

i-Pr)₆(PMe₃)(μ-C₄H₄), 91899-19-3; W₂(OCH₂-*t*-Bu)₆(PMe₃)(μ-C₄H₄), 91899-20-6; W₂(O-*i*-Pr)₆(py)₂, 70178-75-5; W₂(O-*i*-Pr)₆(py)₂(μ-C₂H₂), 82281-73-0; W₂(OCH₂-*t*-Bu)₆(HNMe₂)₂, 83437-02-9; W₂(OCH₂-*t*-Bu)₆(py)₂, 88608-50-8; W₂(O-*t*-Bu)₆, 57125-20-9; W₂(O-*t*-Bu)₆(py)(μ-C₂H₂), 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, W₂(O-*i*-Pr)₆(μ-C₄H₄)(C₂H₂), and MSC Report No. 82089, W₂(O-*i*-Pr)₆(μ-C₄Me₄)(C₂Me₂), 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

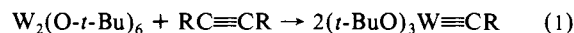
W₂(O-*t*-Bu)₆(CHCHC(Ph)N), W₂(O-*i*-Pr)₇(CH₂CHC(Ph)N), W₂(OCH₂-*t*-Bu)₆(N(CMe)₄N)(py), and W₂(O-*i*-Pr)₇(NHC(Me)CHCHC(Me)N)

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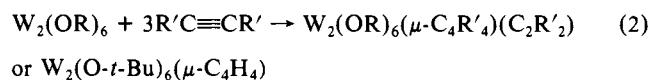
Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405. Received April 3, 1984

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 W₂(O-*t*-Bu)₆(CHCHC(Ph)N), I, which is formed in the reaction between W₂(O-*t*-Bu)₆(μ-C₂H₂)(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=C(CH)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 W₂(O-*i*-Pr)₇(CH₂CHC(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 → ROWCH₂-. 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 W₂(OCH₂-*t*-Bu)₆(N(CMe)₄N)(py), III, which is formed in the reaction between W₂(OCH₂-*t*-Bu)₆(py)₂(μ-C₂Me₂) 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 W₂(O-*i*-Pr)₇(NHC(Me)CHCHC(Me)N), IV, is closely related to III. IV is formed in the reaction between W₂(O-*i*-Pr)₆(py)₂(μ-C₂H₂) 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 ¹H and ¹³C 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*1̄. 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*1̄. 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 *P*2₁/*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 *P*2₁/*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.

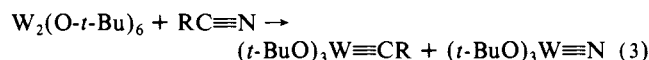


R = Me, Et, Pr



R = *i*-Pr and CH₂-*t*-Bu; R' = H or Me

Acetonitrile and benzonitrile have also been reported² to react with the *tert*-butoxide in a metathesis-like manner (eq 3).



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

(1) Part 5. Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.*, preceding paper in this issue.

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

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

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

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

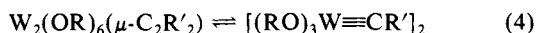
Table I. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(O-t-Bu)_6(CHCHC(Ph)N)$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}, \text{\AA}^2$
W(1)	7763.2 (1)	8068.6 (2)	9047.2 (2)	12
W(2)	7312.1 (1)	5811.5 (2)	7398.4 (2)	11
C(3)	6942 (3)	9627 (7)	10075 (7)	17
C(4)	6253 (3)	9850 (6)	9402 (7)	18
C(5)	6197 (3)	8835 (6)	8118 (6)	16
N(6)	6854 (2)	7766 (5)	7836 (5)	14
C(7)	5571 (3)	8833 (6)	7112 (7)	17
C(8)	5660 (4)	8057 (7)	5661 (7)	20
C(9)	5063 (4)	8127 (7)	4736 (8)	25
C(10)	4377 (4)	8959 (7)	5217 (8)	26
C(11)	4290 (3)	9702 (7)	6649 (8)	26
C(12)	4869 (3)	9648 (7)	7578 (7)	22
O(13)	8503 (2)	8435 (4)	10472 (4)	17
C(14)	8931 (3)	9387 (7)	11260 (7)	23
C(15)	9674 (4)	8754 (8)	10602 (10)	37
C(16)	8964 (4)	9492 (8)	12793 (8)	32
C(17)	8600 (4)	10837 (7)	11154 (8)	27
O(18)	8129 (2)	8653 (4)	7811 (4)	16
C(19)	7926 (4)	9509 (7)	6913 (7)	22
C(20)	8622 (5)	9830 (9)	6740 (9)	36
C(21)	7342 (4)	10854 (7)	7635 (8)	28
C(22)	7648 (4)	8648 (8)	5514 (8)	30
O(23)	7814 (2)	6269 (4)	9424 (4)	14
C(24)	8241 (3)	5500 (6)	10331 (7)	19
C(25)	8046 (4)	4118 (7)	9896 (7)	23
C(26)	9043 (4)	5207 (7)	10107 (7)	24
C(27)	8058 (4)	6428 (8)	11868 (7)	24
O(28)	8257 (2)	4695 (4)	6779 (4)	17
C(29)	8900 (3)	4379 (6)	5994 (6)	17
C(30)	9319 (4)	5459 (8)	6721 (7)	25
C(31)	8670 (4)	4420 (8)	4514 (7)	26
C(32)	9344 (4)	2905 (7)	5913 (8)	29
O(33)	6632 (2)	5266 (4)	8071 (4)	15
C(34)	6045 (3)	5611 (6)	9019 (6)	18
C(35)	6011 (4)	4201 (8)	9064 (8)	31
C(36)	6190 (4)	6632 (8)	10476 (8)	32
C(37)	5346 (4)	6259 (8)	8376 (8)	30
O(38)	6951 (2)	5350 (4)	5489 (4)	14
C(39)	6742 (3)	4121 (6)	4483 (6)	19
C(40)	5964 (4)	4263 (7)	4734 (7)	25
C(41)	6809 (4)	4172 (7)	3013 (7)	23
C(42)	7225 (4)	2771 (7)	4632 (7)	21

Table II. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(O-i-Pr)_7(CH_2CHC(Ph)N)$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}, \text{\AA}^2$
W(1)	2810.8 (2)	381.0 (3)	427.9 (4)	15
W(2)	2241.8 (2)	-1792.2 (3)	-60.2 (4)	18
C(3)	4139 (5)	659 (8)	-823 (10)	21
C(4)	4451 (5)	-84 (7)	-2454 (9)	21
C(5)	3941 (5)	-930 (7)	-2765 (8)	18
N(6)	3153 (4)	-964 (6)	-1476 (7)	18
C(7)	4116 (6)	-1802 (7)	-4275 (10)	25
C(8)	3490 (9)	-2341 (8)	-4590 (12)	37
C(9)	3655 (10)	-3170 (9)	-6050 (14)	48
C(10)	4461 (10)	-3426 (10)	-7136 (13)	58
C(11)	5086 (10)	-2901 (11)	-6831 (12)	54
C(12)	4944 (8)	-2098 (10)	-5419 (11)	40
O(13)	2496 (3)	1484 (5)	-206 (6)	17
C(14)	2034 (6)	1562 (9)	-974 (11)	30
C(15)	1701 (11)	2792 (13)	-450 (17)	78
C(16)	2546 (13)	1173 (17)	-2656 (15)	108
O(17)	2834 (4)	1503 (5)	2262 (6)	23
C(18)	3262 (8)	2594 (10)	2498 (12)	47
C(19)	3080 (17)	3519 (17)	2105 (29)	124
C(20)	3326 (19)	2916 (15)	3864 (29)	142
O(21)	2804 (3)	-938 (5)	1371 (6)	17
C(22)	2765 (5)	-1097 (7)	2765 (9)	22
C(23)	3543 (5)	-579 (7)	2877 (10)	23
C(24)	1982 (6)	-553 (10)	4189 (10)	34
O(25)	1529 (3)	-258 (5)	1276 (7)	22
C(26)	697 (5)	-60 (9)	2511 (11)	31
C(27)	609 (6)	1250 (10)	3411 (12)	40
C(28)	88 (6)	-474 (10)	1878 (14)	44
O(29)	2881 (3)	-3204 (5)	-765 (7)	23
C(30)	3754 (5)	-3459 (8)	-1548 (10)	26
C(31)	4002 (6)	-3781 (8)	-490 (11)	31
C(32)	3928 (8)	-4476 (9)	-2995 (12)	41
O(33)	1410 (3)	-2535 (5)	1546 (7)	27
C(34)	1220 (6)	-3742 (9)	1676 (13)	38
C(35)	310 (9)	-3918 (14)	2338 (21)	86
C(36)	1564 (8)	-4001 (10)	2643 (14)	48
O(37)	1719 (4)	-2225 (5)	-1343 (8)	32
C(38)	1195 (7)	-3171 (9)	-1646 (14)	44
C(39)	1677 (8)	-4335 (10)	-2607 (16)	52
C(40)	814 (10)	-2752 (11)	-2467 (19)	81

because of thermodynamic factors since simple adducts of $Mo_2(OR)_6$ are obtained under analogous conditions.^{6,7} The role of steric factors in partitioning reactions according to (1) or (2) is not yet understood, and it appears that by a judicious choice of alkoxide and acetylene substituent an equilibrium between a dimetallatetrahydride and a methylidyne complex may be established (eq 4).^{8,9}



We describe here the products obtained from the reactions between alkyne adducts of ditungsten hexaalkoxides and nitriles. Our purpose in exploring these reactions was to determine whether or not C-C bond formation occurs in analogy to (2) or metathesis reactions analogous to (1) and (4) occur involving coordinated alkynes and/or nitriles. A preliminary report concerning one of these compounds has appeared.¹⁰

(6) Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. *J. Am. Chem. Soc.* **1983**, *105*, 6162.

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

(8) Evidence for this type of equilibrium has been presented for R = *t*-Bu and R' = H: Part 4: Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.*, preceding in this issue.

(9) The alkylidyne complex is represented as a dimer based on the observed structure for $(MeC \equiv (t-BuO)_2W(\mu-O-t-Bu)_2W(O-t-Bu)_2 \equiv CMe)_2$: Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903.

(10) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1983**, 967.

Results and Discussion

Syntheses. Relatively few alkyne adducts of ditungsten hexaalkoxides are known because the metathesis reaction 1 or the alkyne coupling reaction 2 can preclude their isolation. The alkyne adducts $W_2(O-t-Bu)_6(py)(\mu-C_2H_2)$, $W_2(O-i-Pr)_6(py)_2(\mu-C_2H_2)$, and $W_2(OCH_2-t-Bt)_6(py)_2(\mu-C_2Me_2)$ were used in this study.⁸

In hydrocarbon solvents at room temperature $W_2(O-t-Bu)_6(py)(\mu-C_2H_2)$ reacts with 1 equiv of nitrile, RCN, to give $W_2(O-t-Bu)_6(CHCHC(R)N)$ compounds where R = Ph (I) and Me (Ib). The compounds are extremely soluble in hydrocarbon solvents resulting in low yields as crystalline solids. The ¹H NMR spectra of the products obtained by stripping the reaction mixtures in vacuo show, however, that formation of the 1:1 alkyne/nitrile coupled compounds is essentially quantitative. In the presence of excess nitrile a further reaction occurs but no compound has been characterized as yet.

Compound I reacts with excess 2-propanol to give $W_2(O-i-Pr)_7(CH_2CHC(Ph)N)$, II. Again this appears to be a quantitative reaction. Formation of II is readily understood in terms of the combined reactions of alcoholysis, in which *t*-BuO ligands are exchanged for *i*-PrO ligands, and the addition of *i*-PrOH across the tungsten-carbon double bond, $W=CHR + i-PrOH \rightarrow (i-PrO)WCH_2R$. The former reaction is a standard type of reaction in alkoxide chemistry,¹¹ but the latter appears to be without precedent. It is, however, not a surprising reaction. Schrock and Fellmann¹² reported the addition of HCl across a tantalum-carbon

(11) Bradley, D. C.; Mehrotra, R. C.; Gaur, P. In "Metal Alkoxides"; Academic Press: New York, 1978.

(12) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.

