Metal Alkoxides—Models for Metal Oxides. 5.[1] Coupling of Alkyne Ligands in Reactions Involving Ditungsten Hexaalkoxides: An Alternative to the Metathesis Reaction $M{\equiv}M + -C{\equiv}C- \rightarrow 2M{\equiv}C$

Malcolm H. Chisholm,* David M. Hoffman, and John C. Huffman

Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405. *Received February 2, 1984*

Abstract: $W_2(O\text{-}t\text{-}Bu)_6$ and $W_2(OR)_6(py)_2$, where R = *i*-Pr or CH_2-*t*-Bu, react in hydrocarbon solvents at ambient temperatures with ethyne (≥3 equiv) to give the compounds $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)$ and $W_2(OR)_6(\mu\text{-}C_4H_4)(C_2H_2)$, respectively. The same compounds are produced from reactions involving the ethyne adducts $W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)$ and $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_2H_2)(py)_2$ and ethyne, and an intermediate $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(py)$ has been isolated and shown to be isomorphous and isostructural with its previously characterized molybdenum analogue. The nature of the C-C coupling has been investigated by using the labeled ethynes $^{13}C_2H_2$ and $^{12}C_2D_2$ and found to occur without C–C or C–H rupture. Analogous reactions employing MeC≡CMe lead to the alkylidyne complex $(t\text{-}BuO)_3W{\equiv}CMe$ or $W_2(OR)_6(\mu\text{-}C_4Me_4)(C_2Me_2)$ compounds, where R = *i*-Pr and CH_2-*t*-Bu. These new compounds provide models for the cyclotrimerization and/or polymerization of alkynes at a dimetal center, though the elimination of the hydrocarbon fragment does not readily occur from the ditunsten center. These observations are contrasted with earlier findings in the chemistry of $Mo_2(OR)_6$ compounds. Single-crystal X-ray studies reveal the connectivity $(RO)_3W(\mu\text{-}\eta^1,\eta^4\text{-}C_4R'_4)(OR)W(OR)_2(\eta^2\text{-}C_2R'_2)$ for the compounds where R = *i*-Pr and R′ = H and Me. One tungsten atom is in a distorted octahedral environment being coordinated to three terminal OR ligands, a bridging OR ligand, and forming two W–C σ bonds (W–C = 2.13 (2) Å, averaged) to the $\mu\text{-}C_4R'_4$ ligand. This tungsten atom lies in a plane with the four carbon atoms of the $\mu\text{-}C_4$ ligand. The other tungsten atom is coordinated to one bridging and two terminal OR ligands, the η^2-alkyne (W–C = 2.07 (2) Å, averaged, and with C–C–C angle = 136 (3)°, averaged) and the four carbon atoms of the $\eta^4\text{-}C_4R'_4$ ligand (W–C = 2.40 (2) Å, averaged). The $\eta^2\text{-}C_2$ and $\eta^4\text{-}C_4$ ligands are aligned at right angles to one another. The W–W distances, 2.877 (1) (R′ = H) and 2.851 (1) Å (R′ = Me), are interpretable in terms of the existence of W–W single bonds. A qualitative bonding scheme is presented based on structural parameters and symmetry considerations. Low-temperature limiting NMR spectra are consistent with expectations based on the solid-state structures, but the molecules are fluxional showing two distinct processes: (1) rotation about the W–η^2-alkyne bond and (2) site exchange of the two terminal OR ligands and the $\eta^2\text{-}C_2R'_2$ ligand at one tungsten atom. Crystal data for $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)(C_2H_2)$ at −160 °C: a = 14.754 (7) Å, b = 12.125 (6) Å, c = 9.011 (4) Å, α = 105.51 (2)°, β = 88.66 (3)°, γ = 60.53 (2)°, Z = 2, d_{calcd} = 1.83 g cm^{-3}, and space group $P\bar{1}$. Crystal data for $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4Me_4)(C_2Me_2)$ at −169 °C: a = 16.352 (14) Å, b = 16.036 (12) Å, c = 26.335 (18) Å, Z = 8, d = 1.70 g cm^{-3}, and space group *Pcab*.

Previously we reported[2] reactions between $Mo_2(OR)_6(M{\equiv}M)$ compounds (R = *t*-Bu, *i*-Pr, and CH_2-*t*-Bu) and alkynes (HC≡CH, MeC≡CH, and MeC≡CMe) and the isolation of compounds of formula $Mo_2(OR)_6(py)_2(\mu\text{-alkyne})$, where R = *i*-Pr and CH_2-*t*-Bu, and $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_4H_4)$. No isolable products or NMR detectable compounds were formed for R = *t*-Bu. In the preceding paper we described[1] the preparation and characterization of related alkyne adducts $W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)$, $W_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}C_2H_2)$, and $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2(\mu\text{-}C_2Me_2)$ that revealed strikingly different structures as a function of alkoxy group and alkyne substituent. Schrock and co-workers[3] observed the metathesis-like reaction (eq 1) in reactions between $W_2(O\text{-}t\text{-}Bu)_6$ and dialkylacetylenes and more recently Cotton et al. observed related C≡C cleavages using PhC≡CPh[4] and EtC≡CEt[5] under somewhat different reaction conditions.

$$W_2(O\text{-}t\text{-}Bu)_6 + RC{\equiv}CR \rightarrow 2(t\text{-}BuO)_3W{\equiv}CR \quad (1)$$

R = Me, Et, and Pr

(1) Part 4. Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C., submitted for publication in *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 4389.

(3) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

(4) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* **1983**, *2*, 1167.

(5) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* **1983**, *2*, 1340.

We describe here related reactions wherein C–C coupling is favored over (1). A preliminary report of some aspects of this work has appeared.[6]

Results and Discussion

$W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)$. Hydrocarbon solutions of $W_2(O\text{-}t\text{-}Bu)_6$ react very rapidly with ethyne to give a brown waxy solid, which based on NMR spectroscopy and subsequent reactions, can reliably be established as $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)$. Addition of only 1 equiv of ethyne leads to a 1:1 mixture of this compound and the starting material, although in the presence of pyridine a simple ethyne adduct, $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_2H_2)(py)\cdot{}^1/_2py$, can be isolated as a crystalline compound and was described in detail in the preceding paper.[1] Addition of 1 equiv of ethyne to the μ-ethyne adduct leads to rapid formation of $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)$. In the presence of excess ethyne, black-insoluble polyacetylene is always formed but no further W_2-containing compounds have been detected. Though the NMR characterization of $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)$ leaves little doubt concerning its formulation, we have been unable to obtain a crystalline sample. However, treatment with excess *i*-PrOH in the presence of PMe_3 has allowed the isolation of the crystalline compound $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)(PMe_3)$, for which characterization by elemental analyses and NMR spectroscopy provide further evidence for our formulation of the $\mu\text{-}C_4H_4$ ligand in the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and ethyne.

The ^{1}H NMR spectra of $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)$ in toluene-d_8 in the temperature range −80 to +25 °C show four *t*-Bu resonances

(6) Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C.; Leonelli, J. *J. Chem. Soc., Chem. Commun.* **1983**, 589.

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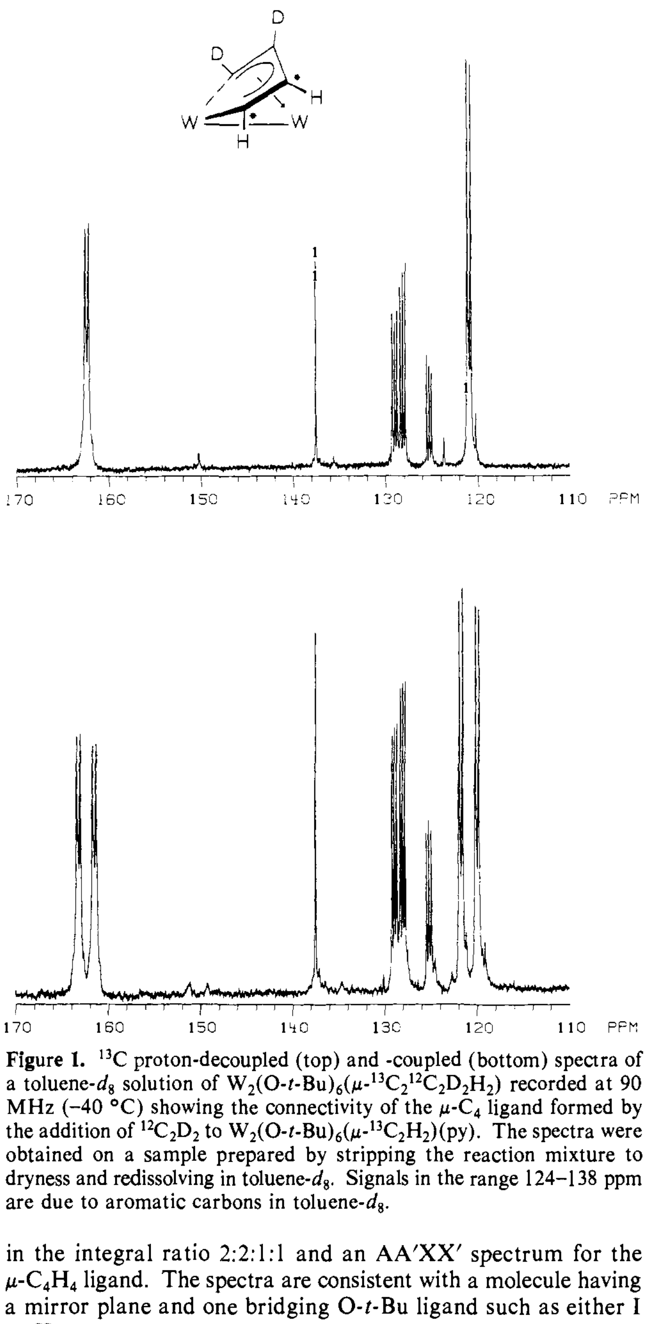
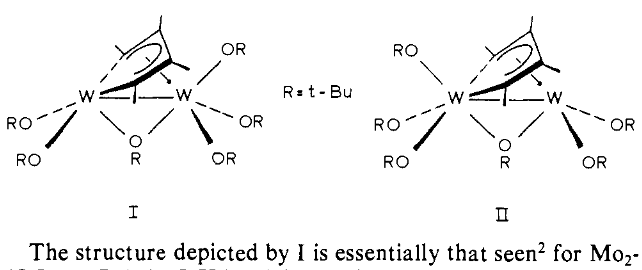


Figure 1. ^{13}C proton-decoupled (top) and -coupled (bottom) spectra of a toluene-d_8 solution of $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}^{13}C_2{}^{12}C_2D_2H_2)$ recorded at 90 MHz (−40 °C) showing the connectivity of the μ-C_4 ligand formed by the addition of $^{12}C_2D_2$ to $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}^{13}C_2H_2)(py)$. The spectra were obtained on a sample prepared by stripping the reaction mixture to dryness and redissolving in toluene-d_8. Signals in the range 124–138 ppm are due to aromatic carbons in toluene-d_8.

in the integral ratio 2:2:1:1 and an AA′XX′ spectrum for the μ-C_4H_4 ligand. The spectra are consistent with a molecule having a mirror plane and one bridging O-t-Bu ligand such as either I or II.



I II

The structure depicted by I is essentially that seen[2] for $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(py)$ but having a vacant coordination site in place of the M–py bond. The structure II is related to that seen for $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4R_4)(C_2R_2)$ compounds but lacks the η^2-C_2R_2 ligand.

