Alkyne Adducts of Ditungsten Hexaneopentoxide and Alkylidyne-Capped Tritungsten Compounds Supported by Neopentoxide Ligands

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Alkynes (1 equiv) are shown to react with $W_2(ONp)_6(py)_2$, where Np = neopentyl and py = pyridine, in hydrocarbon solvents at or below room temperature to give 1:1 alkyne adducts of formula $W_2(ONp)_6(py)_n(\mu\text{-}C_2R_2)$, where R = H and Me for $n = 2$ and R = Et and Ph for $n = 1$. The molecular structure of the ethyne adduct is related to that reported previously [*J. Am. Chem. Soc.* **1984**, *106*, 6794] for $W_2(ONp)_6(py)_2(\mu\text{-}C_2Me_2)$ having one bridging OR ligand uniting formally octahedrally and trigonal bipyramidally coordinated tungsten atoms (W–W = 2.6095 (16) Å), where the $\mu\text{-}C_2H_2$ ligand (C–C = 1.39 (3) Å) is considered to occupy a single coordination site at each metal center. The molecular structure of the diethylacetylene adduct is shown to have structural features similar to that seen for $W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)$ in which two trigonal bipyramidally coordinated tungsten atoms are united by a common axial (μ-OR) and equatorial ($\mu\text{-}C_2Et_2$) ligand: W–W = 2.5719 (12) Å and for $\mu\text{-}C_2Et_2$ C–C = 1.40 (2) Å. The NMR data for the diphenylacetylene adduct indicate that it adopts a structure in solution akin to that found for the diethylacetylene adduct. Reactions employing $Me_3SiC{\equiv}CSiMe_3$ failed to yield isolable 1:1 adducts and addition of PMe_3 gave the phosphine adduct $W_2(ONp)_6(PMe_3)_2$. Chemical evidence is presented for an equilibrium involving the 1:1 alkyne adducts and alkylidyne species: $W_2(ONp)_6(py)_n(\mu\text{-}C_2R_2) \rightleftharpoons 2(NpO)_3W{\equiv}CR + n\text{py}$, where R = Ph, Et, and Me, but not H. The alkyne adducts act as alkylidyne sources in the formation of $W_3(\mu_3\text{-}CR)(ONp)_9$ compounds: $3W_2(ONp)_6(py)_2 + RCCR \xrightarrow{(1)} 2W_3(\mu_3\text{-}CR)(ONp)_9$ and $2W_2(ONp)_6(py)_2 + W_2(ONp)_6(py)_n(\mu\text{-}C_2R_2) \xrightarrow{(2)} 2W_3(\mu_3\text{-}CR)(ONp)_9$. These results are discussed in terms of earlier findings. Crystal data for $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ at −156 °C: $a = 13.711$ (6) Å, $b = 13.843$ (6) Å, $c = 25.414$ (12) Å, $Z = 4$, $d_{calcd} = 1.48$ g cm^{-1}, and space group $Pc2_1n$. Crystal data for $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$ at −158 °C: $a = 11.977$ (4) Å, $b = 17.981$ (9) Å, $c = 11.389$ (4) Å, $\beta = 107.49$ (2)°, $Z = 2$, $d_{calcd} = 1.493$ g cm^{-3}, and space group $P2_1$.

Introduction

Schrock and co-workers[1] first noted the remarkable metathesis reaction shown in eq 1, wherein a W≡W bond and a C≡C bond are cleaved to form two W≡C bonds.

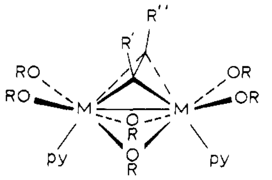
$$W_2(O\text{-}t\text{-}Bu)_6 + RC{\equiv}CR \rightarrow 2(t\text{-}BuO)_3W{\equiv}CR \quad (1)$$

$$R = \text{Me, Et, and Pr}$$

Subsequently[2] Schrock and co-workers extended reactions of type 1 to include a wide variety of substituted acetylenes. The conditions for the reaction shown in (1) are extremely mild (alkane solvents at or below 25 °C) which contrasts with alkylidyne formation from coordinated alkynes at polynuclear metal centers in cluster carbonyl compounds.[3]

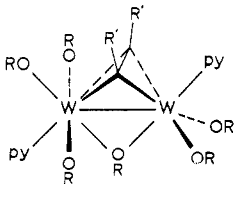
Under somewhat different experimental conditions (toluene, 50–70 °C) Cotton and co-workers[4,5] studied the reactions between $W_2(O\text{-}t\text{-}Bu)_6$ and each of PhC≡CPh and EtC≡CEt with ratios of $W_2{:}C_2R_2$ ranging from 3:1 to 1:1 and obtained a variety of products including those of C—C scission: $W_2(O\text{-}t\text{-}Bu)_4(\mu\text{-}CPh)_2$, $(t\text{-}BuO)_3W{\equiv}CPh$, and $[W_3(O\text{-}t\text{-}Bu)_5(\mu\text{-}O)(\mu\text{-}CEt)O]_2$. Evidently under the more severe reaction conditions *t*-BuO group transfer or decomposition is also encountered.

