crystal and Molecular Structures of $W_2(OPr^i)_6(py)_2(\mu\text{-}C_2H_2)$, $W_2(OCH_2Bu^t)_6(py)_2(\mu\text{-}C_2Me_2)$, and $W_2(OPr^i)_6(\mu\text{-}C_4R_4)(C_2R_2)$, where R = H and Me (py = pyridine)

Malcolm H. Chisholm,* Kirsten Folting, David M. Hoffman, John C. Huffman, and Joseph Leonelli

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

Ethyne and but-2-yne react with hydrocarbon solutions of $W_2(OR)_6$ compounds in the presence of pyridine (py) to produce the compounds $W_2(OR)_6(py)_2(\mu\text{-}C_2R'_2)$, $W_2(OR)_6(\eta\text{-}C_4R'_4)(C_2R'_2)$, or $R'C\equiv W(OR)_3$, depending on the nature of the alkoxy group and the alkyne substituent, R'.

Steric factors are well known to dominate the physicochemical properties of metal alkoxides and the use of bulky alkyl groups may allow the isolation of compounds with metal atoms in unusual co-ordination environments and oxidation states.[1] We note here a most remarkable difference in the products obtained from reactions between $W_2(OR)_6$ compounds and alkynes (HCCH and MeCCMe) as a function of both alkoxy group and alkyne substituent.

Hydrocarbon solutions of $W_2(OBu^t)_6$[2] in the presence of pyridine (py) ($\geqslant 2$ equiv.) and $W_2(OPr^i)_6(py)_2$[2] react with
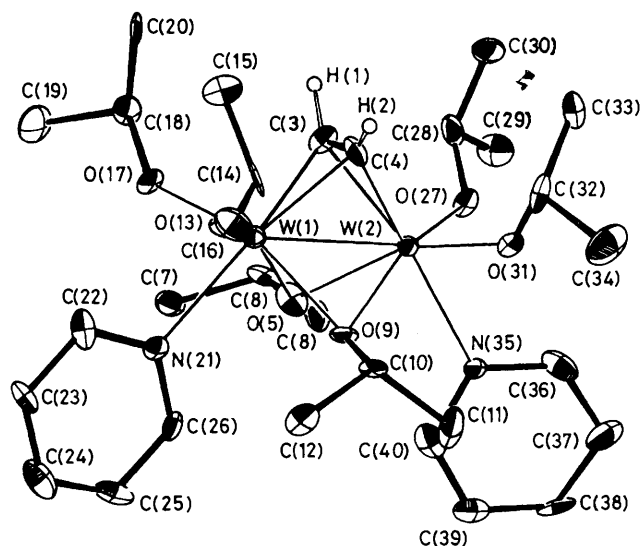
Figure 1. An ORTEP view of the structure of the $W_2(OPr^i)_6(py)_2$-(μ-C_2H_2) molecule. Some pertinent distances (Å) are W–W 2.567(1), W–O (terminal) 1.94(2) (averaged), W–O (bridge) 2.12(4) (averaged), W(1)–C(3), –C(4) 2.10(1), 2.08(1); W(2)–C(3), –C(4) 2.12(2), 2.09(1); W–N 2.31(1) (averaged), C(3)–C(4) 1.39(2).
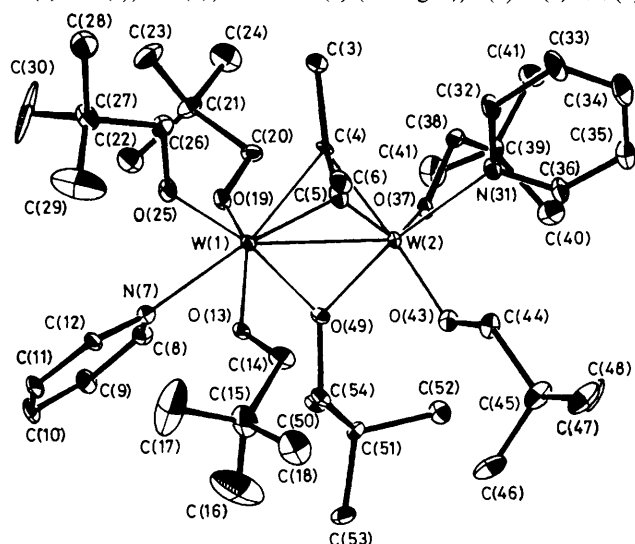