In view of our evidence for a kinetically facile equilibrium between the ethyne adduct $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_2H_2)$ and a methylidyne complex $(t\text{-}BuO)_3W{\equiv}CH$ in toluene-d_8 at 20 °C,[1] we investigated the nature of the C–C coupling process in the reaction between $W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}^{13}C_2H_2)$ and 1 equiv of $^{12}C_2D_2$. The proton-decoupled and -coupled ^{13}C NMR spectra of the resultant $W_2(\mu\text{-}^{13}C_2{}^{12}C_2H_2D_2)$ moiety is shown in Figure 1. This, together

Table I. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(O\text{-}i\text{-}Pr)_6(C_4H_4)(C_2H_2)$ Molecule[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	7465.5 (3)	683.6 (4)	6998 (1)	12
W(2)	7678.3 (3)	1838.6 (4)	6486.5 (5)	11
C(3)	6372 (8)	−356 (10)	7358 (13)	15
C(4)	5944 (8)	409 (10)	6451 (14)	19
C(5)	6486 (8)	141 (10)	5048 (12)	16
C(6)	7350 (8)	−845 (10)	4812 (13)	16
C(7)	8687 (9)	1194 (11)	6981 (15)	22
C(8)	8676 (8)	509 (10)	5632 (14)	16
O(9)	7122 (5)	1332 (7)	9194 (8)	15
C(10)	7595 (9)	1650 (10)	10545 (13)	20
C(11)	7397 (10)	2962 (11)	11090 (15)	30
C(12)	7233 (9)	1188 (13)	11780 (14)	29
O(13)	6694 (5)	2195 (7)	6626 (9)	15
C(14)	6866 (8)	3347 (10)	7123 (13)	17
C(15)	7114 (9)	3666 (11)	5696 (15)	24
C(16)	5947 (8)	4290 (11)	8090 (15)	23
O(17)	8459 (5)	−862 (7)	7561 (9)	14
C(18)	9387 (8)	−1086 (10)	8114 (13)	16
C(19)	9408 (8)	−1605 (12)	9464 (14)	22
C(20)	10196 (8)	−1873 (10)	6833 (13)	16
O(21)	7570 (5)	−2280 (7)	8339 (8)	13
C(22)	7059 (8)	7091 (11)	8927 (14)	21
C(23)	6375 (12)	−2060 (14)	10344 (18)	44
C(24)	7798 (9)	−3980 (11)	9315 (14)	24
O(25)	8781 (5)	−2839 (7)	5007 (8)	15
C(26)	8954 (8)	−3467 (10)	3388 (12)	16
C(27)	9229 (9)	−4817 (11)	3189 (14)	25
C(28)	9753 (10)	−3208 (12)	2614 (14)	28
O(29)	7048 (5)	−2968 (7)	5579 (8)	15
C(30)	6193 (8)	−2812 (11)	4790 (14)	20
C(31)	5382 (8)	−2786 (12)	5836 (15)	24
C(32)	6449 (9)	−3820 (13)	3306 (14)	25

[a] Isotropic values for those atoms refined anistropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

with ^1H NMR spectra, show that the μ-C_4 ligand is formed by a simple coupling of C–C bonds. This is not preceded by or followed by C–C and/or C–H scrambling reactions.

$W_2(OR)_6(\mu\text{-}C_4R'_4)(C_2R'_2)$ Compounds. Syntheses. Hydrocarbon solutions of $W_2(OR)_6L_2$ compounds (R = i-Pr and $CH_2\text{-}t$-Bu and L = py or $HNMe_2$)[7] react with ethyne and but-2-yne (≥3 equiv) to give compounds of formula $W_2(OR)_6(\mu\text{-}C_4R'_4)(C_2R'_2)$, which are air sensitive, crystalline, and extremely soluble in hydrocarbon solvents. The high solubility in hydrocarbons causes problems in obtaining good yields by crystallization from these solvents, and reactivity toward a number of other common organic solvents (those containing OH, C=O, or active C—X bonds) precludes their use. By ^1H NMR spectroscopy their formation appears to be quantitative according to eq 2.

$$W_2(OR)_6L_2 + 3R'C{\equiv}CR' \rightarrow W_2(OR)_6(\mu\text{-}C_4R'_4)(C_2R'_2) + 2L \quad (2)$$

The same compounds are formed from the reactions of $W_2(OR)_6(\mu\text{-}C_2R'_2)(py)_2$ with 2 equiv of alkyne, and, in the reaction between $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and ethyne (2 equiv), the intermediate $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(py)$ can be isolated. Attempts to prepare related isopropoxy and but-2-yne derivatives lead to mixtures of products. Presumably the successful isolation of μ-$C_2R'_2$- and μ-$C_4R'_4$-containing compounds, which are intermediates in (2), rests on a careful balance of steric factors, even when (1) is not favored. The favorable binding of pyridine, or other donor ligands, can suppress otherwise facile C–C coupling reactions. It is thus worthy of note that $W_2(O\text{-}i\text{-}Pr)_6L_2$ (L = py, PMe_3, $HNMe_2$) and $W_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}C_2H_2)$ react with ethyne (2 or 1 equiv, respectively) to give a mixture of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_2H_2)L_2$, $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)L$, and $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}$

(7) For listings and discussions of M–M and M–O distances in the Chemistry of molybdenum and tungsten alkoxides see: Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

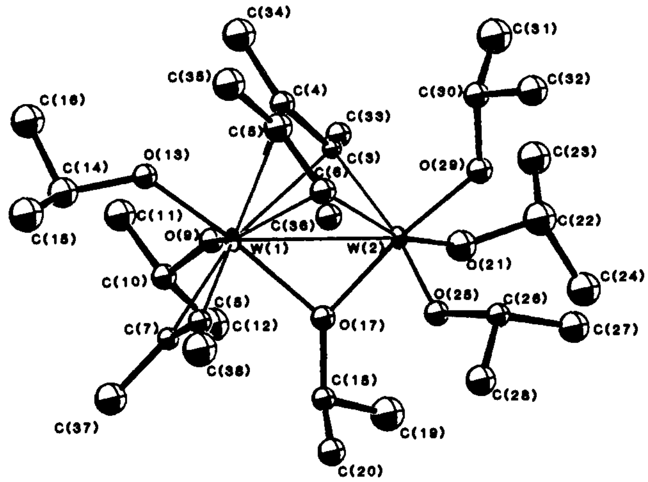


Figure 2. An ORTEP view of the $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4Me_4)(\eta^2\text{-}C_2Me_2)$ molecule showing the atom number scheme used in the tables. The same number scheme is used for the structurally related $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)$ molecule, which lacks carbon atoms numbered 34 through 38 shown here.

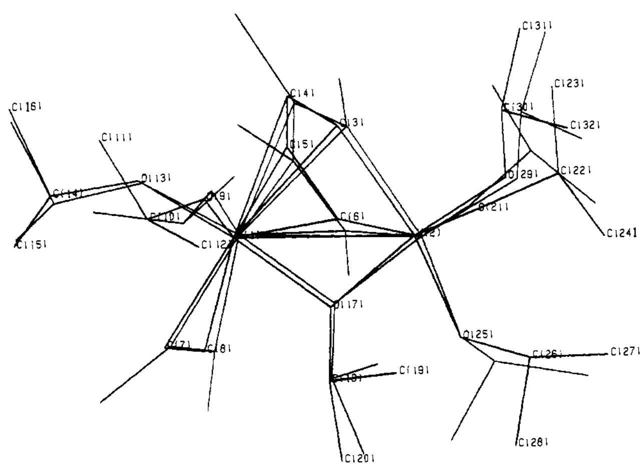


Figure 3. Best superposition of the two $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4R_4)(\eta^2\text{-}C_2R_2)$ molecules (R = Me and H), shown in stick form.

$C_4H_4)(C_2H_2)$ compounds from which we have been unsuccessful in isolating $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)L$. However, the alcoholysis reaction involving $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)$ in the presence of PMe_3 affords a route to $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)(PMe_3)$.

Crystal and Molecular Structures. $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4R'_4)(C_2R'_2)$ Where R = H and Me. Fractional coordinates and isotropic thermal parameters are given in Tables I and II for the compounds where R = H and Me, respectively. An ORTEP view of the $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4Me_4)(C_2Me_2)$ molecule is shown in Figure 2. The numbering scheme for the $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)(C_2H_2)$ molecule is the same but lacks carbons C(33) through C(38), which are methyl carbons derived from dimethylacetylene. A comparison of pertinent bond distances and angles for the two compounds is given in Tables III and IV, respectively. Finally, stereoviews of the superimposition of the two molecules are shown in Figure 3. The two compounds are thereby shown to be remarkably similar in structure.

The following points are worthy of particular note. (1) The W–W distances, 2.87 and 2.85 Å, are outside the range observed for W–W triple and double bonds.[7] They are at most single-bond distances. (2) The W(2)–C(3) and W(2)–C(6) distances are typical for tungsten–carbon σ bonds, while the η^4-carbon to W(1) distances are typical of those found for $\eta^5\text{-}C_5H_5\text{-}W$ bonds.[8] The C–C distances within the $\mu\text{-}C_4$ ring are equivalent to within 3σ at 1.40 Å, typical again of $\eta^5\text{-}C_5H_5$ and η^4-conjugated diene distances. (3) The $W\text{–}\eta^2\text{-}C_2R'_2$ distances, 2.06–2.09 Å, are notably shorter than the $W\text{–}\eta^4$ carbon distances, and the C–C–H and

(8) Comp. Organometallic Chem., Volume 3, Ch. 27.2.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(O\text{-}i\text{-}Pr)_6(C_4Me_4)(C_2Me_2)$ Molecule[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^3
W(1)	2748.9 (4)	823.2 (4)	3284.2 (3)	9
W(2)	2374.8 (4)	9839.1 (4)	4155.7 (3)	9
C(3)	3462 (8)	585 (9)	4091 (7)	9 (3)
C(4)	4037 (9)	390 (9)	3728 (7)	15 (3)
C(5)	3787 (10)	−278 (10)	3403 (8)	19 (3)
C(6)	3023 (9)	−604 (10)	3505 (8)	16 (3)
C(7)	1884 (9)	1147 (9)	2752 (7)	11 (3)
C(8)	1973 (9)	353 (9)	2722 (7)	12 (3)
O(9)	2815 (6)	1954 (6)	3548 (5)	14 (2)
C(10)	2564 (9)	2769 (9)	3435 (8)	15 (3)
C(11)	3310 (10)	3327 (11)	3422 (8)	24 (4)
C(12)	1965 (11)	3076 (11)	3828 (8)	27 (4)
O(13)	3613 (6)	1032 (6)	2812 (5)	14 (2)
C(14)	3640 (10)	1626 (10)	2393 (8)	22 (3)
C(15)	3484 (11)	1122 (12)	1893 (9)	29 (4)
C(16)	4466 (10)	1993 (11)	2390 (9)	27 (4)
O(17)	1736 (6)	696 (6)	3776 (5)	14 (2)
C(18)	912 (9)	1019 (9)	3763 (8)	13 (3)
C(19)	617 (11)	1227 (12)	4289 (9)	28 (4)
C(20)	335 (9)	402 (10)	3497 (8)	18 (3)
O(21)	2161 (6)	357 (7)	4805 (5)	22 (2)
C(22)	2255 (11)	78 (11)	5334 (9)	26 (4)
C(23)	2905 (10)	604 (11)	5595 (8)	26 (4)
C(24)	1429 (11)	178 (11)	5576 (9)	26 (4)
O(25)	1495 (6)	−924 (6)	4025 (5)	14 (2)
C(26)	1321 (8)	−1781 (9)	4159 (8)	13 (3)
C(27)	1025 (10)	−1800 (11)	4694 (8)	22 (4)
C(28)	684 (10)	−2121 (10)	3788 (8)	21 (3)
O(29)	2872 (6)	−1061 (6)	4541 (5)	16 (2)
C(30)	3654 (9)	−1452 (10)	4501 (8)	16 (3)
C(31)	4231 (11)	−1081 (12)	4878 (9)	29 (4)
C(32)	3554 (10)	−2375 (11)	4582 (8)	22 (4)
C(33)	3607 (9)	1319 (10)	4440 (7)	15 (3)
C(34)	4860 (10)	770 (11)	3667 (9)	26 (4)
C(35)	4343 (10)	−621 (11)	2983 (9)	25 (4)
C(36)	2727 (9)	−1395 (9)	3207 (7)	16 (3)
C(37)	1409 (10)	−1765 (11)	2450 (9)	24 (4)
C(38)	1673 (10)	−365 (11)	2402 (9)	28 (4)

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.*, **1959**, *12*, 609.