Previously we have found[6,7] that 1:1 alkyne adducts of $W_2(OR)_6$ compounds can be isolated with pyridine of ligation in one of three structural types shown.



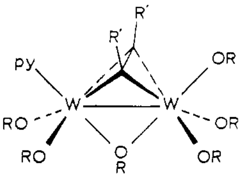
M=Mo or W	R=i-Pr	R'=R''=H
M=Mo	R=i-Pr	R'=H R''=Me
		R'=R''=Me
M=Mo	R=Np	R'=R''=H

I



R=Np R'=Me

II



R=t-Bu R'=H

III

Alkyne adducts of types I, II, and III are capable of undergoing C–C coupling in their reactions with alkynes[8]

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

(2) Schrock, R. R.; Listemann, M. L. *Organometallics* **1985**, *4*, 74.

(3) (a) Shapley, J. R.; Chi, Y. *Organometallics* **1985**, *4*, 1900. (b) Clauss, A. D.; Shapley, J. R.; Wilker, C. N.; Hoffmann, R. *Organometallics* **1984**, *3*, 619.

(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.

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

(7) Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

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or nitriles.[9] In the case of $W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)$ (III) we found evidence[7] for an equilibrium involving the methylidyne compound (eq 2) while in the reactions between $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ and MeC≡CMe we found a competition[10,11] between C–C coupling (eq 3) and C–C scission reactions leading to alkylidyne-capped W_3 compounds (eq 4).

$$W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2) \rightleftharpoons 2(t\text{-}BuO)_3W{\equiv}CH + py \quad (2)$$

$$W_2(O\text{-}i\text{-}Pr)_6(py)_2 + 3MeC{\equiv}CMe \rightarrow W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4Me_4)(\eta^2\text{-}C_2Me_2) + 2py \quad (3)$$

$$3W_2(O\text{-}i\text{-}Pr)_6(py)_2 + MeC{\equiv}CMe \rightarrow 2W_3(\mu_3\text{-}CMe)(O\text{-}i\text{-}Pr)_9 + 6py \quad (4)$$

An alternate synthesis for the ethylidyne-capped-W_3 compounds was established[11] (eq 5), which lends support to the initial C–C scission in reaction 4.

$$(t\text{-}BuO)_3W{\equiv}CMe + W_2(O\text{-}i\text{-}Pr)_6(py)_2 \xrightarrow[\text{hexane}/i\text{-PrOH}]{25\ ^\circ\text{C}} W_3(\mu_3\text{-}CMe)(O\text{-}i\text{-}Pr)_9 + 2py \quad (5)$$

More recently Schrock and co-workers have extended their study of alkoxides of tungsten and, in particular, have reported[12] that $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ (prepared in situ) and EtC≡CEt (1 equiv) gives an essentially quantitative reaction leading to propylidyne formation (eq 6).

$$W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2 + 2py + EtC{\equiv}CEt \xrightarrow[\text{pentane}]{-20\ ^\circ\text{C}} [(i\text{-}PrO)_3W{\equiv}CEt]_2 \quad (6)$$

Clearly the reaction leading to C–C scission is influenced by the nature of the alkyl substituents on the acetylene and the alkoxide ligand. As part of our continuing interest in the chemical reactivity of the M≡M bond in W_2^{6+} and Mo_2^{6+} compounds, we have determined to unravel the intricate steps associated with the C≡C and M≡M metathesis reaction. We describe here reactions between symmetrically substituted alkynes, RC≡CR, where R = H, Me, Et, Ph, and Me_3Si, and $W_2(ONp)_6(py)_2$ and show that 1:1 alkyne adducts can be isolated for all but when R = Me_3Si. We also present evidence that these 1:1 alkyne adducts, except for R = H, are in fact in equilibrium with reactive alkylidyne species.

Results and Discussion

Syntheses. Alkyne Adducts. The 1:1 alkyne adducts were prepared by a common procedure summarized in (7).

$$W_2(ONp)_6(py)_2 + RC{\equiv}CR \xrightarrow[\text{hexane}]{0\text{–}20\ ^\circ\text{C}} W_2(ONp)_6(py)_x(\mu\text{-}C_2R_2) + (2 - x)py \quad (7)$$

R = H, Me, Et, and Ph

Reaction 7 allows formation of the alkyne adducts, where R = H, Me, Et, and Ph, in near quantitative yield by ^1H NMR spectroscopy though isolated crystalline yields are only in the range 20–50% based on tungsten. The lower isolated crystalline yields reflect (i) the high solubility of the alkyne adducts and (ii) mechanical loss in handling small samples by Schlenk and drybox techniques. Attempts to prepare an alkyne adduct where R = $SiMe_3$ failed to give a crystalline sample. It is possible that a 1:1 alkyne adduct is formed reversibly in reaction 7 for R = $SiMe_3$ since, by ^1H NMR spectroscopy, some reaction does appear to occur. However, addition of PMe_3, which was added in the hope of stabilizing such a 1:1 alkyne adduct, led to the isolation of the known compound $W_2(ONp)_6(PMe_3)_2$.