Figure 2. An ORTEP view of the structure of the $W_2(OCH_2Bu^t)_6$-(py)$_2$(μ-C_2Me_2) molecule. Some pertinent distances (Å) are: W–W 2.602(1), W(1)–O(13), –O(19), –O(25), –O(49), –N(7), –C(4), –C(5) 1.97(1), 1.95(1), 1.94(1), 2.12(1), 2.32(1), 2.17(1), 2.23(1); W(2)–O(37), –O(43), –O(49), –N(31), –C(4), –C(5) 1.94(1), 1.97(1), 2.025(7), 2.24(1), 2.09(1), 2.04(1); C(4)–C(5) 1.374(15).

ethyne to give $W_2(OR)_6(py)_2(\mu$-$C_2H_2)$ compounds.† These are spectroscopically analogous to the previously characterized compound $Mo_2(OPr^i)_6(py)_2(\mu$-$C_2H_2)^3$ and, in the solid state, the tungsten compound is isomorphous and isostructural.‡ An ORTEP view of the $W_2(OPr^i)_6(py)_2(\mu$-$C_2H_2)$ molecule is given in Figure 1. Note the molecule has virtual C_{2v} symmetry and

there is a pair of bridging OPr^i ligands. In solution, these compounds are fluxional and show rapid terminal $\rightleftharpoons$ bridge OR group exchange at room temperature on the ^1H n.m.r. time-scale but, at low temperatures, spectra are consistent with those expected from considerations of the solid state structure.

As previously noted by Schrock and co-workers,[4] hydrocarbon solutions of $W_2(OBu^t)_6$, with or without added pyridine, react under comparable conditions with MeCCMe to give $(Bu^tO)_3W\equiv CMe$. The cleavage of the $W\equiv W$ and $C\equiv C$ bonds in this metathesis-like reaction is quite striking. In contrast, we have found the addition of one equivalent of MeCCMe to $W_2(OCH_2Bu^t)_6(py)_2$ in hexane produces a blue crystalline compound, $W_2(OCH_2Bu^t)_6(py)_2(\mu$-$C_2Me_2)$.† The molecular structure determined by an X-ray study‡ differs quite remarkably from that of $W_2(OPr^i)_6(py)_2(\mu$-$C_2H_2)$. A view of this neopentoxy compound is given in Figure 2. Note the presence of only one alkoxy bridge which results in pseudo-octahedral and trigonal bipyramidal co-ordination for the two different tungsten atoms. The bridging alkyne ligand is also quite asymmetrically disposed to the two metal atoms as shown by the W–C distances. In [$^2H_8$]toluene solution, the ^1H n.m.r. spectrum at room temperature is consistent with that expected based on the structure shown in Figure 2. Specifically, there are four types of OR ligands in the integral ratio 2:2:1:1 and the methyne protons appear as two AB quartets (4H, 4H) and two singlets (2H, 2H). The latter are readily assigned to the alkoxy ligands contained in the virtual mirror plane of the molecule, and the former to the two pairs of terminal OR groups not contained in this plane of symmetry.

Addition of R'CCR' ($\geqslant 3$ equiv.) to hydrocarbon solutions of $W_2(OR)_6(py)_2$ yields crystalline compounds $W_2(OR)_6$-(μ-$C_4R'_4)(C_2R'_2)$ (R' = H, Me, R = Pr^i; R' = Me, R = CH_2Bu^t). Addition of HCCH ($\geqslant 2$ equiv.) to hydrocarbon solutions of $W_2(OBu^t)_6$ leads to an unstable green compound which has a ^1H n.m.r. spectrum indicative of $W_2(OBu^t)_6$-(μ-C_4H_4) having a structure akin to that of $Mo_2(OCH_2Bu^t)_6$-(μ-$C_4H_4)(py)$ in which the site occupied by py in the latter molecule is vacant, viz. $(Bu^tO)_2W(\mu$-$C_4H_4)(\mu$-$OBu^t)W(OBu^t)_3$.