Table III. Selected Bond Distances (Å) for the Molecules $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4R_4)(C_2R_2)$ Where R = H (I) and Me (II)

A	B	I	II
W(1)	W(2)	2.877 (1)	2.851 (1)
W(1)	O(9)	1.910 (7)	1.945 (10)
W(1)	O(13)	1.931 (7)	1.911 (11)
W(1)	O(17)	2.152 (7)	2.112 (11)
W(1)	C(3)	2.419 (11)	2.453 (18)
W(1)	C(4)	2.421 (12)	2.507 (16)
W(1)	C(5)	2.398 (11)	2.469 (16)
W(1)	C(6)	2.372 (11)	2.404 (16)
W(1)	C(7)	2.092 (13)	2.059 (16)
W(1)	C(8)	2.063 (11)	2.092 (17)
W(2)	O(17)	2.004 (7)	1.995 (10)
W(2)	O(21)	1.903 (7)	1.933 (14)
W(2)	O(25)	1.901 (7)	1.920 (10)
W(2)	O(29)	1.923 (8)	1.942 (11)
W(2)	C(3)	2.105 (11)	2.150 (14)
W(2)	C(6)	2.140 (11)	2.137 (18)
O(9)	C(10)	1.445 (13)	1.402 (18)
O(13)	C(14)	1.458 (13)	1.460 (22)
O(17)	C(18)	1.434 (13)	1.443 (17)
O(21)	C(22)	1.420 (13)	1.473 (24)
O(25)	C(26)	1.426 (13)	1.446 (18)
O(29)	C(30)	1.445 (13)	1.428 (18)
C(3)	C(4)	1.402 (16)	1.377 (23)
C(4)	C(5)	1.380 (16)	1.430 (24)
C(5)	C(6)	1.392 (16)	1.381 (22)
C(7)	C(8)	1.280 (17)	1.285 (21)

Table IV. Selected Bond Angles (deg) for the $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4R_4)(C_2R_2)$ Molecules Where R = H (I) and Me (II)

A	B	C	I	II	A	B	C	I	II
O(9)	W(1)	O(13)	93.1 (3)	91.6 (4)	O(17)	W(2)	O(29)	171.3 (3)	173.1 (4)
O(9)	W(1)	O(17)	83.9 (3)	85.1 (4)	O(17)	W(2)	C(3)	91.8 (4)	90.6 (5)
O(9)	W(1)	C(3)	80.2 (3)	79.0 (5)	O(17)	W(2)	C(6)	92.7 (3)	95.0 (6)
O(9)	W(1)	C(4)	95.5 (4)	92.6 (5)	O(21)	W(2)	O(25)	117.0 (3)	107.3 (5)
O(9)	W(1)	C(5)	128.6 (3)	125.7 (5)	O(21)	W(2)	O(29)	86.6 (3)	86.2 (5)
O(9)	W(1)	C(6)	142.4 (3)	142.3 (6)	O(21)	W(2)	C(3)	88.1 (4)	88.9 (6)
O(9)	W(1)	C(7)	94.8 (4)	92.6 (5)	O(21)	W(2)	C(6)	160.2 (4)	160.5 (5)
O(9)	W(1)	C(8)	130.1 (4)	128.5 (5)	O(25)	W(2)	O(29)	88.1 (3)	86.1 (4)
O(13)	W(1)	O(17)	171.8 (3)	174.4 (4)	O(25)	W(2)	C(3)	154.9 (4)	163.8 (6)
O(13)	W(1)	C(3)	106.9 (3)	103.8 (5)	O(25)	W(2)	C(6)	82.8 (4)	90.9 (5)
O(13)	W(1)	C(4)	76.3 (3)	74.4 (5)	O(29)	W(2)	C(3)	94.2 (4)	96.3 (5)
O(13)	W(1)	C(5)	74.3 (3)	72.5 (5)	O(29)	W(2)	C(6)	95.1 (3)	87.9 (6)
O(13)	W(1)	C(6)	103.8 (4)	100.7 (5)	C(3)	W(2)	C(6)	72.1 (4)	73.2 (6)
O(13)	W(1)	C(7)	90.0 (4)	91.2 (5)	W(1)	O(9)	C(10)	137.5 (7)	141.0 (11)
O(13)	W(1)	C(8)	93.4 (4)	92.9 (6)	W(1)	O(13)	C(14)	125.6 (6)	129.0 (9)
O(17)	W(1)	C(3)	80.2 (3)	80.0 (5)	W(1)	O(17)	W(2)	87.5 (3)	87.9 (4)
O(17)	W(1)	C(4)	111.6 (3)	110.3 (5)	W(1)	O(17)	C(18)	132.9 (6)	133.1 (11)
O(17)	W(1)	C(5)	113.5 (3)	113.1 (5)	W(2)	O(17)	C(18)	137.9 (6)	138.3 (10)
O(17)	W(1)	C(6)	83.0 (3)	84.6 (5)	W(2)	O(21)	C(22)	137.0 (7)	133.5 (10)
O(17)	W(1)	C(7)	82.7 (4)	84.4 (5)	W(2)	O(25)	C(26)	136.3 (6)	135.1 (9)
O(17)	W(1)	C(8)	82.8 (3)	85.6 (6)	W(2)	O(29)	C(30)	131.3 (6)	131.5 (10)
C(3)	W(1)	C(4)	33.7 (4)	32.2 (5)	W(1)	C(3)	W(2)	78.6 (3)	76.2 (5)
C(3)	W(1)	C(5)	58.0 (4)	56.8 (6)	W(1)	C(3)	C(4)	73.2 (7)	76.1 (11)
C(3)	W(1)	C(6)	62.9 (4)	63.5 (6)	W(2)	C(3)	C(4)	120.4 (8)	119.5 (11)
C(3)	W(1)	C(7)	162.6 (4)	162.9 (6)	W(1)	C(4)	C(3)	73.1 (6)	71.7 (9)
C(3)	W(1)	C(8)	143.1 (4)	147.8 (5)	W(1)	C(4)	C(5)	72.4 (7)	71.8 (9)
C(4)	W(1)	C(5)	33.3 (4)	33.4 (6)	C(3)	C(4)	C(5)	114.1 (10)	113.0 (14)
C(4)	W(1)	C(6)	57.7 (4)	57.8 (5)	W(1)	C(5)	C(4)	74.3 (7)	74.8 (9)
C(4)	W(1)	C(7)	163.2 (4)	164.8 (6)	W(1)	C(5)	C(6)	72.0 (6)	71.0 (9)
C(4)	W(1)	C(8)	134.0 (4)	137.7 (5)	C(4)	C(5)	C(6)	113.1 (10)	115.3 (17)
C(5)	W(1)	C(6)	33.9 (4)	32.9 (5)	W(1)	C(6)	W(2)	79.1 (4)	77.6 (5)
C(5)	W(1)	C(7)	133.7 (4)	137.7 (6)	W(1)	C(6)	C(5)	74.1 (6)	76.1 (10)
C(5)	W(1)	C(8)	100.7 (4)	104.4 (6)	W(2)	C(6)	C(5)	120.1 (8)	118.5 (13)
C(6)	W(1)	C(7)	118.2 (4)	122.2 (6)	W(1)	C(7)	C(8)	70.8 (7)	73.4 (11)
C(6)	W(1)	C(8)	82.7 (4)	86.6 (6)	W(1)	C(8)	C(7)	73.3 (8)	70.6 (11)
C(7)	W(1)	C(8)	35.9 (5)	36.0 (6)	C(8)	C(7)	C(37)		133.3 (17)
O(17)	W(2)	O(21)	87.3 (3)	93.0 (5)	C(7)	C(8)	C(38)		139.0 (17)
O(17)	W(2)	O(25)	89.1 (3)	87.5 (4)					

Table V. Summary of Angles (deg) Subtended at W(1) in $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4R_4)(C_2R_2)$ Compounds (I, R = H; II, R = Me) Assuming X Represents the Midpoint of the η^4-C_4 Carbons and Y the Midpoint of the η^2-C_2 Alkyne Carbons

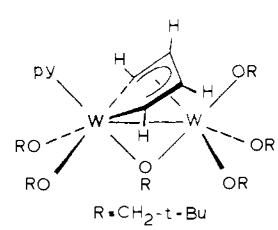
atom	atom	atom	I	II	assignt[a]
O(9)	W(1)	O(13)	93.0	91.6	ae
O(9)	W(1)	Y	112.44	110.7	ee
O(9)	W(1)	X	112.4	110.4	ee
O(9)	W(1)	O(17)	83.9	85.1	ae
O(13)	W(1)	Y	91.8	92.2	ae
O(13)	W(1)	X	90.4	87.4	ae
O(13)	W(1)	O(17)	171.8	174.4	aa
Y	W(1)	X	134.9	138.8	ee
O(17)	W(1)	Y	82.5	84.7	ae
O(17)	W(1)	X	97.8	98.0	ae

[a] Based on an idealized trigonal bipyramid: aa = 180°, ae = 90°, and ee = 120°.

C–C–C angles of the alkyne ligand are in the range 133–139°, quite markedly bent from linearity. The acetylenic C–C distance, 1.28 Å, while significantly longer than in a typical free alkyne, 1.21 Å, are not nearly lengthened as much as the μ-C_2R_2 alkynes discussed previously.[1,2] (4) The terminal W–OR distances, which fall within the range 1.90–1.93 Å, are typical of W–O distances having some π-character[7] while the distances to the bridging OR ligand, O(17), are longer and asymmetric with the W(2)–O(17) distances being more than 0.1 Å shorter than the W(1)–O(17) distances. (5) The local geometry about W(2) is easily seen to approximate that of an octahedron. The geometry about W(1) may also be viewed as a distorted octahedral one if the η^4-C_4 ligand is viewed as a diene occupying two coordination sites. In these descriptions the M–M bond is not counted.

An alternative description of the coordination geometry about W(1) can be based on the trigonal bipyramid, if the η^4-C_4R_4 ligand is considered to occupy one coordination site and the η^2-alkyne ligand another. By defining the midpoint of the η^4-C_4R_4 ligand as a point X, the averaged positions of the four η^4-carbon atoms, and the midpoint of the alkyne η^2-carbons as Y, then X and Y occupy equatorial sites of a trigonal bipyramid with O(17) of the bridging OR ligand and O(13) as axial positions. The angles subtended at W(1) using this five-coordinate model are given in Table V. The distortions from an idealized trigonal bipyramid are toward a square-based bipyramid with the η^4-C_4R_4 ligand X occupying the apical position.

$W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_4H_4)$ was shown to be isomorphous and isostructural with its molybdenum analogue. The molecular structure is shown schematically in III. In view of the disorder



III

associated with the neopentoxy ligands, described previously for the molybdenum compound, a full refinement was not undertaken since the quality of the structural determination would not have revealed crystallographically significant differences in metal–ligand distances. The fact that $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_4H_4)$ is isomorphous and isostructural with its molybdenum analogue is, however, noteworthy in that the solution properties of the two compounds differ as described later in this paper.