Alkylidyne-Capped Compounds. $W_3(\mu_3\text{-}CR)(ONp)_9(py)_x$. Three methods of preparation were found and these are summarized in eq 8–10.[13]

$$W_2(ONp)_6(py)_2 + (t\text{-}BuO)_3W{\equiv}CR \xrightarrow[\text{hexane/NpOH}]{25\ ^\circ\text{C}} W_3(\mu_3\text{-}CR)(ONp)_9(py)_x + 3t\text{-}BuOH \quad (8)$$

$$3W_2(ONp)_6(py)_2 + RC{\equiv}CR \xrightarrow[\text{hexane}]{25\ ^\circ\text{C}} 2W_3(\mu_3\text{-}CR)(ONp)_9(py)_x + (6 - x)py \quad (9)$$

$$W_2(ONp)_6(py)_n(\mu\text{-}C_2R_2) + 2W_2(ONp)_6(py)_2 \xrightarrow[\text{hexane}]{25\ ^\circ\text{C}} 2W_3(\mu_3\text{-}CR)(ONp)_9(py)_x + (4 + n - x)py \quad (10)$$

None of these reactions is applicable for the case when R = H for reasons outlined later. Reaction 8 has a direct parallel with reaction 5. Care must be taken to allow for $W_3(\mu_3\text{-}CR)$ formation prior to alcoholysis. If $(t\text{-}BuO)_3W{\equiv}CR$ and neopentanol are allowed to react in hexane at room temperature, $W(ONp)_6$ and RCH_3 are formed. In reaction 8, if neopentanol is omitted, some $W_3(\mu_3\text{-}CR)(ONp)_9(py)_x$ is still formed. Presumably this occurs by alkoxide group scrambling reactions which could involve intermolecular exchange between W–O-*t*-Bu and W–ONp groups or could be catalyzed by the presence of free alcohol. The latter will always be present in trace amounts due to adventitious hydrolysis reactions. The methylidyne compound $(t\text{-}BuO)_3W{\equiv}CH$ is not an isolable compound, and the synthesis of $W_3(\mu_3\text{-}CH)(ONp)_9(py)_x$ by the preparative route of reaction 8 has not been achieved.

Reactions 9 and 10 are based on the premise that the alkyne adducts $W_2(ONp)_6(py)_n(\mu\text{-}C_2R_2)$, where R = Me and *n* = 2 and *R* = Et and Ph and *n* = 1, are present in equilibrium with a reactive alkylidyne species, $(NpO)_3W{\equiv}CR$, and that this reacts with $W_2(ONp)_6(py)_2$. Reactions 9 and 10 do not work for R = H, and for R = Me formation of the ethylidyne capped compound is slow and inefficient. When reaction 9 is monitored with time by ^1H NMR spectroscopy, the formation of the alkyne adduct is seen rapidly for R = Me while for R = Et and Ph, alkyne adduct formation and alkylidyne formation are competitive.

Mechanistic Considerations. The above results are consistent with a reaction scheme summarized in (11).

$$W{\equiv}W + RC{\equiv}CR \rightarrow W_2(\mu\text{-}C_2R_2) \quad (11i)$$

$$W_2(\mu\text{-}C_2R_2) \rightleftharpoons 2W{\equiv}CR \quad (11ii)$$

$$W{\equiv}W + W{\equiv}CR \rightarrow W_3(\mu_3\text{-}CR) \quad (11iii)$$

In general, reaction 11i proceeds rapidly to the right to give the alkyne adducts. However, bulky substituents on the alkyne such as Me_3Si may surpress this. Similarly for the bulky combinations of R = Ph and *t*-BuO, no reaction occurs at room temperature.[1]

The equilibrium involving the alkyne adducts and the alkylidyne species is dependent on the nature of the alk-

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[9] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6815.

[10] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 3683.

[11] Chisholm, M. H.; Folting, K.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1234.

[12] Schrock, R. R.; Pedersen, S. F.; Freudenberger, J. H. *Bull. Soc. Chim. Fr.* **1985**, 349.

[13] Chisholm, M. H.; Conroy, B. K.; Huffman, J. C.; Marchant, N. S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 446.