Table III. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(OCH_2-t-Bu)_6(N(CMe)_4N)(py)$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}, \text{\AA}^2$
W(1)	3529.1 (2)	2279.3 (3)	3453.6 (4)	11
W(2)	3741.0 (2)	2688.5 (3)	1558.3 (4)	10
N(3)	3466 (4)	3146 (6)	4219 (9)	12
C(4)	3319 (6)	3915 (8)	4210 (14)	21
C(5)	3693 (7)	4399 (10)	5190 (15)	32
C(6)	2857 (6)	4189 (8)	3328 (13)	22
C(7)	2746 (8)	5073 (10)	3359 (15)	39
C(8)	2448 (6)	3702 (8)	2435 (13)	18
C(9)	1855 (6)	3908 (9)	2270 (13)	26
C(10)	2559 (5)	3123 (7)	1779 (11)	15
C(11)	2101 (5)	2589 (8)	1021 (12)	20
N(12)	3092 (4)	2891 (6)	1905 (9)	16
N(13)	2754 (4)	1790 (7)	3503 (9)	16
C(14)	2421 (5)	2215 (9)	3941 (11)	19
C(15)	1923 (6)	1958 (9)	3919 (12)	19
C(16)	1748 (6)	1214 (8)	3452 (13)	22
C(17)	2104 (6)	762 (9)	3043 (13)	26
C(18)	2591 (6)	1080 (8)	3080 (12)	17
O(19)	3858 (4)	1406 (6)	4496 (8)	19
C(20)	3824 (5)	1247 (8)	5638 (12)	16
C(21)	4061 (6)	441 (9)	6069 (11)	19
C(22)	3656 (4)	-189 (9)	5336 (13)	25
C(23)	4623 (6)	325 (11)	6032 (14)	31
C(24)	4081 (7)	379 (10)	7364 (12)	26
O(25)	3545 (3)	1529 (5)	1951 (7)	9
C(26)	3864 (5)	837 (7)	2067 (12)	15
C(27)	3624 (6)	263 (9)	1043 (12)	20
C(28)	3037 (6)	47 (9)	912 (16)	31
C(29)	3643 (6)	638 (8)	-114 (12)	20
C(30)	3987 (7)	-470 (9)	1348 (14)	27
O(31)	4267 (4)	2515 (5)	3290 (8)	19
C(32)	4802 (5)	2217 (8)	3830 (10)	15
C(33)	5173 (5)	2738 (9)	4817 (11)	18
C(34)	5192 (7)	3557 (11)	4314 (14)	35
C(35)	5745 (6)	2373 (11)	5241 (14)	33
C(36)	4949 (6)	2766 (10)	5826 (11)	23
O(37)	3991 (3)	3720 (5)	1608 (8)	17
C(38)	3804 (6)	4439 (8)	1938 (13)	22
C(39)	4012 (6)	5134 (8)	1410 (14)	26
C(40)	4628 (7)	5180 (10)	1903 (16)	36
C(41)	3805 (8)	5102 (9)	100 (14)	35
C(42)	3761 (7)	5886 (10)	1759 (18)	41
O(43)	3354 (3)	2615 (5)	-122 (7)	15
C(44)	2775 (5)	2652 (10)	-838 (12)	22
C(45)	2724 (5)	2802 (8)	-2142 (11)	17
C(46)	3001 (6)	2165 (10)	-2591 (11)	27
C(47)	2111 (7)	2853 (12)	-2814 (14)	40
C(48)	2995 (6)	3606 (9)	-2209 (11)	26
O(49)	4368 (3)	2313 (5)	1145 (7)	13
C(50)	4478 (6)	2464 (9)	94 (12)	24
C(51)	5069 (5)	2328 (9)	247 (11)	20
C(52)	5144 (6)	2409 (10)	-938 (13)	30
C(53)	5436 (8)	2890 (11)	1135 (14)	39
C(54)	5240 (6)	1500 (10)	694 (14)	30

double bond at -78°C , $(t\text{-BuCH}_2)_3\text{Ta}=\text{CH}-t\text{-Bu} + \text{HCl} \rightarrow (t\text{-BuCH}_2)_4\text{TaCl}$, and more recently Rothwell and Chamberlin reported¹³ the intramolecular addition of a C-H bond across a tantalum-carbon double bond to generate an alkyl and a cyclo-metalated ligand.

$W_2(OCH_2-t-Bu)_6(py)_2(\mu-C_2Me_2)$, in hydrocarbon solvents, reacts with acetonitrile (1 equiv) to give a mixture of $W_2(OCH_2-t-Bu)_6(N(CMe)_4N)(py)$, III, and unreacted $W_2(OCH_2-t-Bu)_6(py)_2(C_2Me_2)$. The compound III is easily prepared in reactions involving an excess of acetonitrile. In related reactions involving $W_2(O-i-Pr)_6(py)_2(\mu-C_2H_2)$ with acetonitrile, no pure crystalline compound could be isolated, but crystallization from 2-propanol yields $W_2(O-i-Pr)_7(NHC(Me)CHCHC(Me)N)$, IV.

(13) Chamberlain, L. R.; Rothwell, A. P.; Rothwell, I. P., submitted for publication.

(14) For a discussion of M-OR and M-M distances in related compounds see: Chisholm, M. H. *Polyhedron* 1983, 2, 681.

Table IV. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(O-i-Pr)_7(NHC(Me)CHCHC(Me)N)$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}, \text{\AA}^2$
W(1)	3114.1 (4)	1902.3 (2)	9576.4 (2)	11
W(2)	1682.3 (4)	3023.4 (2)	8794.7 (2)	12
N(3)	2927 (8)	717 (5)	9359 (4)	15
C(4)	2510 (10)	196 (7)	8799 (6)	23
C(5)	2514 (12)	345 (7)	8177 (6)	23
C(6)	2992 (11)	1040 (8)	7897 (6)	25
C(7)	3108 (10)	1826 (6)	8075 (5)	14
N(8)	2757 (8)	2132 (5)	8596 (4)	14
C(9)	2094 (12)	-624 (7)	8971 (6)	25
C(10)	3568 (13)	2456 (8)	7687 (7)	31
O(11)	4946 (6)	2029 (4)	9857 (4)	16
C(12)	5716 (10)	2587 (7)	9615 (6)	18
C(13)	6668 (11)	3046 (8)	10230 (7)	28
C(14)	6388 (12)	2096 (8)	9237 (7)	29
O(15)	3312 (6)	1558 (4)	10506 (3)	15
C(16)	4264 (10)	1003 (7)	10937 (5)	18
C(17)	5201 (12)	1464 (8)	11545 (6)	27
C(18)	3589 (13)	317 (8)	11160 (7)	32
O(19)	1136 (6)	2101 (4)	9337 (4)	18
C(20)	71 (11)	1939 (7)	9565 (7)	26
C(21)	-89 (12)	1006 (8)	9571 (7)	32
C(22)	296 (13)	2317 (9)	10242 (7)	33
O(23)	2968 (6)	3165 (4)	9789 (3)	13
C(24)	2940 (10)	3764 (6)	10288 (5)	16
C(25)	3428 (12)	4563 (7)	10123 (6)	23
C(26)	3710 (12)	3457 (7)	11006 (6)	24
O(27)	2543 (7)	3799 (4)	8447 (4)	19
C(28)	2362 (11)	4581 (7)	8123 (6)	20
C(29)	1375 (12)	4511 (7)	7401 (7)	26
C(30)	3692 (12)	4861 (8)	8144 (7)	31
O(31)	575 (7)	3826 (4)	9025 (3)	16
C(32)	-513 (12)	4313 (7)	8632 (6)	25
C(33)	-1781 (12)	3944 (8)	8664 (7)	33
C(34)	-307 (13)	5163 (8)	8922 (8)	36
O(35)	167 (7)	2796 (4)	8007 (4)	18
C(36)	-307 (12)	2077 (7)	7618 (7)	32
C(37)	-1680 (13)	1946 (8)	7515 (9)	52
C(38)	-170 (14)	2199 (9)	6899 (7)	40

Compound IV is closely related to III, and it is reasonable to view its formation in the reaction involving $W_2(O-i-Pr)_6(py)_2(\mu-C_2H_2)$ and acetonitrile by the addition of *i*-PrOH across a W-N double bond: $W_2(O-i-Pr)_6(N(CMe)_4N) + i\text{-PrOH} \rightarrow W_2(O-i-Pr)_7(NHC(Me)CHCHC(Me)N)$.

As with reactions involving $W_2(OR)_6$ compounds and alkynes the reaction products are dependent on the nature of the OR ligands. In the present case it is reasonable to suppose that compounds analogous to I are intermediates in the formation of III and IV; i.e., the linking of the alkyne and nitrile fragments proceeds via a five-membered metallacycle to the seven-membered metallacycle. The latter reaction involves the formal insertion of a $C\equiv N$ group into a $W=C$ bond to give an imido(2-) ligand and has a parallel with reactions of Ta=C bonds: $(t\text{-Bu})_3\text{Ta}=\text{CH}(t\text{-Bu}) + \text{MeC}\equiv\text{N} \rightarrow (t\text{-Bu})_3\text{Ta}=\text{NC}(\text{Me})=\text{CH}(t\text{-Bu})$.¹²

Solid-State Structures. Atomic positional parameters for the compounds I, II, III, and IV are given in Tables I, II, III, and IV, respectively. Selected bond distances and angles are given in Tables V through VIII and ORTEP views of the molecules giving the atom number schemes used in the tables are shown in Figures 1, 2, 3, and 4. For brevity these structures are discussed collectively where possible, and crystal data are summarized in Table IX.

General Considerations. In I each tungsten atom is in a five-coordinate environment that corresponds fairly well to a distorted trigonal-bipyramidal geometry. The two tungsten atoms share a common equatorial-axial edge through the agency of an *O-t*-Bu ligand and the nitrogen of the metallacycle. The five-membered metallacycle spans equatorial (C) and axial (N) positions for W(1) while the nitrogen atom occupies an equatorial position for W(2). In compounds II, III, and IV, each tungsten atom is six-coordinate and the local geometry is distorted from octahedral. In each molecule the two tungsten atoms share a face formed by two OR

Table V. Selected Bond Distances (Å) and Angles (deg) for the $W_2(O-t-Bu)_6(CHCHC(Ph)N)$ Molecule

A			B			dist		
W(1)	W(2)	2.674 (1)	O(13)	C(14)	1.434 (7)			
W(1)	O(13)	1.913 (4)	O(18)	C(19)	1.463 (7)			
W(1)	O(18)	1.878 (4)	O(23)	C(24)	1.474 (7)			
W(1)	O(23)	2.058 (4)	O(28)	C(29)	1.444 (7)			
W(1)	N(6)	2.041 (5)	O(33)	C(34)	1.452 (7)			
W(1)	C(3)	1.980 (6)	O(38)	C(39)	1.455 (7)			
W(2)	O(23)	2.107 (4)	N(6)	C(5)	1.407 (7)			
W(2)	O(28)	1.892 (4)	C(3)	C(4)	1.411 (9)			
W(2)	O(33)	1.866 (4)	C(4)	C(5)	1.364 (9)			
W(2)	O(38)	1.910 (4)	C(5)	C(7)	1.479 (8)			
W(2)	N(6)	1.903 (5)						

A			B			C			angle		
W(2)	W(1)	O(13)	136.18 (12)	O(23)	W(2)	N(6)	89.55 (17)				
W(2)	W(1)	O(18)	105.75 (12)	O(28)	W(2)	O(33)	125.97 (17)				
W(2)	W(1)	O(23)	50.87 (11)	O(28)	W(2)	O(38)	91.01 (16)				
W(2)	W(1)	N(6)	45.15 (13)	O(28)	W(2)	N(6)	132.23 (18)				
W(2)	W(1)	C(3)	111.13 (18)	O(33)	W(2)	O(38)	96.29 (16)				
O(13)	W(1)	O(18)	94.79 (17)	O(33)	W(2)	N(6)	100.95 (18)				
O(13)	W(1)	O(23)	89.08 (16)	O(38)	W(2)	N(6)	92.40 (18)				
O(13)	W(1)	N(6)	169.31 (17)	W(1)	O(13)	C(14)	146.2 (4)				
O(13)	W(1)	C(3)	97.98 (22)	W(1)	O(18)	C(19)	143.7 (4)				
O(18)	W(1)	O(23)	140.45 (16)	W(1)	O(23)	W(2)	79.88 (13)				
O(18)	W(1)	N(6)	94.43 (18)	W(1)	O(23)	C(24)	137.6 (3)				
O(18)	W(1)	C(3)	108.10 (21)	W(2)	O(23)	C(24)	138.3 (3)				
O(23)	W(1)	N(6)	87.24 (17)	W(2)	O(28)	C(29)	151.0 (4)				
O(23)	W(1)	C(3)	110.28 (20)	W(2)	O(33)	C(34)	150.1 (4)				
N(6)	W(1)	C(3)	73.92 (23)	W(2)	O(38)	C(39)	133.3 (3)				
W(1)	W(2)	O(23)	49.25 (10)	W(1)	N(6)	W(2)	85.32 (18)				
W(1)	W(2)	O(28)	94.02 (13)	W(1)	N(6)	C(5)	120.4 (4)				
W(1)	W(2)	O(33)	119.87 (12)	W(2)	N(6)	C(5)	146.4 (4)				
W(1)	W(2)	O(38)	129.37 (11)	W(1)	C(3)	C(4)	119.8 (5)				
W(1)	W(2)	N(6)	49.53 (14)	C(3)	C(4)	C(5)	114.7 (5)				
O(23)	W(2)	O(28)	83.72 (16)	N(6)	C(5)	C(4)	109.3 (5)				
O(23)	W(2)	O(33)	88.59 (16)	N(6)	C(5)	C(7)	123.3 (5)				
O(23)	W(2)	O(38)	174.30 (15)	C(4)	C(5)	C(7)	127.3 (5)				

ligands and a nitrogen atom of the metallacycle.