A Qualitative Bonding Description for $W_2(OR)_6(\mu\text{-}C_4R'_4)(C_2R'_2)$ Compounds. As a starting point for an understanding of the

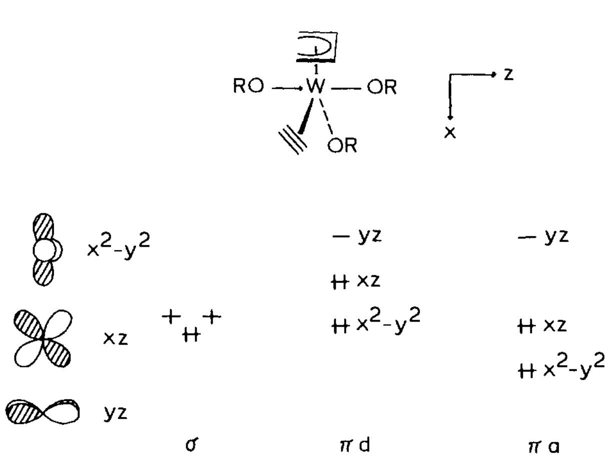
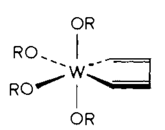
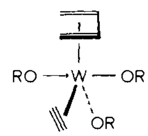


Figure 4. Evolutionary splitting, from left to right, of the t_{2g}-type orbitals from, first, the π-donor influence of the alkoxide and alkyne ligands (πd) and, second, the π-acceptor influence of the alkyne and diene fragments (πa) for the tungsten-containing fragment shown.

bonding in these compounds, we propose that the molecule may be viewed as the sum of two fragments IV and V. W(2) is readily



IV

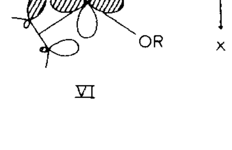


V

seen to be octahedrally coordinated and in this formalism the bridging OR ligand is a uninegative ligand to W(2) and forms a dative bond to W(1), consistent with the respective short and long W to O(17) distances noted previously. The μ-C_4R_4 ligand is a 2− ligand to W(2), a metallacyclopentadiene, and a η^4-diene to W(1). W(2) is thus 6+, d^0, and W(1) is 2+, d^4. At this point the octahedral hexavalent W(2) needs no further comment and we turn our attention to W(1).

As noted previously the geometry about W(1) may be viewed as that of a distorted octahedron in which the diene fragment occupies two adjacent sites and the alkyne one site. In the coordinate system shown in Figure 4, the d orbitals will be split into two sets as a result of forming the six σ bonds (formally t_{2g} and e_g in O_h symmetry). The d_{z^2} and d_{xy} orbitals in the coordinate system shown will be very high in energy having M–L σ* character. Of the d_{xz}, d_{yz}, and $d_{x^2-y^2}$ (the t_{2g} set) only the d_{yz} and d_{xz} orbitals have the appropriate symmetry to interact with filled alkoxy oxygen p orbitals and the alkyne filled π-orbital that is perpendicular to the M–η^2-C_2 plane. The d_{yz} orbital can interact with all three potential π-donor ligands while the d_{xz} orbital can only interact with one alkoxy ligand and the alkyne. We would therefore expect the splitting of the t_{2g}-type orbitals shown in Figure 4 that places the $d_{x^2-y^2}$ lowest and the d_{yz} highest as a result of π-donor interactions.

Next we turn to the π-acceptor interaction with the η^4-C_4 ligand and the alkyne. The highest energy π*-orbital of the C_4-diene fragment has δ symmetry with respect to the metal and may thus interact with the d_{yz} orbital, though we expect this to be a very weak interaction from both energy and overlap considerations. On the other hand the d_{xz} orbital can interact with the LUMO of the C_4-diene, and from both overlap and energy considerations this should be a strong interaction resulting in a net stabilization of the d_{xz} orbital. For the bent alkyne fragment the LUMO interacts strongly with the $d_{x^2-y^2}$, as shown in VI, whereas the other



VI

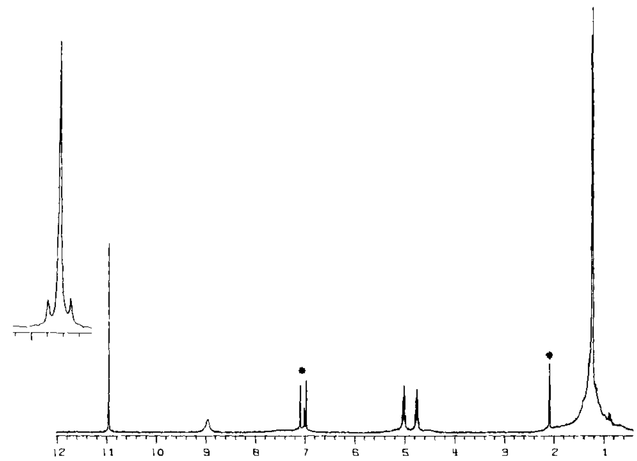
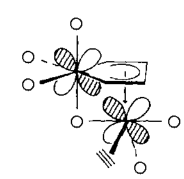


Figure 5. ^{1}H NMR spectrum of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)$ in toluene-d_8 recorded at +21 °C and 360 MHz. The resonances denoted by the asterisk arise from protio impurities in the solvent. The η^2-C_2H_2 signal at δ ~11 is shown at scale expansion in the inset to show the coupling between ^{183}W and ^{1}H.

alkyne π* orbital does not have the proper pseudo symmetry to interact with any metal d orbital. Consequently we predict the splitting of the remnant t_{2g} set to be the "two below one" pattern shown in Figure 4. This is reminiscent of other d^4 octahedral complexes.[9,10]

Lastly, we note that the d_{xz} orbital on W(1) may interact with its counterpart on W(2) as shown in VII below to form M–M σ and σ* bonds. At a distance of 2.85 Å, no other d–d interactions (π and δ type) would be significant.



VII

Several important features emerge from a consideration of this qualitative bonding picture. (1) The observed diamagnetism can be rationalized in terms of the splitting of the t_{2g}-type orbitals. (2) The alkyne can compete with the terminal alkoxy ligands in π-donation to the metal; i.e. the alkyne can contribute more than two electrons to the metal. (3) The observed large bend-back angle of the alkyne (C–C–C or C–C–H) results from metal-to-alkyne back bonding involving only one of the alkyne π* orbitals VI. The C–C–C angle and the lengthening of the C≡C bond are comparable to those well documented in alkyne adducts of zerovalent platinum of formula $L_2Pt(alkyne)$.[11] (4) The observed W–W distance, 2.85 Å, may be reconciled with the formation of a M–M dative bond, W(1)→W(2), which may in turn offset the large difference in formal oxidation states of the two metal atoms, +6 and +2.

NMR Studies. $W_2(OR)_6(\mu\text{-}C_4R'_4)(C_2R'_2)$ Compounds. NMR data are given in the Experimental Section. The ^{1}H NMR spectra obtained for the compounds where R = CH_2-t-Bu and R′ = H and Me in toluene-d_8 at +16 °C are consistent with expectations based on the molecular structures of the isopropoxy compounds described previously. At high temperatures (>80 °C) the spectra broaden as the molecules becomes fluxional. The isopropoxy compound with R′ = H is, however, fluxional at lower tempera-

(9) Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713.
(10) Kubacek, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320.
(11) Comp. Organometallic Chem., Volume 6, Ch. 39, pages 698–699. For a discussion of metal-to-alkyne backbonding and its selective effect on the alkyne C–C–C angles, see: Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858 and references therein.

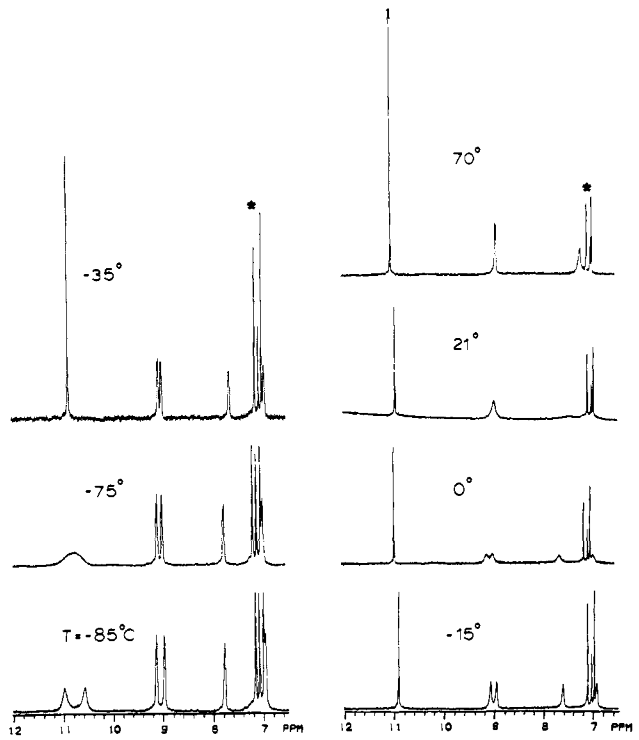


Figure 6. Variable-temperature ^{1}H NMR spectra recorded at 360 MHz in the range 6.5–12 ppm showing the temperature-dependent behavior of the η^2-C_2H_2 and the μ-C_4H_4 signals for the $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)$ molecule. The signals denoted by the asterisk arise from protio impurities in the toluene-d_8 solvent.

tures leading to some fascinating spectral changes with temperature. We describe these in detail and offer our interpretation of the data since similar behavior is expected for the other compounds of formula $W_2(OR)_6(\mu\text{-}C_4R'_4)(C_2R'_2)$ but with different activation parameters.

The ^{1}H NMR spectrum of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)(C_2H_2)$ in toluene-d_8 at 21 °C is shown in Figure 5. The only distinctive features of the spectrum are a sharp downfield resonance at 11 ppm, two septets of equal intensity, and a sharp doublet and several rolls in the base line. The downfield signal, δ 11, is readily assigned to the η^2-C_2H_2 protons, and the appearance of tungsten satellites of the intensity expected for ^{183}W, $I = {}^1/_2$, 14.5% natural abundance, confirms that the alkyne ligand is neither reversibly dissociating nor being transferred intramolecularly between the two tungsten atoms at a rate that is rapid on the NMR time scale. The η^2-C_2H_2 signal retains its coupling to tungsten even at 100 °C, and from separate experiments we find no evidence for alkyne dissociation in these compounds. Specifically, addition of MeC≡CMe to the ethyne derivative and addition of ethyne to the dimethylacetylene derivative do not lead to alkyne exchange.