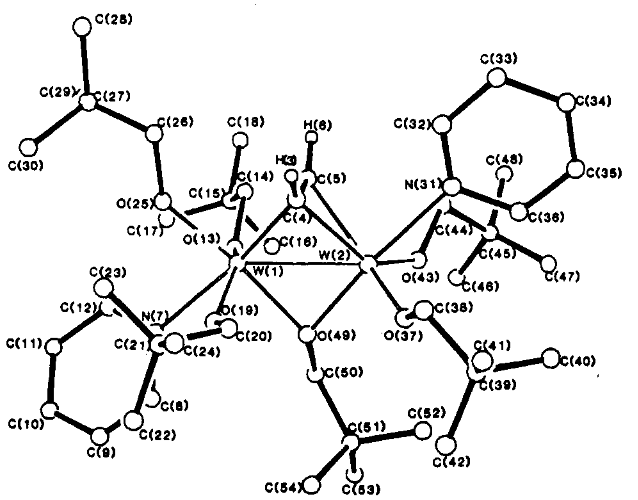

Figure 1. A ball-and-stick drawing of the $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ molecule giving the atom number scheme used in the tables.

oxide and the substituents on the alkyne with bulky combinations favoring the alkylidyne. For *t*-BuO ligands, only the ethyne adduct can be isolated, and in solution there is evidence[7] for a significant concentration of the methylidyne species. For the neopentoxide ligand, isolable alkyne adducts can be obtained for R = H, Me,[7] Et, and Ph. The relative rate of μ_3-alkylidyne formation, which occurs by (11iii), is a qualitative measure of the equilibrium concentration of reactive alkylidyne species which follows the order R = Ph > Et > Me ≫ H. We have, in fact, found no evidence for the formation of a reactive methylidyne neopentoxide of tungsten. Even an NMR tube containing a 1:1 mixture of $W_2(ONp)_6(py)_2(\mu\text{-}C_2D_2)$ and $W_2(ONp)_6(py)_2(\mu\text{-}{*}C_2H_2)$ showed no evidence for the formation of the μ-H*CCD-containing compound after 2 weeks in toluene-d_8 at room temperature.

Physicochemical Properties. The new compounds are dark, hydrocarbon-soluble, air-sensitive crystalline solids. The alkylidyne capped compounds have a tendency to coordinate pyridine both in solution and in the solid state. The crystals of the latter compounds where R = Me and Ph were "tacky" and failed to give satisfactory elemental analysis. The $W_3(\mu_3\text{-}CEt)$-containing compound showed one molecule of pyridine per tritungsten unit. In solution there was ^1H NMR evidence for a dynamic exchange involving reversible coordination to the W_3 center (discussed later). Infrared and NMR data are presented in the Experimental Section. The alkyne adducts are green or blue in solution, and this color arises in absorption maxima at ca. 640 nm. These absorptions do not obey the Beer–Lambert law, and we observe a bleaching effect on going to extremely high dilution. This could be due to trace hydrolysis and/or oxidation by adventitious molecular oxygen. We cannot, therefore, use this as evidence for the existence of an equilibrium of the type 11ii which would be driven to the right upon dilution. The electronic absorption data for the alkyne adducts and the alkylidyne complexes will be presented elsewhere together with results of Fenske–Hall molecular orbital calculations and electrochemical studies.