In I and II, the five atoms forming the metallacycle ligand are planar. The W(2) atoms are not contained in this plane; the geometry about the bridging nitrogen atoms is distorted from trigonal planar to pyramidal, but not to a great extent. Also the central W_2ON unit in I is not planar. These structural features no doubt arise from the steric constraints of the metallacycle being used to bridge the two metal atoms. The seven atoms of the metallacyclic ligands in III and IV are in a puckered ring. In all of the compounds the W–W distances, which fall in the range 2.56–2.67 Å, can be viewed as single-bond distances associated with a W_2^{10+} moiety. For a ready comparison of distances associated with these fused metallacyclic groups, the central units are shown in Figure 5 for compounds I and II and Figure 6 for compounds III and IV.

Bond Distances and Angles Involving RO Ligands. The W–O distances for terminal ligands average 1.90 Å, typical of distances where some oxygen-to-tungsten π bonding is involved. The bridging W–O distances are longer, ca. 2.10 Å, as is generally the case. In every molecule the W–O distances are longer when the RO group is trans to the terminal nitrogen atom of the macrocycle consistent with the high trans influence¹⁵ and π -donor ability of the imido (and in IV the amido) nitrogen ligand. This phenomenon readily explains the large asymmetries seen in some of the W–O distances associated with the bridging OR groups. The W–O–C angles fall in the range 120–150°, again typical for tungsten alkoxides. In general the larger the angle the shorter is the M–O distance since a larger M–O–C angle generally correlates with increased oxygen-to-metal π -donation.

Bond Distances and Angles Involving Nitrogen Atoms. The structural parameters for compounds I through IV span the range for nitrogen ligands of the type described by Nugent and Haymore,¹⁶ namely, imido(2-), NR, which can behave as a terminal

or bridging ligand and donate from four to six electrons, and amido (1-) ligands, NRR' , which also can be either bridging or terminal and may donate from two to four electrons. In III we see, as a reference, a W–N pyridine distance, 2.20 Å, typical of a W–N dative single-bond distance.

The terminal W–N distance, 1.78 (1) Å, in III and the W–N–C angle, 150°, are reconcilable with a terminal imido ligand, RN^{2-} , donating between four and six electrons to tungsten. Upon conversion to a terminal amido ligand, $R(H)N$, in IV, the W–N distance increased to 1.99 (1) Å and the W–N–C angle decreases to 140°. The W–N distance, 1.99 (1) Å, may be taken to indicate a M–N single bond with some further π -bonding, i.e. an amido group donating more than two electrons to tungsten. For a comparison we note the W–N distance in $W_2(NMe_2)_6$ is 1.97 (1) Å (averaged), which corresponds to a W–N bond order of $1^2/3(1\sigma + 2^2/3\pi)$ since four π -bonds are delocalized over the six W–N bonds.¹⁷ In the present cases the imido and amido ligands in III and IV, respectively, are competing with the terminal RO ligands for two of the t_{2g} type orbitals to form π -bonds. The other t_{2g} orbital is principally involved in forming the M–M bond.

The bridging N-to-W distances are also typical of what can be expected for a $\mu-NR^{2-}$ ligand donating between four and six electrons in total. In compounds II and IV the bridge is relatively symmetrical but in I and III the bridge is notably asymmetric suggestive of varying contributions of delocalized and localized forms of bonding represented by V and VI below, respectively.



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Table VI. Selected Bond Distances (Å) and Angles (deg) for the $W_2(O-i-Pr)_7(CH_2CHC(Ph)N)$ Molecule

A	B	dist.	A	B	dist.
W(1)	W(2)	2.5845 (6)	W(2)	N(6)	1.962 (7)
W(1)	O(13)	1.851 (5)	O(13)	C(14)	1.426 (11)
W(1)	O(17)	1.951 (5)	O(17)	C(18)	1.411 (13)
W(1)	O(21)	2.025 (5)	O(21)	C(22)	1.451 (10)
W(1)	O(25)	2.184 (5)	O(25)	C(26)	1.436 (10)
W(1)	N(6)	1.980 (6)	O(29)	C(30)	1.438 (10)
W(1)	C(3)	2.174 (8)	O(33)	C(34)	1.421 (11)
W(2)	O(21)	2.112 (5)	O(37)	C(38)	1.415 (11)
W(2)	O(25)	2.064 (5)	N(6)	C(5)	1.421 (10)
W(2)	O(29)	1.902 (5)	C(3)	C(4)	1.490 (12)
W(2)	O(33)	1.953 (5)	C(4)	C(5)	1.333 (12)
W(2)	O(37)	1.884 (6)	C(5)	C(7)	1.482 (11)

Bond Angles							
A	B	C	angle	A	B	C	angle
W(2)	W(1)	O(13)	116.57 (16)	O(21)	W(2)	N(6)	80.87 (23)
W(2)	W(1)	O(17)	132.40 (17)	O(25)	W(2)	O(29)	164.25 (24)
W(2)	W(1)	O(21)	52.86 (15)	O(25)	W(2)	O(33)	84.28 (22)
W(2)	W(1)	O(25)	50.46 (14)	O(25)	W(2)	O(37)	92.79 (25)
W(2)	W(1)	N(6)	48.73 (19)	O(25)	W(2)	N(6)	94.79 (23)
W(2)	W(1)	C(3)	117.99 (24)	O(29)	W(2)	O(33)	85.82 (24)
O(13)	W(1)	O(17)	97.17 (23)	O(29)	W(2)	O(37)	100.33 (25)
O(13)	W(1)	O(21)	163.56 (22)	O(29)	W(2)	N(6)	93.25 (25)
O(13)	W(1)	O(25)	86.56 (21)	O(33)	W(2)	O(37)	95.50 (28)
O(13)	W(1)	N(6)	98.98 (24)	O(33)	W(2)	N(6)	171.72 (26)
O(13)	W(1)	C(3)	96.5 (3)	O(37)	W(2)	N(6)	92.76 (27)
O(17)	W(1)	O(21)	85.67 (22)	W(1)	O(13)	C(14)	141.2 (5)
O(17)	W(1)	O(25)	103.67 (23)	W(1)	O(17)	C(18)	133.3 (6)
O(17)	W(1)	N(6)	159.01 (25)	W(1)	O(21)	W(2)	77.30 (18)
O(17)	W(1)	C(3)	88.1 (3)	W(1)	O(21)	C(22)	140.7 (5)
O(21)	W(1)	O(25)	77.05 (20)	W(2)	O(21)	C(22)	134.9 (5)
O(21)	W(1)	N(6)	82.64 (23)	W(1)	O(25)	W(2)	74.89 (17)
O(21)	W(1)	C(3)	99.83 (28)	W(1)	O(25)	C(26)	145.9 (6)
O(25)	W(1)	N(6)	90.64 (25)	W(2)	O(25)	C(26)	133.0 (5)
O(25)	W(1)	C(3)	167.46 (28)	W(2)	O(29)	C(30)	134.5 (5)
N(6)	W(1)	C(3)	76.9 (3)	W(2)	O(33)	C(34)	134.3 (6)
W(1)	W(2)	O(21)	49.84 (14)	W(2)	O(37)	C(38)	136.3 (6)
W(1)	W(2)	O(25)	54.65 (15)	W(1)	N(6)	W(2)	81.93 (24)
W(1)	W(2)	O(29)	123.80 (17)	W(1)	N(6)	C(5)	119.9 (5)
W(1)	W(2)	O(33)	125.06 (18)	W(2)	N(6)	C(5)	153.1 (5)
W(1)	W(2)	O(37)	118.61 (18)	W(1)	C(3)	C(4)	109.2 (6)
W(1)	W(2)	N(6)	49.34 (18)	C(3)	C(4)	C(5)	116.8 (7)
O(21)	W(2)	O(25)	77.85 (21)	N(6)	C(5)	C(4)	114.2 (7)
O(21)	W(2)	O(29)	90.11 (22)	N(6)	C(5)	C(7)	118.9 (7)
O(21)	W(2)	O(33)	90.90 (23)	C(4)	C(5)	C(7)	126.9 (8)
O(21)	W(2)	O(37)	168.10 (22)				

The M–N distances in compounds I through IV may be compared to those seen in $[(t-BuO)_2(ArN)Mo(\mu-NAr)]_2$, where Ar = tolyl, which has terminal imido ligands, Mo–N = 1.75 (1) Å and Mo–N–C = 175° (averaged), and bridging imido ligands with distances 1.84 (1) and 2.30 (1) Å,¹⁸ corresponding to the limiting bridging mode depicted by VI.

Why should the μ -imido ligands be symmetrical in II and IV but unsymmetrical in I and III? In part this may be a consequence of charge distribution within the molecule. In compounds I and III the terminal function of the macrocycle is a 2- ligand to W(1) and consequently the formal 2- charge of the bridging imido ligand is mostly associated with W(2). In compounds II and IV, the gross charge associated with the macrocyclic ligands is 3-. The terminal function is amido(1-) in IV and alkyl(1-) in II and so the bridging imido group (2-) may partition its charge equally between W(1) and W(2). Note in both II and IV there are two and three terminal O-*i*-Pr ligands associated with W(1) and W(2), respectively. Other factors may also contribute. In I, the bridging nitrogen atom forms part of an axial (long) and equatorial (short) bridge and in III the presence of the neutral donor pyridine ligand provides an additional problem in the way in which charge is formally assigned to the two tungsten atoms. The nitrogen to tungsten bonding seen in compounds I, II, III, and IV provides

further evidence¹⁶ of the fascinating and subtle ways nitrogen donor ligands can respond to the electronic requirements of a metal.