At −85 °C a low temperature limiting spectrum is consistent with expectation based on the observed solid-state molecular structure that lacks any element of symmetry and has the ethyne ligand coordinated perpendicularly to the plane of the diene ligand. The changes in the region 6.5–12 ppm upon raising the temperature are shown in Figure 6. This is the region of the spectrum where the μ-C_4H_4 and the η^2-C_2H_2 signals are observed. There are four signals, each a multiplet, associated with the μ-C_4H_4 protons at −85 °C, and upon raising the temperature these collapse in a pairwise manner to give above +80 °C two signals, each a part of an AA′XX′ multiplet. The coalescence temperatures of these pairwise collapses differ, but from the observed T_c's and the low temperature chemical shift positions a common activation energy is seen: $\Delta G^\ddagger = 13.6 \pm 0.3$ kcal mol^{-1}. Even at −85 °C the ethyne proton signals are broad, indicating that site exchange is not completely frozen out. [Spectra obtained at lower temperatures were also broad but probably because of other factors such as increased solvent viscosity.] However, assuming that limiting chemical shift values for the two protons had been reached

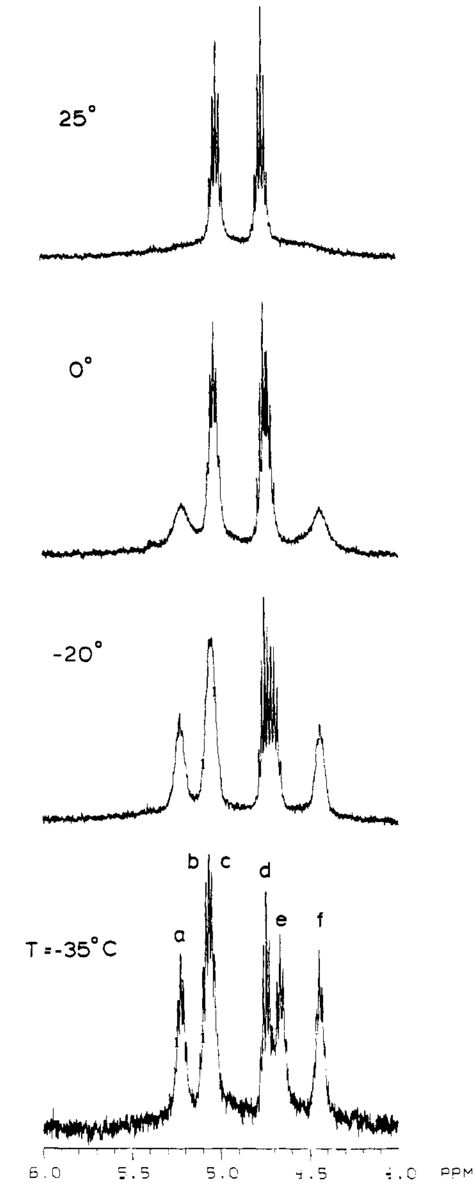
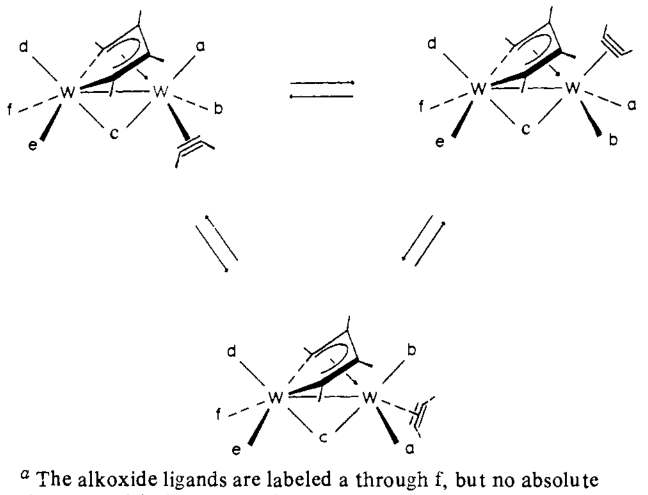


Figure 7. ^{1}H NMR spectra recorded at various temperatures in the range 4.0–6.0 ppm showing the temperature dependence of the methyne signals of the O-i-Pr ligands in a sample of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)$ in toluene-d_8. The labels a through f refer to the text discussion and are not meant to imply any absolute assignment with respect to the labels used in Scheme I.

at −85 °C, and by the observed coalescence temperature, we obtain $\Delta G^\ddagger = 9.4 \pm 0.3$ kcal mol^{-1} for ethyne hydrogen site exchange.

The spectral changes observed in the isopropoxy methyne region are shown in Figure 7. At −35 °C there are six septets, two of which are overlapping, which we shall call, from low field to high field: a, b, c, d, e, and f. The septets b and c at −35 °C are the pair that are overlapping. Upon raising the temperature to −20 °C the chemical shift positions of the septets d and e move together to give a complex overlapping but well-resolved pattern. It is important to recognize this as distinct from the broadening observed for the septets a, b, c, and f, particularly since septets b and c were already overlapping. The interpretation is, however, unequivocal: four of the O-i-Pr ligands are undergoing some sort of site exchange on the NMR time scale at −20 °C while two are not. From the spectral changes in the temperature range −20 to +25 °C it is clear that there is a pairwise exchange: a with f and b with c. Because the chemical shift separation is small for b and c and large for a and f, the former coalesce and sharpen so that at room temperature a single septet is seen for b ⇌ c, while the exchange of a and f produces a roll in the base line. The signals for d and e are accidentally degenerate at 25 °C, but upon raising

Scheme I. Proposed Site Exchanges To Account for the Observed Variable-Temperature ^1H NMR Spectra of the O-*i*-Pr Ligands in $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)^a$



^{a} The alkoxide ligands are labeled a through f, but no absolute assignment with the spectra shown in Figure 7 is intended.

the temperature further they become distinct again. The exchange between a and f is approaching the limiting rapid exchange septet at 90 °C. Again it is possible to obtain an estimate of ΔG^* for the exchange processes a $\rightleftharpoons$ f and b $\rightleftharpoons$ c from their T_c's and low-temperature chemical shifts: 13.7 ± 0.2 and 13.3 ± 0.2 kcal mol^{-1}. Thus, bearing in mind the assumptions inherent in this approach, we see that the activation energy for the process that exchanges O-*i*-Pr ligands in a pairwise manner is the same as that which cause a pariwise exchange of the μ-C_4H_4 protons but is quite different from that which makes the ethyne protons equivalent.

Our interpretation of the above is as follows. The low-energy process is rotation about the tungsten–alkyne bond, and this is distinct from the higher energy process that creates an apparent mirror plane in the molecule. The only plausible interpretation of the latter appears to be a psuedorotation of the ligands at W(1) keeping the bridging OR and μ-C_4H_4 ligands fixed. This is shown in Scheme I. The ligands attached to W(2), the formally 6+ metal center, remain fixed while the pseudo-five-coordinate W(1), formally the 2+, d^4, metal center, is stereochemically labile. This seems in intuitively satisfying interpretation of the dynamic behavior observed. Qualitatively, the spectra observed for the other $W_2(OR)_6(\mu\text{-}C_4R'_4)(C_2R'_2)$ compounds are similar in showing a low-energy process for alkyne rotation but with a higher energy barrier for R′ = Me than H and a higher barrier to OR exchange for R = CH_2-*t*-Bu than *i*-Pr. In all instances alkyne rotation is rapid on the ^1H NMR time scale at +21 °C and 360 MHz.

$W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(py)$ shows a complex ^1H NMR spectrum in solution at 21 °C. The solid-state molecular structure, shown schematically in III, contains a plane of symmetry and the ^1H NMR spectrum for the molybdenum analogue is entirely in accord with the maintenance of the same in solution. We can be confident that we have formulated the tungsten compound correctly on the bases of the observed elemental analyses, solid-state structure, and chemical reactivity. Reaction of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(py)$ with $^{13}C_2H_2$ gives only $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(^{13}C_2H_2)$, and similarly reaction with dimethylacetylene gives $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(C_2Me_2)$. We considered the possibility that $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(py)$ exists in solution in equilibrium with $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)$, a molecule akin to $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)$, and free pyridine. However, the ^1H NMR spectra are unaffected by added pyridine. The most plausible explanation is that $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(py)$ exists in solution in a mixture of isomeric forms, one of which may be reconciled with III based on ^1H NMR data. Interestingly the spectra obtained for $W_2(OCH_2\text{-}t\text{-}Bu)_6(PMe_3)(\mu\text{-}C_4H_4)$ are as expected for III where PMe_3 replaces py. See the Experimental Section.

^{13}C NMR Studies. In order to investigate further the nature of the η^2-C_2H_2-to-W interaction, we prepared the labeled compound $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}^{13}C_2H_2)$ where ^{13}C represents 90 atom % ^{13}C. The ^{13}C NMR spectra recorded in toluene-d_8 at +21 °C are shown in Figure 8. The proton-decoupled spectrum showed a resonance assignable to the η^2-alkyne carbons, which due to rapid rotation are equivalent at this temperature on the NMR time scale, at δ 179.3 with coupling to ^{183}W, J_{WC} = 40 Hz. The extremely low-field carbon chemical shift, together with the low-field proton shift for the ethyne protons, suggests that the ethyne ligand is acting as more than a two-electron donor. On the basis of the Templeton[12] correlation of chemical shift, the alkyne ligand may be formulated as a three electron donor. This is consistent with the notion advanced previously that the alkyne ligand competes with the two other terminal RO ligands in π-donation to W(1).

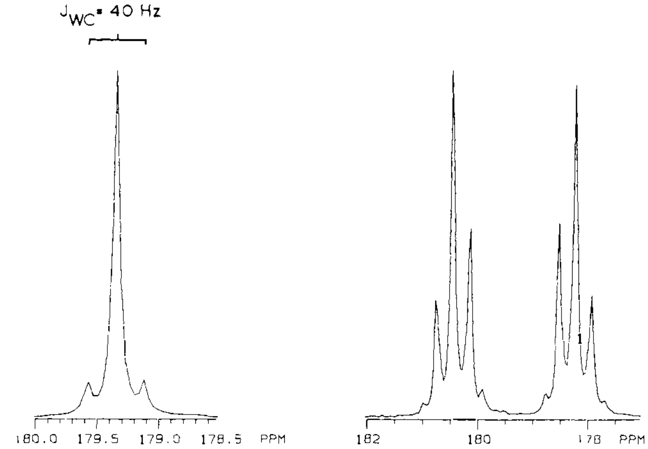


Figure 8. ^{13}C NMR spectra, recorded at +21 °C and 90 MHz with toluene-d_8 as solvent, in the η^2-C_2H_2 carbon region of the sample $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(^{13}C_2H_2)$, where ^{13}C indicates 90 atom % ^{13}C enrichment shown left with proton decoupling and right with proton coupling.

The proton-coupled ^{13}C spectrum of the ethyne ligand in $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(^{13}C_2H_2)$ is also shown in Figure 8. This reveals half of the expected AA′XX′ spectrum, with further satellites due to coupling to ^{183}W, $I = {}^1/_2$, 14.5% natural abundance. Successful simulation of the spectrum gave $^1J_{CH}$ = 198.2 Hz, $^2J_{CH}$ = 4.2 Hz, $^1J_{CC}$ = 54.5 Hz, and $^3J_{HH} \simeq$ 1.0 Hz. $^1J_{CH}$ and $^2J_{CH}$ are necessarily of the same sign, but the relative signs of J_{CC} and J_{HH} are not known. The magnitude of $^1J_{CH}$ and $^1J_{CC}$ are markedly reduced from the values of 249 and 172 Hz observed for free ethyne and are comparable to those for ethylene: $^1J_{CH}$ = 175 Hz and J_{CC} = 68 Hz.[13] The ^1H-coupled spectrum is, however, quite different from that seen for $W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)$ for which a very small ^{13}C–^{13}C coupling (<15 Hz) leads to the fortuitously simple spectrum described previously.[1]

Assignments for the μ-C_4H_4 Ligand. An absolute assignment of ^1H and ^{13}C signals for the μ-C_4H_4 ligand in $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}^{12}C_2{}^{13}C_2H_2D_2)$ (Figure 1) is possible on the basis of the assumption that ^{183}W–^{13}C coupling will be greater to the carbon atoms σ-bonded to W(2) than to the carbon atoms that are π-bonded to W(1). Thus the downfield carbon resonances are assigned to C(3) and C(6), the carbon atoms σ-bonded to W(2). Because of the different ^{13}C–^1H couplings, an assignment of the proton signals is also possible. The hydrogen atoms bonded to C(3) and C(6) are upfield, ca. 7 ppm, relative to those bonded to C(4) and C(5) that occur in the range δ 9–10.