Solid-State and Molecular Structures. Atomic positional parameters for $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ and $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$ are given in Tables I and II, respectively. Selected bond distances and bond angles are given in Table III–VI. A comparison of selected bond distances and bond angles with previously characterized alkyne adduct of $M_2(OR)_6$ compounds (M = Mo and W) is given in Table VII, and the crystal data for the new compounds are summarized in Table VIII.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	2018 (1)	7139[a]	8909.8 (3)	13
W(2)	1492 (1)	6755 (1)	7945.3 (3)	13
C(4)	2791 (17)	6338 (18)	8319 (9)	18 (4)
C(5)	2829 (4)	7305 (16)	8177 (7)	11 (4)
N(7)	1340 (14)	7485 (15)	9722 (8)	23 (4)
C(8)	539 (15)	7000 (15)	9899 (8)	16 (4)
C(9)	199 (19)	7125 (25)	10393 (10)	38 (6)
C(10)	657 (20)	7692 (21)	10747 (11)	33 (5)
C(11)	1439 (21)	8183 (21)	10576 (11)	33 (6)
C(12)	1781 (18)	8098 (19)	10043 (10)	23 (5)
O(13)	1936 (13)	8566 (13)	8911 (7)	26 (3)
C(14)	2563 (20)	9251 (19)	8689 (10)	27 (5)
C(15)	2305 (16)	10303 (16)	8839 (9)	16 (4)
C(16)	1330 (23)	10535 (24)	8607 (12)	41 (6)
C(17)	2320 (21)	10418 (20)	9425 (11)	31 (6)
C(18)	3071 (24)	10929 (24)	8585 (13)	44 (7)
O(19)	1608 (10)	5892 (10)	9204 (5)	12 (3)
C(20)	1713 (17)	4899 (18)	9099 (9)	19 (5)
C(21)	1946 (17)	4343 (17)	9602 (9)	17 (4)
C(22)	1053 (18)	4410 (18)	9955 (10)	23 (5)
C(23)	2798 (19)	4788 (20)	9866 (10)	29 (5)
C(24)	2167 (19)	3294 (18)	9453 (10)	21 (5)
O(25)	3202 (10)	7229 (14)	9325 (5)	22 (3)
C(26)	4209 (15)	6968 (15)	9213 (8)	16 (4)
C(27)	4885 (17)	7312 (20)	9631 (9)	26 (5)
C(28)	5926 (20)	6979 (2)	9482 (10)	38 (6)
C(29)	4835 (25)	8407 (25)	9687 (13)	49 (7)
C(30)	4606 (19)	6810 (24)	10160 (10)	35 (5)
N(31)	2288 (13)	6346 (13)	7193 (7)	12 (3)
C(32)	3190 (16)	6192 (16)	7132 (8)	14 (4)
C(33)	3626 (18)	5915 (18)	6666 (9)	20 (4)
C(34)	3010 (19)	5796 (19)	6222 (10)	24 (5)
C(35)	2065 (18)	5919 (18)	6281 (9)	21 (5)
C(36)	1677 (15)	6215 (16)	6771 (8)	12 (4)
O(37)	928 (10)	5506 (10)	7843 (5)	11 (3)
C(38)	1223 (17)	4538 (18)	7729 (9)	20 (5)
C(39)	390 (17)	3922 (17)	7530 (9)	19 (4)
C(40)	163 (21)	4196 (21)	6976 (11)	32 (6)
C(41)	840 (18)	2868 (19)	7517 (10)	27 (5)
C(42)	−450 (20)	3976 (21)	7884 (11)	32 (5)
O(43)	1056 (11)	7862 (11)	7538 (6)	18 (3)
C(44)	1567 (18)	8548 (18)	7196 (9)	22 (5)
C(45)	797 (16)	9100 (17)	6861 (9)	17 (4)
C(46)	140 (21)	9652 (20)	7209 (10)	29 (5)
C(47)	210 (24)	8440 (25)	6502 (13)	47 (7)
C(48)	1428 (26)	9871 (26)	6554 (13)	48 (7)
O(49)	662 (9)	7197 (12)	8552 (5)	11 (2)
C(50)	−133 (17)	7833 (18)	8588 (9)	24 (5)
C(51)	−1157 (16)	7358 (17)	8490 (9)	22 (5)
C(52)	−1205 (20)	7019 (22)	7931 (11)	41 (6)
C(53)	−1920 (20)	8152 (20)	8539 (10)	30 (5)
C(54)	−1315 (19)	6545 (18)	8885 (10)	28 (5)

[a] Coordinate arbitrarily fixed to define origin.

$W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ adopts a structure in the solid state akin to that seen previously for $W_2(ONp)_6(py)_2(\mu\text{-}C_2Me_2)$.[7] A view of the ethyne adduct is given in Figure 1. The ethyne unit bridges the tungsten atoms in a perpendicular mode, and if this is taken to occupy a single coordination site for each metal atom, then one tungsten is in a pseudooctahedral environment and the other in a trigonal-bipyramidal one with the ethyne in an equatorial position.

$W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$ adopts a structure in the solid state akin to that seen previously for $W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)$.[7] A view of the diethylacetylene adduct is given in Figure 2. Again, if for the sake of defining coordination geometries, the μ-perpendicular ethyne ligand is taken to occupy a single coordination position, X, the central $NO_2W(\mu\text{-}X)(\mu\text{-}O)WO_3$ unit may be described in terms of the fusing of two trigonal-bipyramidal units sharing a