Carbon-to-Tungsten Bonds. W–C bond distances in carbene/alkylidene compounds vary greatly since they are very sensitive to the oxidation state of tungsten, the coordination number and geometry and the nature of the other ligands. In the Casey carbene complex $(CO)_5W=CPh_2$ there are two independent molecules in the unit cell yielding W–C double bond distances of 2.13 (2) and 2.15 (2) Å,¹⁹ whereas in $W(=CHCMe_3)(O)(PEt_3)_2Cl_2$ the W–C double bond distance is 1.882 (14) Å.²⁰ These probably are the longest and shortest known distances for W–C double bonds. In $W(\equiv CMe_3)(=CHCMe_3)-(CH_2CMe_3)(dmpe)$ that contains an alkyl, an alkylidene, and an alkylidyne, the W–C bond distances are, respectively, 2.258 (8), 1.942 (9), and 1.785 (8) Å.²¹ In $Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4$, which is related to the Schrock compound in as much as each metal forms a triple bond, a double and three single bonds, the Mo–C double bond distance is 1.949 (5) Å.²² The W–C distance in I, 1.980 (6) Å, is therefore well within the range expected for

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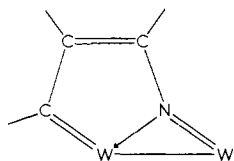
Table VII. Selected Bond Distances (Å) and Angles (deg) for the $W_2(OCH_2-t-Bu)_6(py)(N(CMe)_4N)$ Molecule

Bond Distances						
A	B	dist	A	B	dist	
W(1)	W(2)	2.617 (1)	O(25)	C(26)	1.420 (15)	
W(1)	O(19)	1.943 (9)	O(31)	C(32)	1.409 (14)	
W(1)	O(25)	2.226 (8)	O(37)	C(38)	1.424 (17)	
W(1)	O(31)	2.037 (9)	O(43)	C(44)	1.453 (15)	
W(1)	N(3)	1.778 (11)	O(49)	C(50)	1.412 (16)	
W(1)	N(12)	2.092 (10)	N(3)	C(4)	1.365 (17)	
W(1)	N(13)	2.202 (10)	N(12)	C(10)	1.399 (17)	
W(2)	O(25)	2.135 (8)	C(4)	C(5)	1.491 (21)	
W(2)	O(31)	2.077 (9)	C(4)	C(6)	1.379 (21)	
W(2)	O(37)	1.870 (9)	C(6)	C(7)	1.537 (20)	
W(2)	O(43)	1.922 (8)	C(6)	C(8)	1.476 (20)	
W(2)	O(49)	1.969 (8)	C(8)	C(9)	1.526 (20)	
W(2)	N(12)	1.904 (11)	C(8)	C(10)	1.357 (18)	
O(19)	C(20)	1.432 (15)	C(10)	C(11)	1.524 (18)	

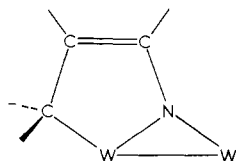
Bond Angles							
A	B	C	angle	A	B	C	angle
W(2)	W(1)	O(19)	125.9 (3)	O(31)	W(2)	O(49)	83.7 (3)
W(2)	W(1)	O(25)	51.6 (2)	O(31)	W(2)	N(12)	97.6 (4)
W(2)	W(1)	O(31)	51.2 (2)	O(37)	W(2)	O(43)	98.3 (4)
W(2)	W(1)	N(3)	108.2 (3)	O(37)	W(2)	O(49)	90.3 (4)
W(2)	W(1)	N(12)	46.1 (3)	O(37)	W(2)	N(12)	98.4 (4)
W(2)	W(1)	N(13)	126.6 (3)	O(43)	W(2)	O(49)	83.8 (3)
O(19)	W(1)	O(25)	87.4 (3)	O(43)	W(2)	N(12)	93.5 (4)
O(19)	W(1)	O(31)	89.7 (4)	O(49)	W(2)	N(12)	171.1 (4)
O(19)	W(1)	N(3)	113.8 (4)	W(1)	O(19)	C(20)	127.1 (8)
O(19)	W(1)	N(12)	159.7 (4)	W(1)	O(25)	W(2)	73.7 (3)
O(19)	W(1)	N(13)	84.0 (4)	W(1)	O(25)	C(26)	124.9 (7)
O(25)	W(1)	O(31)	75.6 (3)	W(2)	O(25)	C(26)	128.0 (7)
O(25)	W(1)	N(3)	158.2 (4)	W(1)	O(31)	W(2)	79.0 (3)
O(25)	W(1)	N(12)	73.9 (4)	W(1)	O(31)	C(32)	134.1 (8)
O(25)	W(1)	N(13)	94.6 (4)	W(2)	O(31)	C(32)	135.6 (8)
O(31)	W(1)	N(3)	98.3 (4)	W(2)	O(37)	C(38)	132.1 (8)
O(31)	W(1)	N(12)	93.2 (4)	W(2)	O(43)	C(44)	132.6 (8)
O(31)	W(1)	N(13)	168.6 (4)	W(2)	O(49)	C(50)	127.5 (8)
N(3)	W(1)	N(12)	85.7 (4)	W(1)	N(3)	C(4)	150.5 (10)
N(3)	W(1)	N(13)	92.9 (4)	W(1)	N(12)	W(2)	81.7 (4)
N(12)	W(1)	N(13)	89.6 (4)	W(1)	N(12)	C(10)	116.7 (8)
W(1)	W(2)	O(25)	54.7 (2)	W(2)	N(12)	C(10)	161.4 (9)
W(1)	W(2)	O(31)	49.8 (2)	N(3)	C(4)	C(5)	114.9 (13)
W(1)	W(2)	O(37)	113.5 (3)	N(3)	C(4)	C(6)	120.0 (13)
W(1)	W(2)	O(43)	134.8 (3)	C(5)	C(4)	C(6)	125.1 (13)
W(1)	W(2)	O(49)	125.1 (2)	C(4)	C(6)	C(7)	115.8 (14)
W(1)	W(2)	N(12)	52.3 (3)	C(4)	C(6)	C(8)	125.7 (13)
O(25)	W(2)	O(31)	76.8 (3)	C(7)	C(6)	C(8)	118.4 (14)
O(25)	W(2)	O(37)	166.3 (3)	C(6)	C(8)	C(9)	114.0 (12)
O(25)	W(2)	O(43)	95.3 (3)	C(6)	C(8)	C(10)	126.0 (13)
O(25)	W(2)	O(49)	92.0 (3)	C(9)	C(8)	C(10)	120.1 (13)
O(25)	W(2)	N(12)	79.8 (4)	N(12)	C(10)	C(8)	123.0 (13)
O(31)	W(2)	O(37)	90.0 (4)	N(12)	C(10)	C(11)	115.9 (11)
O(31)	W(2)	O(43)	165.0 (4)	C(8)	C(10)	C(11)	120.2 (12)

a W-C double bond. Moreover, the W-C bond distance in II, 2.174 (8) Å, which is clearly a single bond, differs by 0.19 Å from that in I, a much greater change than can be reconciled with a change of hybridization at carbon, sp^2 vs. sp^3 , or at tungsten. We conclude that the W-C bond distance in I implies double-bond character.

The Macrocyclic Ligands. A consideration of the W-C and W-N distances together with the C-C and C-N distances within the macrocycles (Figures 5 and 6) allows the formulation of valence bond (VB) descriptions of the five membered rings in compounds I and II as shown in VII and VIII.



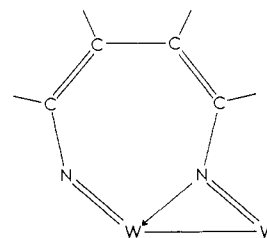
VII



VIII

In compound I there is clearly some delocalization of the π -electrons over the five-membered ring, but in II the C-C and C-N distances imply localization of the double bond between C(4) and C(5) as depicted by the VB description VIII.

A VB description of the seven-membered ring in III can be formulated as IX on the basis of the alternating long and short distances together with the puckering of the ring that generates a C(7)-C(6)-C(8)-C(9) torsion angle of 41.2°. The bond order

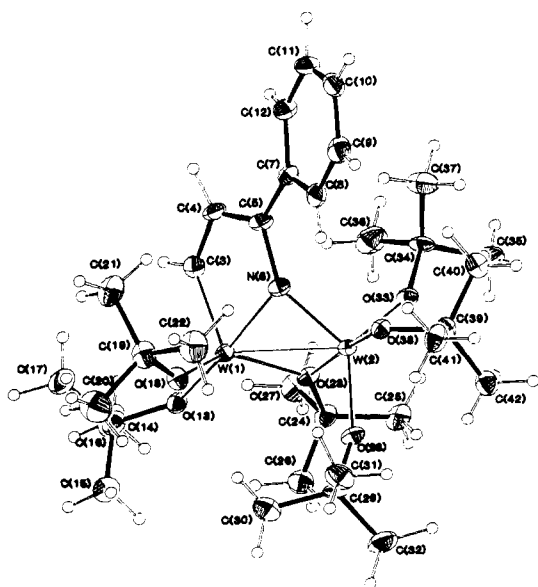


IX

Table VIII. Selected Bond Distances (Å) and Angles (deg) for the $W_2(O-i-Pr)_7(NHC(Me)CHCHC(Me)N)$ Molecule

A	B	dist	A	B	dist
W(1)	W(2)	2.576 (1)	O(15)	C(16)	1.430 (12)
W(1)	O(11)	1.878 (6)	O(19)	C(20)	1.431 (13)
W(1)	O(15)	1.962 (7)	O(23)	C(24)	1.443 (12)
W(1)	O(19)	2.055 (7)	O(27)	C(28)	1.428 (13)
W(1)	O(23)	2.131 (7)	O(31)	C(32)	1.419 (13)
W(1)	N(3)	1.986 (8)	O(35)	C(36)	1.419 (13)
W(1)	N(8)	1.983 (8)	N(3)	C(4)	1.389 (14)
W(2)	O(19)	2.100 (7)	N(8)	C(7)	1.373 (13)
W(2)	O(23)	2.060 (6)	C(4)	C(5)	1.325 (17)
W(2)	O(27)	1.875 (7)	C(4)	C(9)	1.502 (16)
W(2)	O(31)	1.958 (7)	C(5)	C(6)	1.460 (17)
W(2)	O(35)	1.903 (7)	C(6)	C(7)	1.332 (16)
W(2)	N(8)	2.007 (8)	C(7)	C(10)	1.508 (16)
O(11)	C(12)	1.449 (12)			

A	B	C	angle	A	B	C	angle
W(2)	W(1)	O(11)	116.9 (2)	O(23)	W(2)	O(31)	86.0 (3)
W(2)	W(1)	O(15)	131.2 (2)	O(23)	W(2)	O(35)	163.5 (3)
W(2)	W(1)	O(19)	52.5 (2)	O(23)	W(2)	N(8)	93.2 (3)
W(2)	W(1)	O(23)	50.8 (2)	O(27)	W(2)	O(31)	94.6 (3)
W(2)	W(1)	N(3)	124.2 (2)	O(27)	W(2)	O(35)	101.3 (3)
W(2)	W(1)	N(8)	50.2 (2)	O(27)	W(2)	N(8)	90.0 (3)
O(11)	W(1)	O(15)	89.8 (3)	O(31)	W(2)	O(35)	85.7 (3)
O(11)	W(1)	O(19)	164.1 (3)	O(31)	W(2)	N(8)	175.3 (3)
O(11)	W(1)	O(23)	88.8 (3)	O(35)	W(2)	N(8)	93.8 (3)
O(11)	W(1)	N(3)	100.9 (3)	W(1)	O(11)	C(12)	130.1 (6)
O(11)	W(1)	N(8)	95.3 (3)	W(1)	O(15)	C(16)	127.2 (6)
O(15)	W(1)	O(19)	91.0 (3)	W(1)	O(19)	W(2)	76.6 (2)
O(15)	W(1)	O(23)	93.5 (3)	W(1)	O(19)	C(20)	142.6 (7)
O(15)	W(1)	N(3)	85.0 (3)	W(2)	O(19)	C(20)	137.5 (6)
O(15)	W(1)	N(8)	172.7 (3)	W(1)	O(23)	W(2)	75.8 (2)
O(19)	W(1)	O(23)	75.3 (3)	W(1)	O(23)	C(24)	146.4 (6)
O(19)	W(1)	N(3)	95.0 (3)	W(2)	O(23)	C(24)	128.6 (6)
O(19)	W(1)	N(8)	85.5 (3)	W(2)	O(27)	C(28)	142.0 (7)
O(23)	W(1)	N(3)	170.2 (3)	W(2)	O(31)	C(32)	134.0 (7)
O(23)	W(1)	N(8)	91.8 (3)	W(2)	O(35)	C(36)	133.0 (6)
N(3)	W(1)	N(8)	89.0 (4)	W(1)	N(3)	C(4)	140.3 (8)
W(1)	W(2)	O(19)	50.9 (2)	W(1)	N(8)	W(2)	80.4 (3)
W(1)	W(2)	O(23)	53.3 (2)	W(1)	N(8)	C(7)	138.3 (7)
W(1)	W(2)	O(27)	117.1 (2)	W(1)	N(8)	C(7)	141.3 (7)
W(1)	W(2)	O(31)	127.4 (2)	N(3)	C(4)	C(5)	127.0 (11)
W(1)	W(2)	O(35)	123.3 (2)	N(3)	C(4)	C(9)	112.4 (10)
W(1)	W(2)	N(8)	49.4 (2)	C(5)	C(4)	C(9)	120.6 (11)
O(19)	W(2)	O(23)	75.9 (3)	C(4)	C(5)	C(6)	131.7 (11)
O(19)	W(2)	O(27)	167.4 (3)	C(5)	C(6)	C(7)	130.7 (11)
O(19)	W(2)	O(31)	91.7 (3)	N(8)	C(7)	C(6)	123.3 (10)
O(19)	W(2)	O(35)	90.1 (3)	N(8)	C(7)	C(10)	114.9 (9)
O(19)	W(2)	N(8)	83.7 (3)	C(6)	C(7)	C(10)	121.7 (10)
O(23)	W(2)	O(27)	93.6 (3)				

Figure 1. An ORTEP view of the $W_2(O-t-Bu)_6(CHCHC(Ph)N)$ molecule, I, showing the atom number scheme used in the tables.

between C(6) and C(8), the original "triple bond" of the coordinated alkyne, has been reduced to 1.