Concluding Remarks

(1) When the alkoxy ligands are less sterically demanding than *t*-BuO, reactions between $W_2(OR)_6$ compounds and ethyne and 2-butyne lead to alkyne-coupled dinuclear compounds via $W_2(\mu\text{-}C_2R'_2)$ intermediates. The compounds of formula W_2-

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$(OR)_6(\mu\text{-}C_4R'_4)(C_2R'_2)$ appear to be the thermodynamically favored products and are not involved in the metathesis reaction (1).

(2) The compounds of formula $W_2(OR)_6(\mu\text{-}C_4R'_4)(C_2R'_2)$ are the first of their type in organometallic chemistry. A sequence leading to the catalytic cyclotrimerization of alkynes requires insertion of the $\eta^2\text{-}C_2R'_2$ ligand into a W–C bond of the $\mu\text{-}C_4R'_4$ ligand followed by reductive elimination of $C_6R'_6$ from the dimetal center. Neither step is observed in a catalytic manner, but thermal decomposition of $W_2(OR)_6(\mu\text{-}C_4Me_4)(C_2Me_2)$ does yield hexamethylbenzene.

(3) An interesting comparison with the reactivity of $Mo_2(OR)_6$ compounds is seen. The latter are active for the catalytic cyclotrimerization of alkynes, and $Mo_2(\mu\text{-}C_2R'_2)$- and $Mo_2(\mu\text{-}C_4H_4)$-containing compounds were shown to be intermediates in these reactions.[2] This, together with the metathesis reaction (1), which occurs for tungsten but not for molybdenum, is consistent with a general trend that is emerging in the relative reactivities of the M–M multiple bonds of these two elements. Oxidative addition (and oxidative cleavage) is favored for tungsten relative to molybdenum, and reductive elimination occurs more easily for molybdenum.[14-16]

Further studies are in progress.

Experimental Section

Reagents and General Techniques. General procedures and the preparations of $W_2(OR)_6(L)_2$ (R = *i*-Pr or CH_2-*t*-Bu; L = py, $HNMe_2$) and $W_2(O\text{-}t\text{-}Bu)_6$ have been described.[17,18] 2-Butyne was purchased from Farchan and degassed prior to use. Ethyne was purchased from Matheson and was used without purification. Trimethylphosphine was purchased from Strem and degassed prior to use. Dry and oxygen-free hexane, toluene, 2-propanol, and pyridine were used in the preparations. Elemental analyses were performed by Alfred Bernhardt Microanalytisches Laboratorium, West Germany.

^1H NMR spectra were recorded at various temperatures on a Nicolet NT-360 360-MHz spectrometer in dry and oxygen-free toluene-d_8 or benzene-d_6. ^{13}C NMR spectra were recorded on the same instrument at 90 MHz in toluene-d_8. Ethyne-*1,2*-$^{13}C_2$ (90 atom % ^{13}C) was used in the preparation of $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}^{13}C_4H_4)$, $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}^{13}C_2H_2C_2D_2)$ and $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}^{13}C_2H_2)$. The ^{13}C- and ^2H-labeled ethynes were purchased from MSD Isotopes and used without purification. All ^1H NMR chemical shifts are reported in parts per million relative to the CHD_2 quintet of toluene-d_8 set at δ 2.090 or the ^1H impurity in benzene-d_6 set at δ 7.150. ^{13}C NMR chemical shifts are reported in parts per million relative to the ipso carbon of toluene-d_8 set at δ 137.50. The ^{13}C–^1H coupling constants reported were obtained by using gated ^1H decoupling techniques. ^{31}P NMR spectra were recorded on a Varian XL-100 at 40.5 MHz. ^{31}P chemical shifts are reported relative to 85% H_3PO_4.

Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls between CsI or NaCl plates.

$W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4Me_4)(\eta^2\text{-}C_2Me_2)$. In a Schlenk reaction vessel $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ (0.80 g, 0.91 mmol) was dissolved in toluene (10 mL). The solution was frozen at −196 °C, and 2-butyne (2.8 mmol) was condensed into the flask by using a calibrated vacuum manifold. The reaction mixture was allowed to warm to room temperature and then left to stir for 18 h. The toluene was stripped and the residue redissolved in warm *i*-PrOH (5 mL). Cooling at −15 °C for 24 h produced dark green crystals. These were collected by filtration and dried in vacuo. A second crop of crystals was collected by reducing the volume of the filtrate and cooling (total yield 0.5 g, 62%). By ^1H NMR the reaction is quantitative. ^1H NMR (−45 °C): $\delta(OCHMe_2)$ 5.45, 5.17, 5.05, 4.81, 4.77, 4.35 (septets, J_{HH} = 6 Hz); $\delta(C_4Me_4)$ 3.39, 2.87, 2.10, 2.00 (s); $\delta(C_2Me_2)$ 2.71, 2.60 (br s); $\delta(OCHMe_2)$ 1.58, 1.50, 1.33, 1.07, 0.95, 0.47 (d), 1.40–1.47, and 1.27–1.29 (overlapping doublets, J_{HH} = 6 Hz). IR (cm^{-1}): 1720 vw, 1595 vw, 1319 sh, 1312 m, 1259 w, 1160 m, 1115 s, 988 s, 975 s, 940 m, 842 m, 800 w, 767 w, 720 w. Anal. Calcd for $W_2O_6C_{30}H_{60}$: C, 40.74; H, 6.84. Found: C, 40.68; H, 6.71.

$W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)$. The ethyne complex is prepared in an analogous manner. It can also be prepared by adding 2 or more equiv of ethyne to $W_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}C_2H_2)$. ^1H NMR (−60 °C): $\delta(C_2H_2)$ 10.82 (broad resonance (at −85 °C, δ 10.99, 10.58; +21 °C, δ 10.96 ($^2J_{WH}$ = 10.3 Hz))); $\delta(C_4H_4)$ 9.05, 9.02, 7.70, 6.94 (m); $\delta(OCHMe_2)$ 5.20, 5.11, 5.07, 4.73, 4.60, 4.45 (septets, J_{HH} = 6 Hz); $\delta(OCHMe_2)$ 1.57, 1.39, 1.37, 1.25, 1.22, 1.15, 1.00, 0.58 (d), 1.28–1.33 (overlapping doublets, J_{HH} = 6 Hz). IR (cm^{-1}): 1562 w, 1321 m, 1262 w, 1162 m, 1118 s, 986 s, 939 m, 845 m, 803 m, 660 w. Anal. Calcd for $W_2O_6C_{24}H_{48}$: C, 35.97; H, 6.16. Found: C, 35.87; H, 5.89.

$W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4Me_4)(\eta^2\text{-}C_2Me_2)$. In a Schlenk reaction vessel $W_2(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)_2$ (0.30 g, 0.31 mmol) was dissolved in hexane (3 mL). The solution was frozen at −196 °C, and 2-butyne (0.92 mmol) was condensed into the flask using a calibrated vacuum manifold. The reaction mixture was allowed to warm to room temperature and then left to stir for 18 h. The volume was reduced and the solution cooled to −15 °C. After 11 days a small amount of solid was isolated by filtration. The filtrate was reduced in volume and cooled to −15 °C. Dark green crystals were isolated after 3 days (yield 0.07 g, 22%). ^1H NMR (+21 °C): $\delta(OCH_2CMe_3)$ 5.07, 4.99, 4.79, 4.39, 4.35, 4.26, 4.00, 3.96, 3.71, 3.23 (doublets of AB quartets), 4.20 (two overlapping doublets of AB quartets, J_{HH} = 11 Hz); $\delta(C_4Me_4)$ 3.42, 2.69, 2.25, 2.09, (s); $\delta(C_2Me_2)$ 2.78 (br s at −5 °C, δ 2.96 and 2.52); $\delta(OCH_2CMe_3)$ 1.14, 1.12, 1.04, 1.03, 0.98, and 0.71 (s). IR (cm^{-1}): 1712 vw, 1295 vw, 1258 w, 1213 w, 1070 s, 1055 s, 1020 s, 1007 sh, 932 w, 902 w, 752 w, 720 w, 670 sh, 656 m, 646 m, 629 m, 600 w, 520 vw, 510 vw, 480 vw, 455 w, 436 vw, 405 w, 348 vw, 320 vw, 310 vw, 297 vw. Anal. Calcd for $W_2O_6C_{42}H_{84}$: C, 47.92; H, 8.04. Found: C, 47.77; H, 7.96.

$W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)$. In a Schlenk reaction vessel $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ (0.20 g, 0.19 mmol) was dissolved in toluene (3 mL). The solution was frozen at −196 °C, and ethyne (0.57 mmol) was condensed into the flask using a calibrated vacuum manifold. The reaction mixture was allowed to warm to room temperature and then left to stir for 1 h. The toluene was stripped and the residue redissolved in hexane (1 mL). Cooling at −15 °C for 4 days produced dark red crystals. These were collected by removing the hexane with a syringe and drying in vacuo (yield 0.05 g, 27%). ^1H NMR (21 °C) $\delta(C_2H_2)$ 11.26 (s, $^2J_{WH}$ = 10.1 Hz); $\delta(C_4H_4)$ 9.37, 8.38, 7.80, 6.90 (m); $\delta(OCH_2CMe_3)$ 4.61, 3.89, 3.73, 2.91 (doublets of AB quartets), 4.40–4.10 (overlapping doublets of AB quartets); $\delta(OCH_2CMe_3)$ 1.10, 1.08, 1.03, 0.99, 0.97, 0.77 (s). IR (cm^{-1}): 1552 w, 1296 w, 1258 w, 1216 w, 1072 m, 1055 m, 1021 m, 932 w, 905 vw, 848 vw, 802 w, 750 w, 718 w, 675 m, 653 m, 500 vw, 480 vw, 452 w, 405 w, 391 vw, 335 vw, 310 vw. Anal. Calcd for $W_2O_6C_{36}H_{72}$: C, 44.64; H, 7.49. Found: C, 44.47; H, 7.30.

$W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}^{13}C_2H_2)$. This compound was prepared similarly by reacting $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_4H_4)$ with 1 equiv of $^{13}C_2H_2$ in toluene. Crystals were grown from hexane. ^{13}C NMR (21 °C; the ethyne is rotating rapidly on the NMR time scale at 21 °C) $\delta(\eta^2\text{-}^{13}C_2H_2)$ 179.3 (s, J_{WC} = 40.4 Hz). The ^1H and the gate-decoupled ^{13}C NMR spectra each reveal half of the expected AA′XX′ spectrum in the ethyne region (Figure 8). Successful simulation gave $^1J_{CH}$ = 198.2 Hz, $^2J_{CH}$ = 4.2 Hz, J_{CC} = 54.5 Hz, and $^3J_{HH} \simeq$ 1.0 Hz. $^1J_{CH}$ and $^2J_{CH}$ are necessarily of the same sign, but the relative signs of J_{CC} and J_{HH} are not known.

$W_2(OR)_6(\mu\text{-}C_4H_2Me_2)(\eta^2\text{-}C_2R'_2)$ (R = *i*-Pr, R′ = Me; R = CH_2-*t*-Bu, R′ = H) and $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2Me_2)$. These compounds were all prepared in a similar manner. A preparation of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4H_2Me_2)(\eta^2\text{-}C_2Me_2)$ follows: In a small Schlenk flask, $W_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}C_2H_2)$ (0.05 g) was dissolved in toluene (2 mL). The solution was frozen at −196 °C and 2-butyne was condensed into the flask using a calibrated vacuum manifold. The mixture was allowed to warm to room temperature and then stirred for 18 h. The solvent was removed, the residue redissolved in toluene-d_8, and an ^1H NMR spectrum recorded. In all cases the reactions were remarkably clean.