Table II. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	8803.7 (3)	5500^a	6546.0 (3)	13
W(2)	7632.4 (3)	5500 (2)	4247.2 (3)	14
C(3)	11093 (20)	4308 (13)	5499 (21)	48 (4)
C(4)	9849 (15)	4277 (10)	4769 (15)	30 (3)
C(5)	9171 (12)	4962 (9)	4871 (13)	20 (2)
C(6)	9434 (10)	5722 (7)	5042 (10)	15 (2)
C(7)	10516 (15)	6193 (11)	5049 (17)	36 (3)
C(8)	10508 (16)	6993 (10)	5523 (16)	32 (3)
O(9)	8625 (8)	4566 (5)	7145 (9)	20 (2)
C(10)	8049 (16)	3821 (11)	6825 (17)	35 (3)
C(11)	8667 (15)	3230 (10)	7616 (16)	29 (3)
C(12)	8090 (16)	2488 (11)	7049 (17)	33 (3)
C(13)	9956 (15)	3178 (10)	7741 (16)	32 (3)
C(14)	8495 (17)	3328 (12)	8893 (19)	42 (4)
O(15)	8535 (7)	6486 (5)	7165 (8)	15 (1)
C(16)	8063 (10)	7146 (7)	6674 (10)	10 (2)
C(17)	8300 (14)	7738 (10)	7758 (15)	30 (3)
C(18)	7636 (14)	8457 (10)	7201 (15)	30 (3)
C(19)	9602 (16)	7890 (11)	8248 (17)	40 (3)
C(20)	7818 (13)	7460 (9)	8778 (14)	26 (3)
O(21)	10454 (6)	5598 (6)	7475 (6)	14 (1)
C(22)	10757 (9)	5418 (8)	8785 (10)	16 (2)
C(23)	12062 (9)	5630 (7)	9404 (9)	16 (2)
C(24)	12787 (17)	5017 (11)	8967 (18)	37 (4)
C(25)	12443 (16)	6336 (12)	9050 (17)	36 (4)
C(26)	12298 (9)	5434 (10)	10798 (10)	20 (3)
O(27)	6969 (6)	5569 (9)	5711 (6)	14 (1)
C(28)	6043 (10)	5086 (7)	5914 (11)	12 (2)
C(29)	4900 (9)	5541 (21)	5678 (10)	21 (2)
C(30)	4493 (16)	5760 (11)	4358 (17)	44 (4)
C(31)	4015 (15)	4921 (10)	5895 (16)	31 (3)
C(32)	4977 (17)	6144 (12)	6556 (18)	41 (4)
O(33)	7009 (8)	4545 (5)	3723 (8)	17 (2)
C(34)	7236 (14)	3921 (10)	3070 (15)	29 (3)
C(35)	5789 (13)	3529 (9)	2550 (14)	23 (2)
C(36)	5367 (13)	3253 (9)	3590 (14)	25 (3)
C(37)	6050 (20)	2867 (14)	1811 (21)	52 (5)
C(38)	4842 (14)	3965 (10)	1678 (15)	28 (3)
O(39)	6696 (8)	6412 (5)	3646 (8)	18 (2)
C(40)	6895 (13)	7041 (10)	2973 (16)	24 (3)
C(41)	6181 (14)	7602 (9)	2543 (15)	24 (3)
C(42)	5804 (13)	7911 (9)	3669 (13)	23 (2)
C(43)	6441 (14)	8243 (10)	1863 (15)	30 (3)
C(44)	5152 (15)	7146 (11)	1658 (16)	34 (3)
N(45)	7950 (8)	5600 (8)	2416 (8)	19 (2)
C(46)	6965 (10)	5610 (9)	1443 (10)	22 (2)
C(47)	6972 (11)	5689 (8)	263 (12)	22 (3)
C(48)	8010 (14)	5738 (9)	−6 (15)	35 (3)
C(49)	9034 (15)	5745 (10)	974 (16)	40 (4)
C(50)	8952 (12)	5678 (8)	2180 (12)	27 (3)

^{a} Coordinate arbitrarily fixed to define origin.

Table III. Selected Bond Distances (Å) for the $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ Molecule

W(1)	W(2)	2.6095 (16)
W(1)	O(13)	1.979 (17)
W(1)	O(19)	1.963 (14)
W(1)	O(25)	1.940 (14)
W(1)	O(49)	2.070 (12)
W(1)	N(7)	2.314 (20)
W(1)	C(4)	2.146 (24)
W(1)	C(5)	2.181 (19)
W(2)	O(37)	1.911 (14)
W(2)	O(43)	1.943 (15)
W(2)	O(49)	2.012 (12)
W(2)	N(31)	2.274 (17)
W(2)	C(4)	2.099 (24)
W(2)	C(5)	2.070 (20)
O(13)	C(14)	1.40 (3)
O(19)	C(20)	1.41 (3)
O(25)	C(26)	1.456 (24)
O(37)	C(38)	1.43 (3)
O(43)	C(44)	1.47 (3)
O(49)	C(50)	1.40 (3)
C(4)	C(5)	1.39 (3)

Table IV. Selected Bond Distances (Å) for the $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$ Molecule

W(1)	W(2)	2.5719 (12)
W(1)	O(9)	1.848 (20)
W(1)	O(15)	1.970 (18)
W(1)	O(21)	1.950 (6)
W(1)	O(27)	2.120 (6)
W(1)	C(5)	2.296 (14)
W(1)	C(6)	2.107 (11)
W(2)	O(27)	2.055 (6)
W(2)	O(33)	1.895 (12)
W(2)	O(39)	1.989 (12)
W(2)	N(45)	2.237 (9)
W(2)	C(5)	2.012 (14)
W(2)	C(6)	2.112 (12)
O(9)	C(10)	1.50 (3)
O(15)	C(16)	1.360 (25)
O(21)	C(22)	1.462 (12)
O(27)	C(28)	1.480 (16)
O(33)	C(34)	1.417 (22)
O(39)	C(40)	1.425 (21)
C(5)	C(6)	1.402 (22)

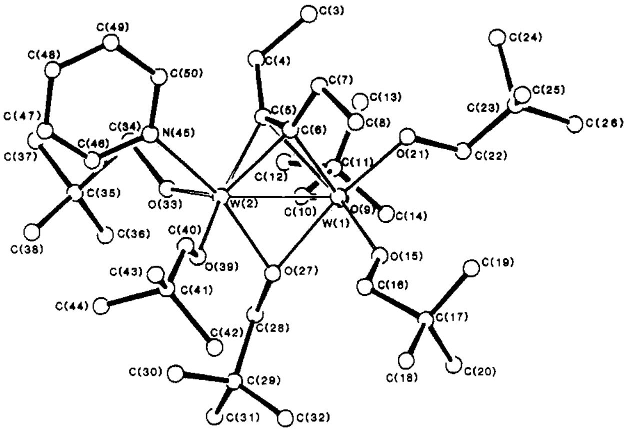

Figure 2. A ball-and-stick drawing of the $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$ molecule giving the atom number scheme used in the tables.

common equatorial (X) and axial (O) edge.