A similar situation is apparent for the carbon backbone of the seven-membered ring in compound IV: the only significant changes involve the nitrogen to tungsten bonding.

Metal-Metal Distances. As noted previously the W-W distances may all be taken as indicative of M-M single bonds. It is interesting to note that the distance in I is significantly longer than the others. This may well reflect the fact that in I the two tungsten atoms are five-coordinate and are fused along an edge whereas in the other compounds the metal atoms are six-coordinate and share a face. The M-M single bond distance in the edge-shared (RO) octahedral complex $W_2Cl_4(OEt)_6$ is 2.715 (1) Å, for example.²³ Of particular interest to us is the comparison of M-M distances of the compounds reported here with those observed in the μ -alkyne adducts of ditungsten hexaalkoxides.⁸ In $W_2(O-t-Bu)_6(py)(\mu-C_2H_2)$, which has five-coordinate tungsten atoms sharing a $\mu-C_2H_2$ ligand and one OR ligand, the W-W distance is 2.665 (1) Å, essentially identical with that in I. In $W_2(O-i-Pr)_6(\mu-C_2H_2)(py)_2$, which has a confacial bioctahedral geometry involving a pair of bridging RO ligands and the alkyne,

(23) Cotton, F. A.; DeMarco, D.; Kolthammer, B. S. W.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 3048.

Table IX. Crystal Data Summary

	I ^a	II	III	IV
empirical Formula	W ₂ C ₃₃ H ₆₁ O ₆ N	W ₂ C ₃₀ H ₅₇ O ₇ N	W ₂ C ₄₃ H ₈₃ N ₃ O ₆	W ₂ C ₂₇ H ₅₈ N ₂ O ₇
color of crystal	black	black	black	magneta
crystal dimens, mm	0.08 × 0.06 × 0.06	0.12 × 0.12 × 0.13	0.04 × 0.04 × 0.05	0.07 × 0.07 × 0.06
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>c</i>
cell dimensions				
temp, °C	-158	-152	-168	-165
<i>a</i> , Å	19.237 (8)	18.346 (3)	26.006 (12)	10.898 (5)
<i>b</i> , Å	10.619 (4)	11.579 (1)	17.056 (7)	16.366 (8)
<i>c</i> , Å	10.180 (3)	10.180 (1)	12.015 (4)	20.942 (12)
α, deg	111.97 (2)	107.08 (1)		
β, deg	97.26 (2)	61.54 (1)	110.29 (2)	111.16 (3)
γ, deg	73.00 (2)	98.19 (1)		
<i>Z</i> (molecules/cell)	2	2	4	4
vol, Å ³	1843.94	1817.33	4998.72	3483.22
<i>d</i> _{calcd} , g/cm ³	1.685	1.666	1.467	1.698
wavelength, Å	0.710 69	0.710 69	0.710 69	0.710 69
mol wt	935.55	911.48	105.85	890.46
linear Ab coeff, cm ⁻¹	64.060	64.993	47.381	67.804
detector to sample dist, cm	22.5	22.5	22.5	22.5
sample to source dist, cm	23.5	23.5	23.5	23.5
av ω scan width at half-height	0.25	0.25	0.25	0.25
scan speed, deg/min	4.0	4.0	4.0	4.0
scan width, deg (+ dispersion)	2.0	2.0	2.0	2.0
individual bgd, s	4	5	3	5
aperture size, mm	3.0 × 4.0	3.0 × 4.0	3.0 × 4.0	3.0 × 4.0
2θ range, deg	6-45	6-45	6-45	6-45
total no. of reflctns collected	6633	5928	8201	6020
no. of unique intensities	4832	4759	6548	4572
no. with <i>F</i> > 3.00 σ(<i>F</i>)	4182	4135	4666	3759
<i>R</i> (<i>F</i>)	0.023	0.033	0.052	0.041
<i>R</i> _w (<i>F</i>)	0.025	0.035	0.049	0.041
goodness of fit for the last cycle	0.708	1.011	1.096	1.094
max Δ/σ for last cycle	0.07	0.05	0.05	0.06

^aI is W₂(O-*t*-Bu)₆(CHCHC(Ph)N), II is W₂(O-*i*-Pr)₇(CH₂CHC(Ph)N), III is W₂(OCH₂-*t*-Bu)₆(N(CMe)₄N)(py), and IV is W₂(O-*i*-Pr)₇(NHC(Me)CHCHC(Me)N).

the W-W distance is 2.567 (1) Å, comparable to the W-W distances seen here for the face-shared compounds II, III, and IV. This may be taken to support the view that in the μ-alkyne adducts the W-W bond distances correlate well with those expected for single bonds.

NMR Studies. The ¹H NMR spectrum of W₂(OCH₂-*t*-Bu)₆(N(CMe)₄N)(py), III, at -20 °C and 360 MHz is consistent with the observed solid-state structure (Figure 3). Specifically, there are six singlets of equal intensity and six AB quartets for the *t*-Bu and CH₂ groups, respectively, of the neopentoxo ligands. The methyl groups of the macrocyclic ligand appear as four singlets of equal intensity and one-third the intensity of the neopentoxo *t*-Bu resonances. In addition, there are signals assignable to the coordinated pyridine ligand. When the sample is warmed to 21 °C, resonances assignable to a second isomer appear, but the low-temperature isomer still dominates. Unfortunately, as the sample is warmed to above room temperature, fluxional processes hinder structural identification of the second isomer.

¹H NMR spectra of W₂(O-*i*-Pr)₇(NHC(Me)CHCHC(Me)N) at 21 °C and 360 MHz reveal the molecule to be fluxional on the NMR time scale. However, at -60 °C the spectrum obtained is consistent with consideration of the observed solid-state structure (Figure 4). The isopropoxy ligands give rise to 14 overlapping doublets (OCHMe₂) in the region 0.9-1.9 ppm (relative to Me₄Si) and seven septets (OCHMe₂) in the region 4.0-5.6 ppm. Two of the methyne septets are obscured by the tight AB quartet arising from the macrocyclic -CHCH- group, as identified from the spectrum of the partially deuterated molecule W₂(O-*i*-Pr)₇(NHC(Me)CDCDC(Me)N). The Me groups on the macrocyclic ligand appear as singlets at 2.11 and 2.50 ppm, and the amido proton (NH) is observed at 9.31 ppm as a singlet and is exchanged with deuterium upon addition of *i*-PrOD.

Unlike our results for compounds III and IV, we have not been successful in obtaining low-temperature limiting spectra for W₂(O-*t*-Bu)₆(CHCHC(R)N) (I) or W₂(O-*i*-Pr)₇(CH₂CHC-

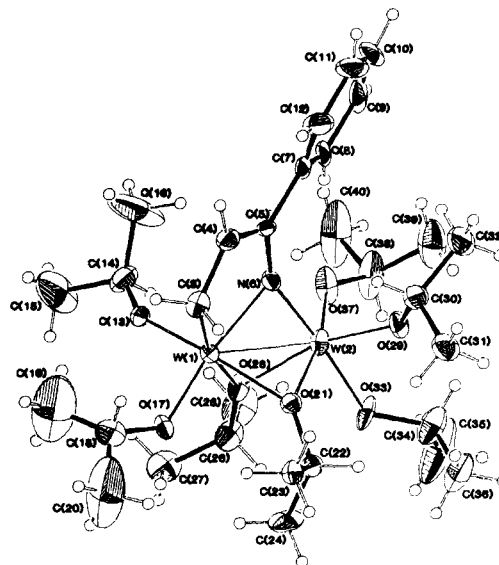


Figure 2. An ORTEP view of the W₂(O-*i*-Pr)₇(CH₂CHC(Ph)N) molecule, II, showing the atom number scheme used in the tables.

(Ph)N) (II) because of their fluxionality (<-90°C). However, detailed ¹H and ¹³C NMR studies of the coordinated macrocyclic ligand at 21 °C have been informative. Data presented in Table X provide a summary of our ¹³C and ¹H NMR results for I and II with further details provided in the Experimental Section. ¹³C NMR spectra were obtained at 90 MHz from toluene-*d*₈ solutions of the ¹³C labeled complexes W₂(O-*t*-Bu)₆(¹³CH¹³CHC(Ph)N) and W₂(O-*i*-Pr)₇(¹³CH₂¹³CHC(Ph)N), each synthesized as outlined in the Experimental Section with ¹³C₂H₂ (92.5 atom % ¹³C). In Table X and subsequent discussions we will refer to the carbons

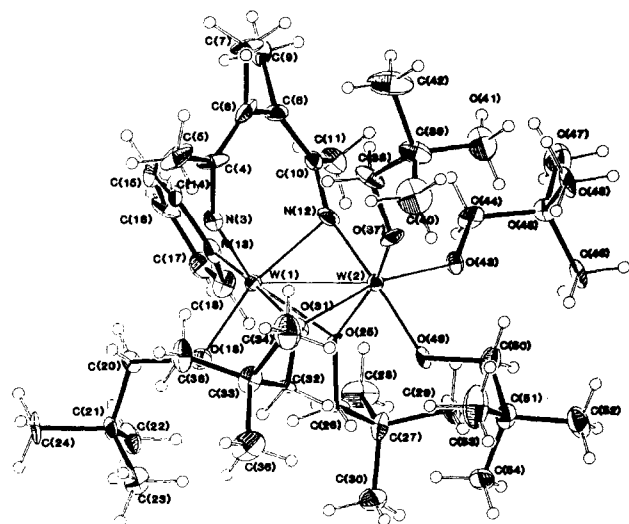


Figure 3. An ORTEP view of the $W_2(OCH_2-t-Bu)_6(py)(N(CMe)_4N)$ molecule, III, showing the atom number scheme used in the tables.

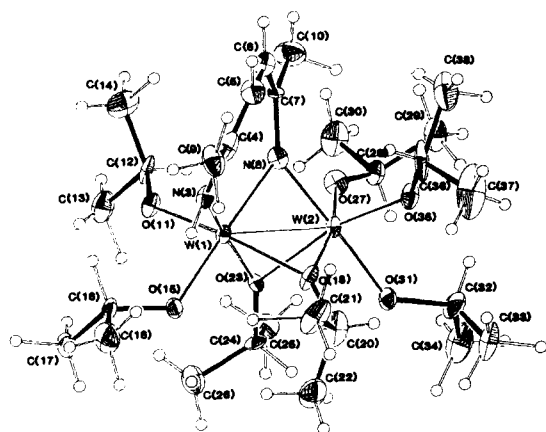
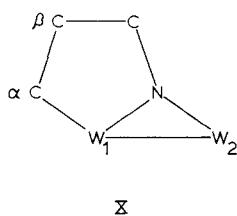


Figure 4. An ORTEP view of the $W_2(O-i-Pr)_7(NHC(Me)CHCHC(Me)N)$ molecule, IV, showing the atom number scheme used in the tables.

and attached hydrogens of the macrocyclic ligand using the labeling scheme shown in X.



We begin by discussing the ^{13}C data for I, for the ^{13}C NMR results simplify interpretation of the 1H NMR spectra. As Table X reports and Figure 7a shows, $C_{\alpha\beta}$ appear as a simple AX pattern in the $^{13}C\{^1H\}$ spectrum. The observed chemical shift of C_{α} , 225.1 ppm and the $^{183}W-^{13}C$ coupling constant, $^1J_{WC_{\alpha}} = 151.9$ Hz (^{183}W , $I = 1/2$, 14.3% natural abundance), are consistent with our formulation of the W-C bond as a double bond and should be compared to the chemical shifts and coupling constants in the pertinent alkylidene complexes.^{20,24} The C_{β} chemical shift of 132.8 ppm falls in the range expected for a sp^2 -hybridized aromatic carbon atom.²⁵ $^1J_{C_{\alpha}C_{\beta}}$ is 49.7 Hz, midway between $^1J_{CC}$ for organic ethane and ethylene. Gate-decoupling reveals (Figure

(24) Schrock, R. R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73. Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774. Kress, J.; Wasolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514.