$W_2(O\text{-}i\text{-}Pr)_6(C_4H_2Me_2)(C_2Me_2)$. ^1H NMR (21 °C): $\delta(C_4H_2Me_2)$ 8.96, 6.75 (d, J_{HH} = 6.9 Hz); $\delta(C_4H_2Me_2)$ 2.77, 2.09 (s); $\delta(C_2Me_2)$ 2.80 (s); $\delta(OCHMe_2)$ 5.27, 5.20, 5.11, 4.97, 4.76, 4.32 (septets, J_{HH} = 6 Hz); $\delta(OCHMe_2)$ 1.58, 1.19, 1.12, 0.99, 0.90, 0.56 (d, J_{HH} = 6 Hz), 1.36–1.42, 1.28–1.31 (overlapping doublets).

$W_2(OCH_2\text{-}t\text{-}Bu)_6(C_4H_2Me_2)(C_2H_2)$. ^1H NMR (21 °C) $\delta(C_2H_2)$ 11.27 (s); $\delta(C_4H_2Me_2)$ 9.68, 6.82 (d, J_{HH} = 6.9 Hz); $\delta(OCH_2CMe_3)$ 5.20, 5.06, 4.86, 4.52, 4.49, 4.39, 4.31, 4.12, 4.04, 3.86, 3.70, 3.24 (doublets of AB quartets, J_{HH} = 11 Hz); $\delta(C_4H_2Me_2)$ 2.59, 2.12 (s); $\delta(OCH_2CMe_3)$ 1.07, 0.96, 0.88, 0.70 (s), 1.10 (overlapping singlets).

$W_2(OCH_2\text{-}t\text{-}Bu)_6(C_4H_4)(C_2Me_2)$. ^1H NMR (21 °C): $\delta(C_4H_4)$ 9.08, 8.37, 7.82, 6.78 (m); $\delta(OCH_2CMe_3)$ 4.80, 4.30, 4.24, 3.69, 2.71 (doublets of AB quartets, J_{HH} = 11 Hz), 4.12–4.21, 3.95–4.05 (overlapping doublets of AB quartets); $\delta(C_2Me_2)$ 2.89 (slightly broadened singlet); $\delta(OCH_2CMe_3)$ 1.14, 1.12, 1.03, 0.99, 0.97, 0.78 (s).

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Table VI. Crystal Data Summary

	I	II
empirical formula	$W_2O_6C_{24}H_{48}$	$W_2O_6C_{30}H_{60}$
color of cryst	dark brown	black
cryst dimens, mm	0.04 × 0.04 × 0.05	0.10 × 0.09 × 0.11
space group	$P\bar{1}$	*Pcab*
cell dimens		
temp, °C	−160	−169
a, Å	14.754 (7)	16.352 (14)
b, Å	12.135 (6)	16.036 (12)
c, Å	9.011 (4)	26.335 (18)
α, deg	105.51 (2)	
β, deg	88.66 (3)	
γ, deg	70.53 (2)	
Z(molecules/cell)	2	8
vol. Å^3	1455.90	3452.75
d_{calcd}, g/cm^3	1.830	1.702
wavelength, Å	0.71069	0.71069
mol wt	801.35	884.50
linear abs coeff, cm^{-1}	81.048	68.363
detector to sample dist, cm	22.5	22.5
sample to source dist, cm	23.5	23.5
av ω scan width at half-height	0.25	0.25
scan speed, deg/min	4.0	4.0
scan width, deg (dispersion)	2.0	2.0
individual bkgd, s	3	3
aperture size, mm	3.0 × 4.0	3.0 × 4.0
2θ range, deg	6–45	6–45
total no. of reflctns collected	9931	4680
no. of unique intensities	3813	3331
no. with $F > 0.0$	3554	3064
no. with $F > \sigma(F)$	3395	2914
no. with $F > 3.00\sigma(F)$	3188	2720
$R(F)$	0.037	0.053
$R_w(F)$	0.037	0.053
goodness of fit for the last cycle	0.850	1.270
max Δ/σ for last cycle	0.05	0.05

$W_2(OCH_2$-*t*-$Bu)_6(py)(\mu$-$C_4H_4)$. In a Schlenk reaction vessel $W_2(OCH_2$-*t*-$Bu)_6(py)_2$ (0.55 g, 0.52 mmol) was dissolved in hexane (8 mL). The dark red solution was frozen at −196 °C, and ethyne (1.05 mmol) was condensed into the flask using a calibrated vacuum manifold. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. During this time the color changed to dark blue. The solution was reduced in volume to approximately 2 mL and then placed in a freezer at −15 °C. After 24 h a dark blue microcrystalline solid was collected by filtration and dried in vacuo (yield 0.32 g, 60%). ^{1}H NMR (21 °C): $\delta(OCH_2CMe_3)$ 0.98, 1.05, 1.33, 1.48 (singlets with relative intensities 2:2:1:1, respectively); $\delta(OCH_2CMe_3)$ 3.48, 3.76 (doublets of an AB quartet, J_{HH} = 10.8 Hz), 4.23, 4.76 (doublets of an AB quartet, J_{HH} = 10.8 Hz), 4.52, 5.27 (s); $\delta(C_4H_4)$ 5.46, 7.39 (m); δ(py) 6.47 (t), 6.75 (t), 8.31 (d). In addition to these resonances, others, apparently from a second isomer, appear in the spectra of solutions made from pure crystalline samples (see text for discussion). The following resonances have been identified: $\delta(OCH_2CMe_3)$ 0.85, 1.12, 1.25 (s); $\delta(OCH_2CMe_3)$ 4.14 and 4.57 (doublets of an AB quartet, J_{HH} = 10.1 Hz), 3.62, 3.87 (broad doublets of an AB quartet), 4.92, 4.99 (s); $\delta(C_4H_4)$ 5.16, 6.92 (m); δ(py) 6.6, 8.5 (broad resonances). IR (cm^{-1}) 1300 vw, 1258 w, 1213 w, 1150 vw, 1088 m, 1056 s, 1040 sh, 1022 s, 999 sh, 990 m, 932 w, 752 w, 684 w, 676 w, 651 s, 643 sh, 630 sh, 621 w, 452 w, 406 w, 338 w. Anal. Calcd for $W_2O_6NC_{39}H_{75}$: C, 45.85; H, 7.40; N, 1.37. Found: C, 45.75; H, 7.26; N, 1.33.

$W_2(O$-*t*-$Bu)_6(\mu$-$C_4H_4)$. This molecule is made by adding ethyne to $W_2(O$-*t*-$Bu)_6$ dissolved in hexane or toluene. If less than 2 equiv of ethyne are added, starting material and the $W_2(\mu$-$C_4H_4)$ compound are observed. If greater than 2 equiv of ethyne are added, the $W_2(\mu$-$C_4H_4)$ complex is produced along with an insoluble material that is presumably polyethyne. $W_2(O$-*t*-$Bu)_6(\mu$-$C_4H_4)$ can also be synthesized by adding ethyne to a hydrocarbon solution of $W_2(O$-*t*-$Bu)_6(py)(\mu$-$C_2H_2)\cdot{}^1/_2$py. This method was used to prepare $W_2(O$-*t*-$Bu)_6(\mu$-$^{13}C_2H_2C_2D_2)$. All attempts to crystallize $W_2(O$-*t*-$Bu)_6(\mu$-$C_4H_4)$ or an adduct (pyridine or PMe_3) of it failed using a variety of solvents. ^{1}H NMR (220 MHz, 16 °C): $\delta(OCMe_3)$ 1.22, 1.39, 1.84, 1.98 (sharp singlets with relative intensities 2:2:1:1, respectively); $\delta(C_4H_4)$ 6.32, 9.58 (m (AA′XX′)).

$W_2(O$-*t*-$Bu)_6(\mu$-$^{13}C_4H_4)$. $^{13}C\{^1H\}$ NMR (−40 °C): $\delta(^{13}C_4H_4)$ 162.5, 120.9 (m (AA′XX′)).

$W_2(O$-*t*-$Bu)_6(\mu$-$^{13}C_2H_2C_2D_2)$. $^{13}C\{^1H\}$ NMR (−40 °C): $\delta(^{13}C_2H_2C_2D_2)$ 162.3 ($J_{WC} \simeq$ 68 Hz), 120.9 (d, $^1J_{CC}$ = 35.1 Hz (^{1}H coupled: $^1J_{CH} \simeq$ 158 and 160 Hz, respectively)); $\delta(OCMe_3)$ 81.2, 81.8, 82.5, 89.8; $\delta(OCMe_3)$ 31.3, 32.3, 32.5, 33.3.

$W_2(O$-*i*-$Pr)_6(PMe_3)(\mu$-$C_4H_4)$. To a hexane solution of $W_2(O$-*t*-$Bu)_6(\mu$-$C_4H_4)$ (~0.25 mmol) in the presence of excess PMe_3 (~2.5 mmol) was added *i*-PrOH (2 mL). The solution was stirred at room temperature for 3 h. During this time the solution turned intensely blue. The volatiles were removed and *i*-PrOH (1.5 mL) was added. Slight warming (40–50 °C) dissolved the blue solid. Cooling at −15 °C for 2 days produced dark blue crystals that were isolated by removing the *i*-PrOH with a syringe and drying in vacuo. (yield 50 mg, 24%). ^{1}H NMR (21 °C): $\delta(OCHMe_2)$ 1.03, 1.07, 1.32, 1.41, 1.59, 1.86 (doublets of equal intensity, J_{HH} = 6 Hz); $\delta(PMe_3)$ 0.91, (d, J_{PH} = 8.3 Hz); $\delta(OCHMe_2)$ 4.97, 5.12, 5.24, 5.38 (septets, J_{HH} = 6 Hz); $\delta(C_4H_4)$ 5.32, 6.52 (m (the multiplet at δ 5.32 is broadened due to coupling to ^{31}P)). $^{31}P\{^1H\}$ NMR (21 °C): $\delta(PMe_3)$ −23.8 (singlet, $^1J_{WP}$ = 319 Hz). Anal. Calcd for $W_2PO_6C_{25}H_{55}$: C, 35.31; H, 6.52. Found: C, 35.19; H, 6.35.

$W_2(OCH_2$-*t*-$Bu)_6(PMe_3)(\mu$-$C_4H_4)$. In a small Schlenk flask $W_2(OCH_2$-*t*-$Bu)_6(py)(\mu$-$C_4H_4)$ was dissolved in toluene and approximately 2 equiv of PMe_3 was added by using a calibrated vacuum manifold. The mixture was stirred for 18 h. The volatiles were then removed, and the residue was redissolved in benzene-d_6. ^{1}H and ^{31}P NMR revealed clean substitution of PMe_3 for pyridine. ^{1}H NMR (220 MHz, 16 °C): $\delta(PMe_3)$ 0.99 (d, J_{PH} = 9 Hz); $\delta(OCH_2CMe_3)$ 0.93, 1.16, 1.29, 1.49 (singlets with relative intensities 2:2:1:1); $\delta(OCH_2CMe_3)$ 3.91, 4.10, 4.12, 4.62 (doublets of AB quartets, J_{HH} = 11 Hz), 4.78, 5.01 (s); $\delta(C_4H_4)$ 5.25, 6.36 (m (the multiplet at δ 5.25 is broadened due to ^{31}P–^{1}H coupling)). $^{31}P\{^1H\}$ NMR (21 °C): $\delta(PMe_3)$ −21.0 (s, J_{WP} = 310 Hz).