General Remarks on Structures and Bonding. The long W–N(pyridine) distances are consistent with the relatively labile pyridine ligands found from solution NMR studies. The structural features of the central $W_2(\mu\text{-}C_2)$ core are similar to those seen previously[6,7] in alkyne adducts of $M_2(OR)_6$ compounds which have been described in terms of a dimetallatetrahedrane with M–M, M–C, and C–C bonds approaching order one. The W–O and W–O–C angles are indicative of oxygen-to-metal π-bonding for the terminal groups.[14]

NMR Studies. Alkyne Adducts. The low-temperature limiting ^1H NMR spectra in toluene-d_8 are consistent with expectations based on the observed solid state structures for R = H, Me, and Et. The solution data for R = Ph indicate an analogous structure to that observed for R = Et. In no instance was there evidence for an NMR detectable concentration of a $(py)_x(NpO)_3W{\equiv}CR$ species.

The ethyne adducts $M_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ where M = Mo and W adopt different structures in solution. As noted previously,[6] the NMR data for the molybdenum compound are consistent with structural type I which has two alkoxide bridges and two mirror planes of symmetry (C_{2v}). The ^1H NMR data of $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ are indicative of only a mirror plane of symmetry with alkoxide ligands in the ratio 2:2:1:1 with the latter (1:1) being contained on the mirror plane and the former (2:2) lying off

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(14) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

Table V. Selected Bond Angles (deg) for the $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ Molecule

W(2)	W(1)	O(13)	100.9 (5)
W(2)	W(1)	O(19)	95.7 (4)
W(2)	W(1)	O(25)	139.0 (4)
W(2)	W(1)	O(49)	49.3 (3)
W(2)	W(1)	N(7)	140.3 (5)
W(2)	W(1)	C(4)	51.3 (6)
W(2)	W(1)	C(5)	50.2 (5)
O(13)	W(1)	O(19)	149.4 (7)
O(13)	W(1)	O(25)	89.0 (8)
O(13)	W(1)	O(49)	84.9 (7)
O(13)	W(1)	N(7)	76.6 (7)
O(13)	W(1)	C(4)	123.0 (8)
O(13)	W(1)	C(5)	85.7 (8)
O(19)	W(1)	O(25)	95.1 (7)
O(19)	W(1)	O(49)	86.8 (6)
O(19)	W(1)	N(7)	74.2 (6)
O(19)	W(1)	C(4)	87.3 (8)
O(19)	W(1)	C(5)	124.3 (7)
O(25)	W(1)	O(49)	170.9 (6)
O(25)	W(1)	N(7)	80.7 (6)
O(25)	W(1)	C(4)	90.0 (8)
O(25)	W(1)	C(5)	91.8 (7)
O(49)	W(1)	N(7)	91.3 (6)
O(49)	W(1)	C(4)	99.0 (7)
O(49)	W(1)	C(5)	94.5 (6)
N(7)	W(1)	C(4)	158.3 (9)
N(7)	W(1)	C(5)	160.9 (8)
C(4)	W(1)	C(5)	37.4 (9)
W(1)	W(2)	O(37)	115.0 (4)
W(1)	W(2)	O(43)	115.1 (4)
W(1)	W(2)	O(49)	51.3 (3)
W(1)	W(2)	N(31)	135.1 (4)
W(1)	W(2)	C(4)	52.9 (7)
W(1)	W(2)	C(5)	54.1 (5)
O(37)	W(2)	O(43)	121.1 (6)
O(37)	W(2)	O(49)	98.7 (6)
O(37)	W(2)	N(31)	81.6 (6)
O(37)	W(2)	C(4)	98.9 (8)
O(37)	W(2)	C(5)	136.8 (7)
O(43)	W(2)	O(49)	89.7 (6)
O(43)	W(2)	N(31)	84.1 (6)
O(43)	W(2)	C(4)	136.0 (8)
O(43)	W(2)	C(5)	97.7 (7)
O(49)	W(2)	N(31)	172.8 (6)
O(49)	W(2)	C(4)	102.5 (8)
O(49)	W(2)	C(5)	99.8 (6)
N(31)	W(2)	C(4)	84.5 (8)
N(31)	W(2)	C(5)	84.6 (7)
C(4)	W(2)	C(5)	38.9 (9)
W(1)	O(13)	C(14)	129.8 (16)
W(1)	O(19)	C(20)	139.3 (13)
W(1)	O(25)	C(26)	132.2 (12)
W(2)	O(37)	C(38)	139.6 (13)
W(2)	O(43)	C(44)	132.8 (14)
W(1)	O(49)	W(2)	79.5 (4)
W(1)	O(49)	C(50)	133.9 (14)
W(2)	O(49)	C(50)	132.7 (13)
W(1)	C(4)	W(2)	75.8 (8)
W(1)	C(4)	C(5)	72.7 (13)
W(2)	C(4)	C(5)	69.4 (13)
W(1)	C(5)	W(2)	75.7 (6)
W(1)	C(5)	C(4)	70.0 (13)
W(2)	C(5)	C(4)	71.7 (14)