‡ *Crystal data:* (a) $W_2(OPr^i)_6(py)_2(\mu$-$C_2H_2)$ at -165 °C: monoclinic, space group $P2_1/a$, $a = 19.061(11)$, $b = 15.674(7)$, $c = 12.234(5)$ Å, $\beta = 108.08(1)°$, $D_c = 1.737$ g cm^{-3}, $Z = 4$. The structure was solved by Patterson and Fourier techniques using 6155 unique intensities collected on an automated diffractometer using Mo-$K\alpha$ radiation for $6 \leqslant 2\theta \leqslant 50°$. Final refinement utilized anisotropic thermal parameters for all non-hydrogen atoms and converged to $R = 0.056$ and $R_w = 0.049$. (b) $W_2(OCH_2Bu^t)_6(py)_2(\mu$-$C_2Me_2)$ at -160 °C: monoclinic, space group $C2/c$, $a = 37.822(21)$, $b = 12.207(5)$, $c = 22.163(9)$ Å, $\beta = 101.01(2)°$, $D_c = 1.459$ g cm^{-3}, $Z = 8$. The structure was solved by Patterson and Fourier techniques using 6602 unique intensities collected on an automated diffractometer using Mo-$K\alpha$ radiation for $6 \leqslant 2\theta \leqslant 45°$. Final refinement used anisotropic thermal parameters for all non-hydrogen atoms and converged to $R = 0.052$ and $R_w = 0.051$. (c) $W_2(OPr^i)_6(\mu$-$C_4Me_4)(C_2Me_2)$ at -160 °C: orthorhombic, space group *Pcab*, $a = 16.35(1)$, $b = 16.04(1)$, $c = 26.33(2)$ Å, $D_c = 1.702$ g cm^{-3}, $Z = 8$. The structure was solved by Patterson and Fourier techniques using 3331 unique intensities collected on an automated diffractometer using Mo-$K\alpha$ radiation for $6 \leqslant 2\theta \leqslant 45°$. Final refinement used isotropic thermal parameters and converged to $R = 0.053$ and $R_w = 0.053$. (d) $W_2(OPr^i)_6(\mu$-$C_4H_4)(C_2H_2)$ at -160 °C: triclinic, $a = 14.754(7)$, $b = 12.135(6)$, $c = 9.011(4)$ Å, $\alpha = 105.51(2)$, $\beta = 88.66(3)$, $\gamma = 70.53(2)°$, $D_c = 1.83$ g cm^{-3}, $Z = 2$. The structure was solved by Patterson and Fourier techniques using 3183 unique intensities collected on an automated diffractometer using Mo-$K\alpha$ radiation for $6 \leqslant 2\theta \leqslant 45°$. Final refinement used anisotropic thermal parameters for all non-hydrogen atoms and converged to $R = 0.037$ and $R_w = 0.037$. 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.
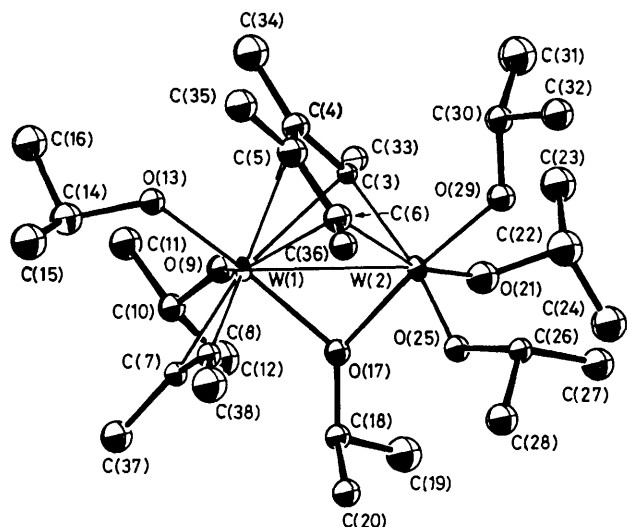
† Standard procedures for the manipulation of air-sensitive materials were used at all times. Reactions were carried out at 1 atm, or less, and at room temperature. Detailed procedures were analogous to those in ref. 3. Satisfactory elemental analyses were obtained.

Added in proof: Since the submission of this manuscript the compound formulated as $W_2(OBu^t)_6(py)_2(\mu$-$C_2H_2)$ has been found to be $W_2(OBu^t)_6(py)(\mu$-$C_2H_2)\cdot\frac{1}{2}py$. It is not isostructural with $W_2(OPr^i)_6(py)_2(\mu$-$C_2H_2)$, but rather has two distorted trigonal bipyramidal W centres with the bridging ethyne co-ordinated perpendicular to the W–W bond.

Figure 3. An ORTEP view of the structure of the $W_2(OPr^i)_6$-(μ-C_4Me_4)(C_2Me_2) molecule. Some pertinent distances (Å) are: W–W 2.852(1), W(1)–O (terminal) 1.93(2) (averaged), W(1)–O(17)2.11(1), W(1)–C(3), –C(4), –C(5), –C(6), –C(7), –C(8)2.45(2), 2.51(2), 2.47(2), 2.40(2), 2.06(2), 2.09(2); W(2)–O (terminal) 1.93(1) (averaged), W(2)–O(17) 1.99(1), W(2)–C(3), –C(6) 2.15(1), 2.14(2); C(7)–C(8) 1.28(2), C(3)–C(4) 1.38(2), C(4)–C(5) 1.43(2), C(5)–C(6) 1.38(2).