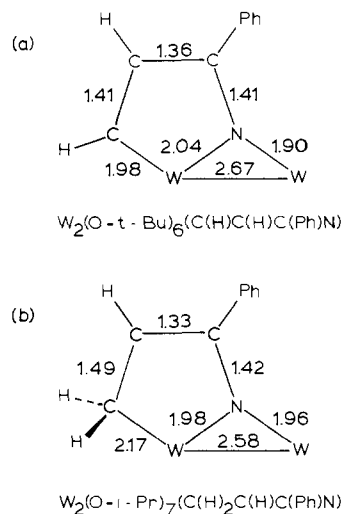


Figure 5. Selected distances (Å) for the $W_2(CHCHC(Ph)N)$ moiety of $W_2(O-t-Bu)_6(CHCHC(Ph)N)$, I (a), and for the $W_2(CH_2CHC(Ph)N)$ moiety of $W_2(O-i-Pr)_7(CH_2CHC(Ph)N)$, II (b). See Tables V and VI for a complete listing of bond distances with esd's. The numbers shown are all within 0.02 Å.

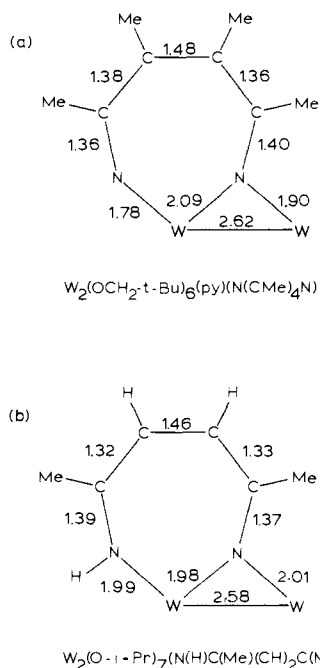


Figure 6. Selected distances (Å) for the $W_2(N(CMe)_4N)$ moiety of $W_2(OCH_2-t-Bu)_6(py)(N(CMe)_4N)$, III (a), and for the $W_2(NHC(Me)CHCHC(Me)N)$ moiety of $W_2(O-i-Pr)_7(NHC(Me)CHCHC(Me)N)$, IV (b). See Tables VII and VIII for a complete listing of bond distances with esd's. The numbers shown are all within 0.02 Å.

7b) $^1J_{C_{\alpha}H_{\alpha}}$ and $^1J_{C_{\beta}H_{\beta}}$ to be 142.9 and 154.0 Hz, respectively, both as expected for near sp^2 -hybridized carbon atoms.

1H NMR spectra of I (Figure 7c) show an AX pattern for H_{α} and H_{β} with doublets at 7.6 and 10.8 ppm ($^3J_{HH} = 5.1$ Hz). The resonance at 7.6 ppm is coupled to two different ^{183}W nuclei, $J_{WH_{\beta}} = 10.7$ and 5.2 Hz. Based upon (a) the chemical shift of H_{α} in the known Schrock-type alkylidenes^{20,24} and (b) a comparison of $^1J_{CH}$ values from the ^{13}C and 1H NMR spectra of the labeled complex (C_{α} and C_{β} assigned as described above), the resonance at 10.8 ppm (without $^{183}W-^1H$ coupling) is assigned to H_{α} . This assignment poses two questions: (a) Why is there no $^{183}W-^{13}C_{\beta}$ coupling, yet we observe two kinds of $^{183}W-^1H_{\beta}$ coupling and (b)

(25) Wehrli, R. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden and Son; London, 1980.

Table X. Summary of ^1H and ^{13}C NMR Results for $\text{W}_2(\text{O}-i\text{-Bu})_6(\text{CHCHC}(\text{Ph})\text{N})$ (I) and $\text{W}_2(\text{O}-i\text{-Pr})_7(\text{CH}_2\text{CHC}(\text{Ph})\text{N})$ (II)^{a,b}

	compd	
	I	II
	^1H Data	
$\delta(\text{H}_\alpha)$	10.78	4.00
$^2J_{\text{W}_1\text{H}_\alpha}$	NO ^c	9.8
$\delta(\text{H}_\beta)$	7.60	7.70
J_{WH_β}	10.7	12.4
J_{WH_β}	5.2	NO
$^3J_{\text{HH}}$	5.1	3.6
	^{13}C Data	
$\delta(\text{C}_\alpha)$	225.1	63.4
$^1J_{\text{W}_1\text{C}_\alpha}$	151.9	111.5
$^1J_{\text{C}_\alpha\text{H}_\alpha}$	142.9	122.6
$^2J_{\text{C}_\alpha\text{H}_\beta}$	NO	<2 ^d
$\delta(\text{C}_\beta)$	132.84	136.05
$^3J_{\text{WC}_\beta}$	NO	NO
$^1J_{\text{C}_\beta\text{H}_\beta}$	154.0	155.9
$^2J_{\text{C}_\beta\text{H}_\alpha}$	2.3 ^d	6.3
$^1J_{\text{C}_\alpha\text{C}_\beta}$	49.7	39.3

^aFor more details see the Experimental Section, where ^1H NMR data are also presented for Ib. ^bAll chemical shifts are in parts per million relative to Me_4Si , and all coupling constants are in hertz. ^cNO = not observed. ^dObserved in the ^1H NMR spectrum of the ^{13}C labeled complex only.

why is there no $^{183}\text{W}-^1\text{H}_\alpha$ coupling? Let us examine the NMR data for II before addressing these questions.

^{13}C and ^1H NMR spectra for II are shown in Figure 8. Upon addition of *i*-PrOH across the $\text{W}-\text{C}_\alpha$ bond in I to form complex II, the chemical shifts and coupling constants for $\text{C}_{\alpha,\beta}$ and $\text{H}_{\alpha,\beta}$ change in a systematic and understandable way: (a) The ^{13}C chemical shift of C_α moves upfield (toward Me_4Si), 225.1 to 63.4 ppm, into the shift range for simple alkyls of tungsten^{20,24,26} while the chemical shift of C_β (136.1 ppm) remains in the region of sp^2 hybridized carbons. (b) The $^{183}\text{W}-^{13}\text{C}_\alpha$ coupling is reduced by 40 Hz to 111.5 Hz and $^1J_{\text{CH}}$ for $\text{C}_\alpha-\text{H}_\alpha$ is also reduced, 142.9 to 122.6 Hz, while that for $\text{C}_\beta-\text{H}_\beta$ remains nearly the same, 154.0 Hz in I vs. 155.9 Hz in II. (c) The ^1H chemical shift of H_α moves upfield from 10.8 to 4.0 ppm while H_β remains approximately the same, 7.6 ppm in I vs. 7.7 ppm in II. These results are interpretable in terms of a rehybridization of C_α from approximately sp^2 to sp^3 , while C_β remains sp^2 .

A curious feature of the ^1H NMR for II is the observation of $^{183}\text{W}-^1\text{H}$ coupling for both H_α and H_β ($J_{\text{WH}_\alpha} = 9.8$ Hz and $J_{\text{WH}_\beta} = 12.4$ Hz). This brings up the questions we posed previously concerning the observed $^{183}\text{W}-^1\text{H}$ couplings to H_β and the near zero $^{183}\text{W}-^{13}\text{C}_\beta$ coupling in I. We suggest that the $^{183}\text{W}-^1\text{H}$ coupling to H_β in complex II and the larger coupling in I is a four-bond coupling from W_2 , $^4J_{\text{W}_2\text{H}_\beta}$. Protonation of C_α in I would presumably little perturb the $^{183}\text{W}_2-^1\text{H}_\beta$ coupling, as is observed. The smaller $^{183}\text{W}-^1\text{H}_\beta$ coupling in I is the three-bond coupling from W_1 , $^3J_{\text{W}_1\text{H}_\beta}$, which becomes too small to observe upon rehybridization of C_α . That tungsten couplings to C_β are not observed in I and II is attributed to a fortuitous cancellation of the coupling constant that remains upon rehybridization of C_α . However, rehybridization of C_α from sp^2 to sp^3 does allow for the observation of $^{183}\text{W}-^1\text{H}_\alpha$ coupling. ^{183}W coupling to the α -hydrogens of alkyl ligands are frequently observed,²⁶ but we have not found any reports of $^{183}\text{W}-^1\text{H}$ coupling in the alkylidenes.^{20,24} Bearing in mind that alternation of the sign of J along a chain is well-known, it could be that $^2J_{\text{W}_1\text{H}_\alpha}$ in I and $^2J_{\text{W}_1\text{C}_\beta}$ in both I and II are close to zero even though the longer range couplings to H_β are larger. In summary unequivocal answers are not available at this time, though the couplings within the macrocyclic rings are fascinating.

^1H NMR data for compound Ib are similar to that for I and

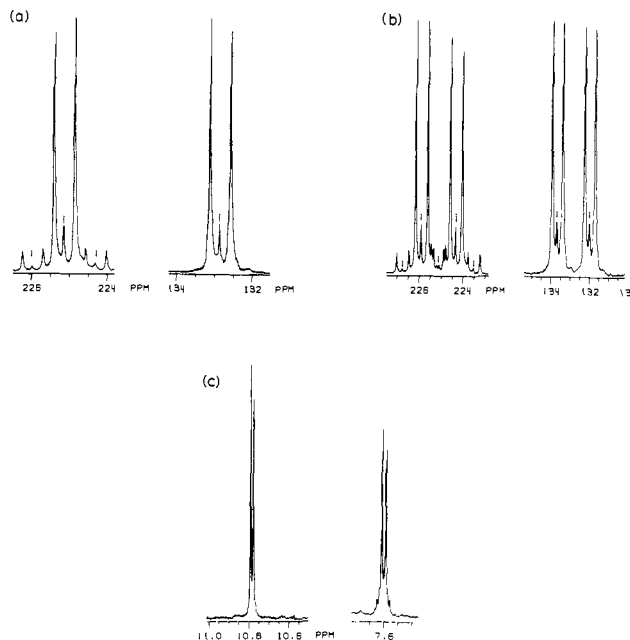


Figure 7. (a) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{W}_2(\text{O}-t\text{-Bu})_6(^{13}\text{CH}^{13}\text{CHC}(\text{Ph})\text{N})$, where ^{13}C represents 92.5 atom % ^{13}C , in toluene- d_8 recorded at 21 $^\circ\text{C}$ and 90 MHz, shown at scale expansion in the regions 223.8–226.5 and 131.5–134.2 ppm. At left is the resonance assigned to C_α and at right the resonance assigned to C_β . The signals denoted by i arise from the $^{13}\text{C}^{12}\text{C}$ isotopomer. (b) Gate ^1H decoupled ^{13}C NMR spectrum shown at scale expansion in the region 222.8–227.5 and 130.2–135.4 ppm for the sample as described in (a). (c) ^1H NMR spectrum of $\text{W}_2(\text{O}-t\text{-Bu})_6(\text{CHCHC}(\text{Ph})\text{N})$ in benzene- d_6 recorded at 21 $^\circ\text{C}$ and 360 MHz, shown at scale expansion in the regions 10.5–11.0 and 7.45–7.73 ppm. At left is the resonance assigned to C_α and at right the resonance assigned to C_β .