Crystallographic Studies. The general operating procedures and listings of programs have been reported previously.[19] Crystal data are summarized in Table VI.

$W_2(O$-*i*-$Pr)_6(\mu$-$C_4H_4)(\eta^2$-$C_2H_2)$. A nearly equidimensional spherical shaped crystal was cleaved from a larger sample and transferred to the goniostat by using standard inert-atmosphere techniques. A systematic search of a limited hemisphere of reciprocal space located no symmetry-related intensities and no systematic absences, indicating a triclinic lattice. The latter was confirmed by subsequent solution and refinement of the structure.

The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares. A difference Fourier phased on non-hydrogen coordinates clearly revealed all hydrogen atoms, and the latter were allowed to vary isotropically in all subsequent cycles.

A ψ-scan indicated less than 5% variation in six reflections, so no attempt was made to correct for absorption. A final difference Fourier was featureless, the largest peaks lying within 0.5 Å of the two tungsten atoms.

$W_2(O$-*i*-$Pr)_6(\mu$-$C_4Me_4)(\eta^2$-$C_2Me_2)$. A suitable sample was obtained by fracturing a larger mass of crystals present in the sample. Standard inert-atmosphere handling techniques employed by the IUMSC were used. A systematic search of a limited hemisphere of reciprocal space revealed orthorhombic symmetry with extinctions which could be indexed as *Pcab*.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. Full-matrix refinement converged rapidly by using isotropic thermal parameters. When the atoms were allowed to vary anisotropically, no improvement was seen in the residual, so only the two metal atoms were assigned anisotropic thermal parameters. Most of the hydrogen atoms were clearly visible in a difference Fourier phased on the non-hydrogen parameters, and fixed, idealized hydrogens were included in final cycles of refinement.

A final difference map was featureless, with three peaks of 1.5–2.2 e/Å^3 located adjacent to the tungsten atoms. ψ-scans of several reflections located near χ = 90° indicated a variation of less than 7%, so no absorption correction was performed.

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Registry No. III, 91899-16-0; $W_2(O$-*i*-$Pr)_6(\mu$-$C_4Me_4)(\eta^2$-$C_2Me_2)$, 87654-13-5; $W_2(O$-*i*-$Pr)_6(\mu$-$C_4H_4)(\eta^2$-$C_2H_2)$, 87654-14-6; $W_2(OCH_2$-*t*-$Bu)_6(\mu$-$C_4Me_4)(\eta^2$-$C_2Me_2)$, 87654-10-2; $W_2(OCH_2$-*t*-$Bu)_6(\mu$-$C_4H_4)(\eta^2$-$C_2H_2)$, 91899-12-6; $W_2(OCH_2$-*t*-$Bu)_6(\mu$-$C_4H_4)(\eta^2$-$^{13}C_2H_2)$, 91899-13-7; $W_2(O$-*i*-$Pr)_6(C_4H_2Me_2)(C_2Me_2)$, 87654-12-4; $W_2(OCH_2$-*t*-$Bu)_6(C_4H_2Me_2)(C_2H_2)$, 91899-14-8; $W_2(OCH_2$-*t*-$Bu)_6(C_4H_4)(C_2Me_2)$, 91899-15-9; $W_2(O$-*t*-$Bu)_6(\mu$-$C_4H_4)$, 87654-11-3; $W_2(O$-*t*-$Bu)_6(\mu$-$^{13}C_2H_2C_2D_2)$, 91899-17-1; $W_2(O$-*t*-$Bu)_6(\mu$-$^{13}C_4H_4)$, 91899-18-2; W$_2$(O-

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i-Pr)$_6$(PMe$_3$)(μ-C$_4$H$_4$), 91899-19-3; W$_2$(OCH$_2$-t-Bu)$_6$(PMe$_3$)(μ-C$_4$H$_4$), 91899-20-6; W$_2$(O-i-Pr)$_6$(py)$_2$, 70178-75-5; W$_2$(O-i-Pr)$_6$(py)$_2$(μ-C$_2$H$_2$), 82281-73-0; W$_2$(OCH$_2$-t-Bu)$_6$(HNMe$_2$)$_2$, 83437-02-9; W$_2$(OCH$_2$-t-Bu)$_6$(py)$_2$, 88608-50-8; W$_2$(O-t-Bu)$_6$, 57125-20-9; W$_2$(O-t-Bu)$_6$(py)(μ-C$_2$H$_2$), 91899-21-7.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, complete listings of bond lengths and bond angles (22 pages). Order information is given on any current masthead page. The complete structure reports, MSC Report No. 82088, W$_2$(O-i-Pr)$_6$(μ-C$_4$H$_4$)(C$_2$H$_2$), and MSC Report No. 82089, W$_2$(O-i-Pr)$_6$(μ-C$_4$Me$_4$)(C$_2$Me$_2$), are available from the Indiana University Chemistry Library in Microfiche form only at a cost of \$2.50 per copy.

Metal Alkoxides—Models for Metal Oxides. 6.[1] The Linking of Alkyne and Nitrile Fragments at Ditungsten Centers. Preparation and Characterization of W$_2$(O-t-Bu)$_6$(CHCHC(Ph)N), W$_2$(O-i-Pr)$_7$(CH$_2$CHC(Ph)N), W$_2$(OCH$_2$-t-Bu)$_6$(N(CMe)$_4$N)(py), and W$_2$(O-i-Pr)$_7$(NHC(Me)CHCHC(Me)N)

Malcolm H. Chisholm,* David M. Hoffman, and John C. Huffman

Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405. *Received April 3, 1984*

Abstract: Alkyne adducts of ditungsten hexaalkoxides react in hydrocarbon solvents with nitriles to give novel dinuclear compounds containing five- or seven-membered heterocyclic rings. In W$_2$(O-t-Bu)$_6$(CHCHC(Ph)N), I, which is formed in the reaction between W$_2$(O-t-Bu)$_6$(μ-C$_2$H$_2$)(py) and PhC≡N (1 equiv), each tungsten atom is in a distorted trigonal-bipyramidal environment. The metal atoms are joined along a common equatorial–axial edge through the agency of an alkoxy ligand and the nitrogen atom of the metallacyclic ligand formed by the coupling of the alkyne and nitrile. Formally this ligand can be counted as a 4− ligand with terminal alkylidene and imido groups: W═CHCH═C(Ph)N═W, where W═C = 1.980 (6) Å, W—N = 2.041 (5) Å, and W═N = 1.903 (5) Å. The W-W distance is 2.674 (1) Å, indicative of a single bond. I reacts with 2-propanol to give W$_2$(O-i-Pr)$_7$(CH$_2$CHC(Ph)N), II, which is the product of the combined reactions of alcoholysis and alcohol addition across the tungsten–carbon double bond: W═CH– + ROH → ROWCH$_2$–. In II each tungsten atom is in a distorted octahedral environment and the two metal atoms share a face formed by two bridging OR ligands and the nitrogen atom of the metallacycle that is now formally a 3− ligand having imido and alkyl attachments to tungsten: W–C = 2.174 (8) Å, W–N = 1.980 (6) and 1.962 (7) Å, and W–W = 2.585 (1) Å. In W$_2$(OCH$_2$-t-Bu)$_6$(N(CMe)$_4$N)(py), III, which is formed in the reaction between W$_2$(OCH$_2$-t-Bu)$_6$(py)$_2$(μ-C$_2$Me$_2$) and MeC≡N (>2 equiv), there is a seven-membered metallacycle that incorporates the 4− ligand derived from 1,4-diamino-1,2,3,4-tetramethyl-1,3-butadiene. The connectivity involves one terminal imido group, W–N = 1.78 (1) Å, and one bridging imido group, W–N(μ) = 1.90 (1) and 2.09 (1) Å. Each tungsten atom is in a distorted octahedral environment, and the W–W distance 2.617 (1) Å corresponds to a M–M single bond. The compound W$_2$(O-i-Pr)$_7$(NHC(Me)CHCHC(Me)N), IV, is closely related to III. IV is formed in the reaction between W$_2$(O-i-Pr)$_6$(py)$_2$(μ-C$_2$H$_2$) and MeC≡N (>2 equiv) in the presence of i-PrOH. The seven-membered metallacycle now has a terminal amido group (1−) and a bridging imido (2−) function, and the addition of ROH across the W═N bond parallels the conversion of I to II. W–N(amido) = 1.986 (8) Å; W–N (μ-imido) = 1.983 (8) and 2.007 (8) Å. Each tungsten is in a distorted octahedral environment with the W–W distance = 2.576 (1) Å. The compounds I through IV have been characterized by variable-temperature ^{1}H and ^{13}C NMR spectroscopy: I, II, and IV are fluxional. Crystal data for I at −158 °C: a = 19.237 (8) Å, b = 10.619 (4) Å, c = 10.180 (3) Å, α = 111.97 (2)°, β = 97.26 (2)°, γ = 73.00 (2)°, Z = 2, d_{calcd} = 1.685 g cm^{-3}, and space group $P\bar{1}$. Crystal data for II at −152 °C: a = 18.346 (3) Å, b = 11.579 (1) Å, c = 10.180 (1) Å, α = 107.08 (1)°, β = 61.54 (1)°, γ = 98.19 (1)°, Z = 2, d_{calcd} = 1.666 g cm^{-3}, and space group $P\bar{1}$. Crystal data for III at −168 °C: a = 26.006 (12) Å, b = 17.056 (7) Å, c = 12.015 (4) Å, β = 110.29 (2)°, Z = 4, d_{calcd} = 1.467 g cm^{-3}, and space group $P2_1/a$. Crystal data for IV at −165 °C: a = 10.898 (5) Å, b = 16.366 (8) Å, c = 20.942 (12) Å, β = 111.16 (3)°, Z = 4, d_{calcd} = 1.698 g cm^{-3}, and space group $P2_1/c$.

Alkynes have been shown to react with ditungsten hexaalkoxides to give a variety of products depending on the specific alkoxy group, the alkyne substituents and the reaction conditions.[1-5] Most notable are the metathesis-like reactions observed for the *tert*-butoxide and dialkylacetylenes (eq 1)[2] and the alkyne coupling reactions (eq 2),[1,5] which occur for less sterically demanding combinations of ligands.

$$\mathrm{W_2(O\text{-}\mathit{t}\text{-}Bu)_6 + RC{\equiv}CR \rightarrow 2(\mathit{t}\text{-}BuO)_3W{\equiv}CR} \quad (1)$$

$$\mathrm{R = Me, Et, Pr}$$

$$\mathrm{W_2(OR)_6 + 3R'C{\equiv}CR' \rightarrow W_2(OR)_6(\mu\text{-}C_4R'_4)(C_2R'_2)} \quad (2)$$

$$\text{or } \mathrm{W_2(O\text{-}\mathit{t}\text{-}Bu)_6(\mu\text{-}C_4H_4)}$$

$$\mathrm{R = \mathit{i}\text{-}Pr \text{ and } CH_2\text{-}\mathit{t}\text{-}Bu;\ R' = H \text{ or } Me}$$

Acetonitrile and benzonitrile have also been reported[2] to react with the *tert*-butoxide in a metathesis-like manner (eq 3).

$$\mathrm{W_2(O\text{-}\mathit{t}\text{-}Bu)_6 + RC{\equiv}N \rightarrow (\mathit{t}\text{-}BuO)_3W{\equiv}CR + (\mathit{t}\text{-}BuO)_3W{\equiv}N} \quad (3)$$

These metathesis-like reactions occur for ditungsten hexaalkoxides but not for related dimolybdenum compounds, presumably

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