(A)   (B)
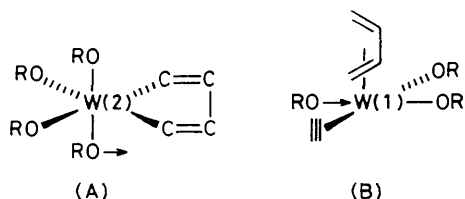
The addition of two equivalents of alkyne to the $W_2(OR)_6(py)_2$-(μ-$C_2R'_2$) compounds (R = Pr^i, R' = H; R = CH_2Bu^t, R' = Me) leads to the appropriate $W_2(OR)_6(\mu$-$C_4R'_4)(C_2R'_2)$ compound. Furthermore, addition of MeCCMe (2 equiv.) to $W_2(OPr^i)_6(py)_2(\mu$-$C_2H_2)$ gives $W_2(OPr^i)_6(\mu$-$C_4H_2Me_2)(C_2Me_2)$.

The molecular structures of the isopropoxy compounds were determined‡ for R' = H and Me and a view of the $W_2(OPr^i)_6(\mu$-$C_4Me_4)(C_2Me_2)$ molecule is given in Figure 3. The change of alkyne substituent, H for Me, produces little difference in the structural parameters in these compounds.

$W_2(OR)_6(\mu$-$C_4R'_4)(C_2R'_2)$ compounds can be viewed as the sum of two halves, (A) and (B). This leads to a formal oxidation state of +6 for W(2) and +2 for W(1). The local geometry about W(1) may be viewed as a pseudo-square-based pyramid if the diene ligand is considered to occupy one site, namely the apical position. The geometry about W(2) is easily recognized as octahedral.

Low-temperature limiting ^1H n.m.r. spectra for $W_2(OR)_6$-(μ-$C_4R'_4)(C_2R'_2)$ compounds (R = Pr^i, R' = H, Me; R = CH_2Bu^t, R' = Me) are consistent with those expected from considerations of the observed solid state structures. Upon raising the temperature, two dynamic processes are observed in the spectra of the $W_2(OPr^i)_6(\mu$-$C_4H_4)(C_2H_2)$ compound: (i) alkyne rotation and (ii) a higher energy process which generates an apparent molecular plane of symmetry containing the two tungsten atoms. A plausible interpretation of the latter is that the groups attached to W(2) are rigid on the n.m.r. timescale, but that the terminal alkyne and OR ligands attached to W(1) undergo site exchange. Since the local co-ordination geometry about W(1) may be viewed as a square-based pyramid in which the diene and μ-OR fragments occupy fixed positions, a facile interconversion of the remaining positions may be envisaged through trigonal bipyramidal intermediates. This dynamic exchange process does not involve dissociation of the alkyne ligand, nor is this ligand scrambled between W(1) and W(2) since for $W_2(OPr^i)_6(\mu$-$C_4H_4)(C_2H_2)$, the ^1H resonance of the terminal ethyne ligand (δ 11.0) is flanked by satellites due to coupling to ^{183}W, $J(^{183}W-^1H)$ = 10.3 Hz, of the expected intensity for ^{183}W having a natural abundance of 14.5%.

It should be noted that, although the coupling of alkyne groups at dimetal centres is well documented,[5] these are the first compounds in which two alkynes are coupled and a third is present as a terminal alkyne ligand. In view of the fact that $Mo_2(OPr^i)_6(py)_2(\mu$-$C_2H_2)$ and $Mo_2(OCH_2Bu^t)_6(\mu$-$C_4H_4)(py)$ have been shown[3] to be intermediates in the catalytic cyclotrimerization of acetylene(s) to give benzene(s), it is likely that molybdenum analogues of $W_2(OR)_6(\mu$-$C_4R'_4)(C_2R'_2)$ compounds are involved.

It is clear that even the most subtle change in alkoxy group or alkyne substituent may greatly influence the nature of these reactions.

References

1 D. C. Bradley, R. C. Mehrotra, and P. D. Gaur, 'Metal Alkoxides,' Academic Press, New York, 1978.
2 M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, D. Little, and P. E. Fanwick, *Inorg. Chem.*, 1979, **18**, 2321.
3 M. H. Chisholm, K. Folting, J. C. Huffman, and I. P. Rothwell, *J. Am. Chem. Soc.*, 1982, **104**, 4389.
4 R. R. Schrock, M. L. Listermann, and L. G. Sturgeoff, *J. Am. Chem. Soc.*, 1982, **104**, 4291.
5 S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodwood, *J. Chem. Soc., Chem. Commun.*, 1978, 221.