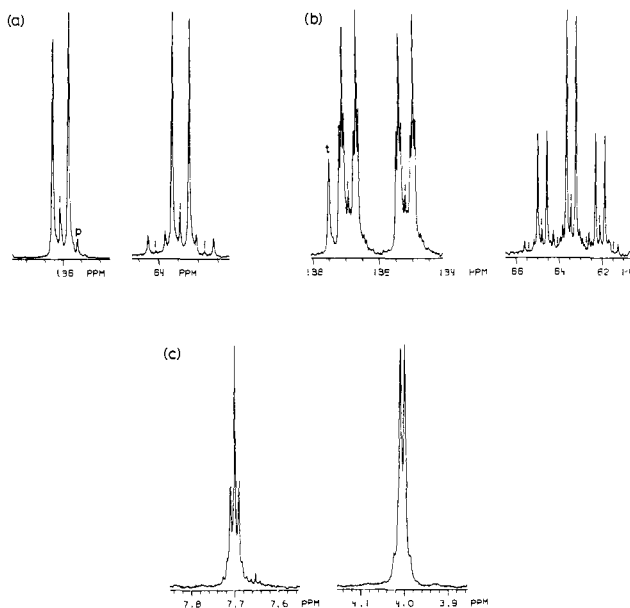


Figure 8. (a) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{W}_2(\text{O}-i\text{-Pr})_7(^{13}\text{CH}_2^{13}\text{CHC}(\text{Ph})\text{N})$, where ^{13}C represents 92.5 atom % ^{13}C , in toluene- d_8 recorded at 21 $^\circ\text{C}$ and 90 MHz, shown at scale expansion in the regions 134.7–137.4 and 62.2–64.7 ppm. At left is the resonance assigned to C_β and at right the resonance assigned to C_α . The signals denoted by i and p arise from the $^{13}\text{C}^{12}\text{C}$ isotopomer and a carbon atom of the phenyl ring attached to the macrocycle, respectively. (b) Gate ^1H decoupled ^{13}C NMR spectrum shown at scale expansion in the regions 134.1–138.0 and 60.5–66.5 ppm for the sample described in (a). The resonance arising from the ipso carbon of the toluene- d_8 solvent is denoted by t. (c) ^1H NMR spectrum of $\text{W}_2(\text{O}-i\text{-Pr})_7(\text{CH}_2\text{CHC}(\text{Ph})\text{N})$ in benzene- d_6 recorded at 21 $^\circ\text{C}$ and 360 MHz, shown at scale expansion in the regions 7.56–7.84 and 3.86–4.16 ppm. At left is the resonance assigned to C_β and at right the resonance assigned to C_α .

the reader is referred to the Experimental Section for details.

We mentioned earlier that we have been unsuccessful in obtaining a low-temperature limiting spectrum for the complexes I and II. However, the ^{13}C experiments described above do show unequivocally that the fluxional processes for I and II cannot entail transfer of C_α from one W center to the other since the intensities of the ^{183}W satellites for C_α are consistent with it seeing only one ^{183}W nucleus (Figures 7 and 8). The fluxionality must therefore involve bridge opening and closing of the alkoxide ligands of the type which leads to complete RO scrambling between the two tungsten atoms. In compound II the helicity of the macrocyclic ligand is also changed on the NMR time scale since the C_α hydrogen atoms are equivalent at room temperature but at low temperatures they collapse into the base line in anticipation of their expected diastereotopic nature in the frozen out structure.

Concluding Remarks

The reactions between μ -alkyne adducts of ditungsten hexaalkoxides and nitriles have led to the isolation of novel compounds containing macrocyclic ligands bonded to the two metal atoms, one of which is a part of the ring, while the other metal atom is exocyclic. The formation of five- vs. seven-membered rings, the coupling of the alkyne fragment with either one or two nitrile ligands, is sensitive to the size of the OR ligand. Similar results are anticipated for other combinations of ligands. This work shows that formation of carbon-carbon bonds and additional metal-ligand bonds is favored over the metathesis-like reactions 1 and 3 when steric factors permit. An obvious parallel is seen with the alkyne coupling reaction 2, and compound III provides a model for the step in the cyclotrimerization of alkynes at a dinuclear metal center which follows from $\text{M}_2(\text{OR})_6(\mu\text{-C}_4\text{H}_4)(\eta^2\text{-C}_2\text{H}_2)$ and precedes the final C-C coupling and reductive elimination of benzene.^{1,7}

Finally we note that within the last three papers of this series we have seen an extensive organometallic chemistry supported by RO ligands. Starting with the simple addition of alkynes to $\text{W}_2(\text{OR})_6$ compounds we have seen the formation of tungsten-alkylidyne, -alkylidene, and -alkyl bonds along with alkyne adducts (μ perpendicular and η^2), coupled fragments $\mu\text{-C}_4\text{R}_4$, and the heterocyclic ligands described here.

Experimental Section

Reagents and General Techniques. General procedures and the preparation of $\text{W}_2(\text{O-}t\text{-Bu})_6$, $\text{W}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{C}_2\text{H}_2)$, and $\text{W}_2(\text{OCH}_2\text{-}t\text{-Bu})_6(\text{py})_2(\text{C}_2\text{Me}_2)$ have been described.⁸ Ethyne was purchased from Matheson and was used without purification. Dry and oxygen-free hexane, toluene, 2-propanol, acetonitrile, and pyridine were used in the preparations. Benzonitrile was purchased from MCB Reagents and used without purification. 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- $^{13}\text{C}_2$ (92.5 atom % ^{13}C) was used in the preparations of $\text{W}_2(\text{O-}t\text{-Bu})_6((^{13}\text{CH})_2\text{C}(\text{Ph})\text{N})$ and $\text{W}_2(\text{O-}i\text{-Pr})_7(^{13}\text{CH}_2^{13}\text{CHC}(\text{Ph})\text{N})$. The ^{13}C -labeled ethyne was 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 toluene- d_8 isopropyl carbon set at δ 137.5. The ^{13}C - ^1H coupling constants reported were obtained by using gated ^1H decoupling techniques.

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

$\text{W}_2(\text{O-}t\text{-Bu})_6((\text{CH})_2\text{C}(\text{Ph})\text{N})$. In a Schlenk reaction vessel $\text{W}_2(\text{O-}t\text{-Bu})_6$ (0.50 g, 0.62 mmol) was dissolved in hexane/pyridine (10 mL/1 mL). The solution was frozen at -196°C , and ethyne (0.62 mmol) was condensed into the flask by using a calibrated vacuum manifold. The reaction mixture was warmed rapidly to 0°C and stirred at that temperature for 0.5 h. During this time the red solutions turned the characteristic green color of $\text{W}_2(\text{O-}t\text{-Bu})_6(\text{py})(\mu\text{-C}_2\text{H}_2)$. The volatiles were quickly removed, and the residue was redissolved in toluene (5 mL) at 0°C . Benzonitrile (63 μL , 0.62 mmol) was then added by microsyringe

and the solution allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 2 h (after 0.25 h the solution turned dark red) and then stripped to yield an oily red solid. The solid was redissolved in a minimal amount of hexane (2 mL). Cooling at -15°C for 4 days yielded dark red crystals (yield 0.16 g, 27%) which were collected by filtration and dried *in vacuo*.

A second crop of crystals could not be obtained. However, removing the volatiles from the filtrate, adding *i*-PrOH (2 mL), stirring for 5 h, and then cooling at -15°C for 3 days allowed isolation of black crystalline $\text{W}_2(\text{O-}i\text{-Pr})_7(\text{CH}_2\text{CHC}(\text{Ph})\text{N})$ (yield 0.15 g, 27%). ^1H NMR (21 $^\circ\text{C}$, benzene- d_6) δ ($\text{CHCHC}(\text{Ph})\text{N}$) 10.78 and δ ($\text{CHCHC}(\text{Ph})\text{N}$) 7.60 (d, $J_{\text{HH}} = 5.2$ Hz) (the resonance at δ 7.6 shows coupling to two different ^{183}W nuclei: $J_{\text{WH}} = 10.7$ and 5.2 Hz); δ ($(\text{CH})_2\text{C}(\text{Ph})\text{N}$) 7.77, 7.30, 6.92 (pseudo-first-order doublet, triplet, and triplet of relative intensities 2:2:1, respectively); δ (OCMe_3) 1.50 (sharp s). IR (cm^{-1}): 1725 vw, 1591 m, 1571 vw, 1500 m, 1259 m, 1234 s, 1172 s, 1105 vw, 1073 vw, 1026 m, 950 s, 884 s, 797 m, 782 m, 776 m, 719 s, 690 m, 677 m, 642 m, 610 m, 567 m, 549 m, 510 w, 480 m, 431 m, 395 w, 366 m, 272 m. Anal. Calcd for $\text{W}_2\text{O}_6\text{NC}_{33}\text{H}_{61}$: C, 42.37; H, 6.57; N, 1.50. Found: C, 42.46; H, 6.21; N, 1.54.

$\text{W}_2(\text{O-}t\text{-Bu})_6((^{13}\text{CH})_2\text{C}(\text{Ph})\text{N})$. ^{13}C NMR (21 $^\circ\text{C}$, toluene- d_8): δ ($^{13}\text{CH}^{13}\text{CHC}(\text{Ph})\text{N}$) 225.11 ($J_{\text{WC}} = 151.9$ Hz, $J_{\text{CC}} = 49.7$ Hz, $J_{\text{CH}} = 142.9$ Hz); δ ($^{13}\text{CH}^{13}\text{CHC}(\text{Ph})\text{N}$) 132.84 ($J_{\text{CH}} = 154.0$ Hz, $J_{\text{CC}} = 49.7$ Hz, $J_{\text{CH}} = 2.3$ Hz); δ (OCMe_3) = 82.56; δ (OCMe_3) 31.98.

$\text{W}_2(\text{O-}t\text{-Bu})_6((\text{CH})_2\text{C}(\text{Me})\text{N})$. Purple-red crystalline samples of this complex are prepared in a procedure analogous to that described above for the phenyl derivative (yield 32%). If one starts with isolated crystalline $\text{W}_2(\text{O-}t\text{-Bu})_6(\text{py})(\mu\text{-C}_2\text{H}_2)$ and 1 equiv of acetonitrile, ^1H NMR spectroscopy reveals almost quantitative formation of the insertion product. ^1H NMR (21 $^\circ\text{C}$, toluene- d_6): δ ($\text{CHCHC}(\text{Me})\text{N}$) 10.85; δ ($\text{CHCHC}(\text{Me})\text{N}$) 6.66 (d, $J_{\text{HH}} = 5.1$ Hz (the resonance at δ 6.66 is broadened due to coupling with the Me protons, and decoupling of the methyl protons signal reveals a sharp doublet with coupling to two different ^{183}W nuclei, $J_{\text{WH}} = 10.5$ and 4.5 Hz); δ ($(\text{CH})_2\text{C}(\text{Me})\text{N}$) 3.18 (slightly broadened singlet); δ (OCMe_3) 1.53 (sharp s). IR (cm^{-1}): 1635 vw, 1299 w, 1258 w, 1234 m, 1172 s, 1064 w, 1022 m, 1009 m, 996 s, 986 s, 952 s, 912 s, 894 s, 875 s, 781 w, 786 m, 778 m, 708 m, 680 w, 668 w, 594 w, 576 w, 566 w, 542 m, 512 w, 480 w, 369 w, 304 w, 270 w. Anal. Calcd for $\text{W}_2\text{O}_6\text{NC}_{28}\text{H}_{59}$: C, 38.50; H, 6.81; N, 1.60. Found: C, 38.22; H, 6.62; N, 1.73.

$\text{W}_2(\text{O-}i\text{-Pr})_7(\text{CH}_2\text{CHC}(\text{Ph})\text{N})$. $\text{W}_2(\text{O-}t\text{-Bu})_6((\text{CH})_2\text{C}(\text{Ph})\text{N})$ was prepared as described above and isolated as the crude product by removing the reaction solvent toluene. *i*-PrOH (4 mL) was then added and the mixture warmed slightly ($30\text{--}40^\circ\text{C}$) for 1–2 min to dissolve the solid. The waxy red solid slowly dissolved in *i*-PrOH, and a black crystalline solid began to precipitate from solution. The mixture was stirred for 2 h and then filtered to yield black crystals (0.10 g). The filtrate was reduced in volume, warmed slightly to dissolve some precipitate, and then left to stand at room temperature for 3 h. Cooling at 5°C overnight yielded more black crystals which were isolated by filtration (0.14 g, total yield 42%). (The first crop of crystals isolated was slightly impure product by ^1H NMR.) ^1H NMR (21 $^\circ\text{C}$, benzene- d_6): δ ($\text{CH}_2\text{CHC}(\text{Ph})\text{N}$) 4.00 (d, $J_{\text{HH}} = 3.6$ Hz, $J_{\text{WH}} = 9.8$ Hz); δ ($\text{CH}_2\text{CHC}(\text{Ph})\text{N}$) 7.70 (t, $J_{\text{HH}} = 3.6$ Hz, $J_{\text{WH}} = 12.4$ Hz); δ ($\text{CH}_2\text{CHC}(\text{Ph})\text{N}$) 8.07, 7.29, 7.15 (pseudo-first-order doublet, triplet, and triplet, respectively, with relative intensities 2:2:1), δ (OCHMe_2) 5.1 (broad resonance); δ (OCHMe_2) 1.3 (broad resonance). IR (cm^{-1}): 1599 w, 1491 w, 1331 m, 1322 m, 1318 m, 1277 w, 1162 m, 1110 s, 1030 w, 989 s, 974 s, 959 s, 949 s, 912 w, 843 s, 760 m, 718 m, 691 m, 650 w, 608 m, 596 m, 579 m, 561 w, 505 w, 469 m, 456 m, 438 w, 380 w, 362 vw, 321 w, 288 w. Anal. Calcd for $\text{W}_2\text{O}_7\text{NC}_{30}\text{H}_{57}$: C, 39.53; H, 6.30; N, 1.54. Found: C, 39.50; H, 6.17; N, 1.50.

$\text{W}_2(\text{O-}i\text{-Pr})_7(^{13}\text{CH}_2^{13}\text{CHC}(\text{Ph})\text{N})$. ^{13}C NMR (21 $^\circ\text{C}$, toluene- d_8): δ ($^{13}\text{CH}_2^{13}\text{CHC}(\text{Ph})\text{N}$) 63.42 ($J_{\text{WC}} = 111.5$ Hz, $J_{\text{CC}} = 39.9$ Hz, $J_{\text{CH}} = 122.6$ Hz, $J_{\text{CH}} < 2$ Hz); δ ($^{13}\text{CH}_2^{13}\text{CHC}(\text{Ph})\text{N}$) 136.05 ($J_{\text{CH}} = 155.9$ Hz, $J_{\text{CC}} = 39.3$ Hz, $J_{\text{CH}} = 6.3$ Hz); δ (OCHMe_2) 62.06, 61.62; δ (OCHMe_2) 25.08.

$\text{W}_2(\text{OCH}_2\text{-}t\text{-Bu})_6(\text{N}(\text{CMe})_4\text{N})$. To a blue solution of $\text{W}_2(\text{OCH}_2\text{-}t\text{-Bu})_6(\text{py})(\mu\text{-C}_2\text{Me}_2)$ (0.39 g, 0.35 mmol) in toluene (7 mL) was added acetonitrile (36.8 μL , 0.70 mmol). The reaction mixture was stirred 18 h during which time the color changed to red-brown. The solution was reduced in volume and then kept at -15°C for 2 d. This produced dark red crystals which were collected by filtration and dried *in vacuo* (0.16 g). Reducing the volume of the filtrate and cooling yielded a second crop of crystals (0.025 g, total yield 47%). ^1H NMR (-20°C , toluene- d_8): δ ($\text{N}(\text{CMe})_4\text{N}$) 2.26, 1.96, 1.85, 1.27 (s); δ (OCH_2CMe_3) 1.39, 1.24, 1.13, 1.10, 1.07, 1.04, (s); δ (OCH_2CMe_3) 3.75 (d), 4.22–5.02 (overlapping doublets of AB quartets); δ (py) 8.26 (d, 6.55, (t), 6.28 (t)). IR (cm^{-1}): 1608 w, 1574 w, 1393 s, 1368 s, 1360 s, 1339 s, 1285 w, 1263 w, 1238 vw, 1219 m, 1153 w, 1092 s, 1070 s, 1043 s, 1025 s, 1007 s, 933 w, 905

w, 805 w, 760 s, 694 s, 668 s, 655 s, 650 s, 641 s, 622 w, 601 w, 574 w, 517 w, 496 w, 455 m, 410 m, 387 w, 340 w, 325 w, 307 w. Anal. Calcd for $W_2O_6N_3C_43H_{83}$: C, 46.70; H, 7.57; N, 3.80. Found: C, 46.48; H, 7.43; N, 3.72.

$W_2(O-i-Pr)_7(NHC(Me)(CH)_2C(Me)N)$. To a solution of $W_2(O-i-Pr)_6(py)_2(\mu-C_2H_2)$ (0.43 g, 0.47 mmol) dissolved in toluene (5 mL) was added acetonitrile (0.75 mL, 14 mmol). The solution was stirred for 18 h. The volatiles were then removed, and the residue was redissolved in warm (40–50 °C) *i*-PrOH (3 mL). Cooling the solution at –15 °C for 24 h produced dark red crystals (0.31 g, yield 73%) which were collected by filtration and dried in vacuo. A second crop was collected by reducing the volume of the filtrate and cooling. A satisfactory analysis was not obtained for crystalline samples of this compound. 1H NMR (–60 °C, toluene- d_8): $\delta(OCHMe_2)$ 1.87, 1.68, 1.61, 1.56, 1.52, 1.46, 1.39, 1.30, 1.27, 1.15 (d, $J_{HH} = 6$ Hz), 0.94–0.90 (overlapping doublets); $\delta(OCHMe_2)$ 4.00, 4.75, 5.08, 5.14, 5.29 (septets, $J_{HH} = 6$ Hz) (two more septets are obscured by an AB quartet from the metallacycle ring $(CH)_2$ protons. The septets are observed by substituting deuterium in the ring positions: δ 5.55 and 5.49; $\delta(NHC(Me)(CH)_2C(Me)N)$ 9.31 (s); $\delta(NHC(Me)(CH)_2C(Me)N)$ 2.50 and 2.11 (s); $\delta(NHC(Me)(CH)_2C(Me)N)$ 5.51, 5.58 (doublets of an AB quartet, $J_{HH} = 8.7$ Hz). IR (cm^{-1}): 3318 w, 1601 w, 1562 w, 1329 m, 1311 m, 1255 w, 1219 w, 1195 w, 1157 m, 1112 s, 993 m, 977 s, 959 s, 839 m, 784 w, 738 w, 715 w, 667 w, 642 w, 599 m, 585 m, 550 w, 469 w, 450 w, 427 w, 412 w, 378 w, 296 w.

Crystallographic Studies. General operating procedures and listings of programs used at the Indiana University Molecular Structure Center have been described.²⁷ Crystal data are summarized in Table IX.

$W_2(O-t-Bu)_6(CHCHC(Ph)N)$. The sample that was examined consisted of numerous clumps of small crystals as well as several larger poorly formed crystals. One of the larger crystals was cleaved under nitrogen to form a near equidimensional fragment. The fragment was then affixed to a glass fiber with silicone grease and transferred to the goniostat where it was cooled to –158 °C for characterization and data collection. All handling was performed in an inert atmosphere.

A systematic search of a limited hemisphere of reciprocal space failed to reveal any systematic absences or symmetry-related intensities, and the space group was assigned to $P\bar{1}$. Although statistical tests indicated a noncentric space group, successful solution and refinement confirmed the centrosymmetric choice.

Direct methods failed to locate the tungsten atoms properly and insisted on placing one peak at the origin. In all solutions, however, there were pairs of atoms corresponding to a vector 2.67 Å, and all were aligned similarly. Two such peaks were used to phase the data assuming the noncentric space group $P1$, and the resultant Fourier revealed two additional pairs of peaks, centrosymmetrically located around the two input peaks. Using one of these pairs the origin for $P\bar{1}$ was calculated and a Fourier phased on the resulting metal positions clearly located all remaining non-hydrogen atoms. Hydrogen atoms were located in a difference Fourier phased on the refined coordinates of the non-hydrogen atoms and were included in the final refinement. Thermal parameters (isotropic for H; anisotropic for W, C, N, and O) as well as positional parameters and an overall scale factor were varied in the final full-matrix least squares.

A final difference Fourier consisted of two peaks (1.1 and 1.4 $e/\text{Å}^3$) at the two metal sites, and all other peaks were less than 0.7 $e/\text{Å}^3$. ψ scans of several reflections indicated no need for an absorption correction.

$W_2(O-i-Pr)_7(CH_2CHC(Ph)N)$. A small fragment of the dark red crystalline material was cleaved under nitrogen to form a nearly equidimensional cube and transferred to the goniostat by using standard inert-atmosphere handling techniques.

A systematic search of a limited hemisphere of reciprocal space revealed no systematic absences or symmetry, indicating a triclinic space group. Statistical tests and the successful solution and refinement of the structure confirmed the space group to be $P\bar{1}$.

Some difficulty was encountered in locating the tungsten atom positions, as was the case for the $W_2(O-t-Bu)_6(CHCHC(Ph)N)$ structure.

(27) Chisholm, M. J.; Foltling, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

In this case there was an ambiguity in determining the origin, even on going to the $P1$ symmetry to generate the center of inversion. The origin was finally fixed by using a Patterson function. All remaining atoms were located by Fourier techniques. Hydrogen atoms were clearly visible in a difference synthesis phased on the refined non-hydrogen atoms. Attempts to refine all hydrogens led to problems for those associated with the $-OCHMe_2$ groups terminated by O(13) and O(17), with several hydrogens converging to unrealistic positions. Examination of the thermal ellipsoids at this point revealed that these groups are highly anisotropic, explaining the difficulty. For this reason the final cycles used hydrogen atoms as fixed atom contributors for all $-OR$ groups and only those associated with the $CH_2CHC(C_6H_5)N$ were allowed to vary (H(1) thru H(8)).

A final difference Fourier was featureless, the largest peak being 0.95 $e/\text{Å}^3$ located near W(1). ψ scans of several reflections were flat, and no absorption correction was deemed necessary.

$W_2(OCH_2-t-Bu)_6(py)(N(CMe)_4N)$. A suitable crystal was obtained by fracturing a larger sample until a nearly equidimensional fragment with no discernible faces was obtained. A systematic search of a limited hemisphere of reciprocal space revealed a monoclinic lattice.

The structure was solved by direct methods and Fourier techniques and refined by full-matrix least squares. Difference maps successfully located approximately half of the hydrogen atoms, with at least one for each of the methyls. Final refinement included fixed hydrogen contributors assuming idealized geometry.

A final difference Fourier contained a peak of 1.2 $e/\text{Å}^3$ near W(1), and all other peaks were less than 0.9 $e/\text{Å}^3$ and uniformly dispersed. ψ scans indicated no absorption correction was necessary.

$W_2(O-i-Pr)_7(NHC(Me)CHCHC(Me)N)$. A suitable fragment of less than 0.1 mm maximum dimension was cleaved from a larger crystal and transferred to the goniostat by using standard inert-atmosphere handling techniques. A systematic search of a limited hemisphere of reciprocal space revealed a monoclinic space group.

The structure was solved by direct methods and Fourier techniques and was refined by full-matrix least squares. Hydrogen atoms were located in a difference Fourier and were included in the final cycles of refinement. While most of the hydrogens were "well-behaved", it should be noted that a few of the methyl hydrogens are rather distorted from their idealized locations.

A ψ scan of several intense reflections indicate no absorption correction was necessary, the largest deviation being less than 7%. A final difference Fourier synthesis revealed the largest peak was 0.75 $e/\text{Å}^3$.

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Registry No. I, 92011-36-4; II, 92011-38-6; III, 88658-53-1; IV, 92011-40-0; $W_2(O-t-Bu)_6((^{13}CH)_2C(Ph)N)$, 92011-37-5; $W_2(O-t-Pr)_7(^{13}CH_2^{13}CHC(Ph)N)$, 92011-39-7; $W_2(O-t-Bu)_6((CH)_2C(Me)N)$, 92011-41-1; $W_2(OCH_2-t-Bu)_6(N(CMe)_4N)$, 92011-43-3; $W_2(O-t-Bu)_6(py)(\mu-C_2H_2)$, 91899-21-7; $W_2(O-i-Pr)_6(py)_2(\mu-C_2H_2)$, 82281-73-0; $W_2(O-t-Bu)_6$, 57125-20-9; $W_2(OCH_2-t-Bu)_6(py)(\mu-C_2Me_2)$, 92011-42-2; $PhC\equiv N$, 100-47-0; $MeC\equiv N$, 75-05-8.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, complete listings of bond lengths and bond angles (95 pages). Ordering information is given on any current masthead page. The complete structure reports, MSC Report No. 83009, $W_2(OCH_2-t-Bu)_6(py)(N(CMe)_4N)$, MSC Report No. 83026, $W_2(O-i-Pr)_7(NHC(Me)CHCHC(Me)N)$, MSC Report No. 83107, $W_2(O-t-Bu)_6(CHCHC(C_6H_5)N)$, and MSC Report No. 83113, $W_2(O-i-Pr)_7(CH_2CHC(C_6H_5)N)$, are available from the Indiana University Chemistry Library in Microfiche form only at a cost of \$2.50 per copy.