the mirror plane. It was this unexpected difference that prompted us to determine the molecular structures of $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ in the solid state. We have also recorded spectra for the compounds $M_2(ONp)_6(py)_2(\mu\text{-}{}^*C_2H_2)$, where *C represents 92 mol% ^{13}C. For M = Mo the $\mu\text{-}^{13}C$ signal is at ca. 160 ppm whereas for M = W, the $\mu\text{-}^{13}C$ signal is at ca. 130 ppm. Careful inspection of the spectra, however, reveal that in both samples there are resonances at ca. 160 and 130 ppm assignable to $\mu\text{-}{}^*C_2H_2$ carbons. The compounds $M_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}C_2H_2)$, which are known to adopt the $(\mu\text{-}OR)_2$ structure I, show carbon signals at ca. 160 ppm, and we suggest that this region is indicative of the moiety $M_2(\mu\text{-}{}^*C_2H_2)(\mu\text{-}OR)_2$ while that at ca. 130 ppm corresponds to $M_2(\mu\text{-}C_2H_2)(\mu\text{-}OR)$ containing compounds. For M = Mo, there is an equilibrium in solution involving the structural types I and II with I being favored over II by ca. 10:1, while for M = W, the situation is reversed. See Figure 3. Upon warming the toluene-d_8 solutions of $M_2(ONp)_6(py)_2(\mu\text{-}{}^*C_2H_2)$ from −60 °C, the signals of the minor isomer initially broaden and then disappear into the base line. These changes have only a minor influence on the major $\mu\text{-}{}^*C_2H_2$ carbon signal. Our interpretation of this is that dynamic exchange involves the interconversion of I and II with the equilibrium concentration of the respective isomers changing little with temperature.

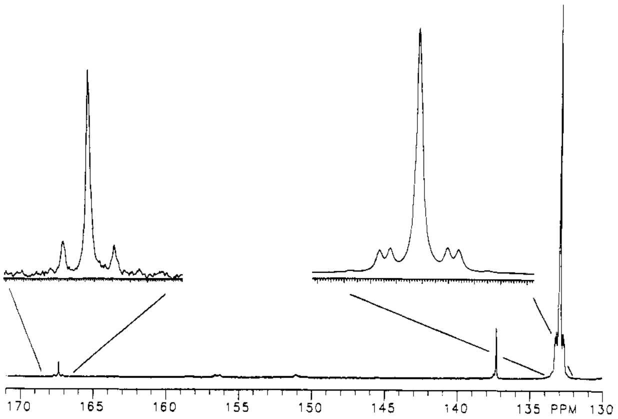


Figure 3. $^{13}C\{^1H\}$ NMR spectrum recorded at −35 °C, 75.4 MHz, of the two isomers of $W_2(ONp)_6(py)_2(\mu\text{-}{}^*C_2H_2)$, where *C represents 92 atom % ^{13}C, dissolved in toluene-d_8 in the region 170–130 ppm. The resonances arising from the $W_2(\mu\text{-}{}^*C_2H_2)$ moiety of the minor isomers (δ 167.4), I, and the major isomer (δ 133.0), II, are shown at scale expansion in the insets. The signal at δ 137.3 arises from the ipso-carbon of toluene-d_8. Note the coupling to two inequivalent ^{183}W nuclei for the major isomer II.

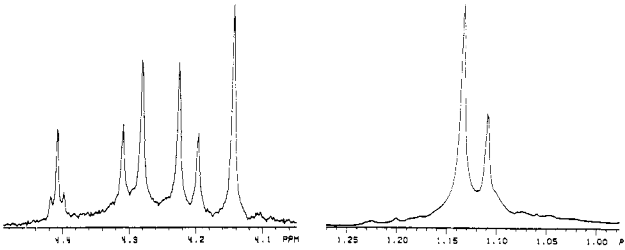
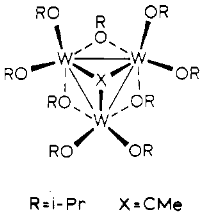


Figure 4. ^1H NMR spectrum recorded at 22 °C, 360 MHz, of the alkylidyne methyl, neopentoxy methylene, and neopentoxy methyl regions of $W_3(ONp)_9(\mu\text{-}CMe)(py)_x$ in benzene-d_6.

$W_3(\mu_3\text{-}CR)(ONp)_9(py)_x$ compounds displayed ^1H NMR spectra consistent with expectations based on the observed solid-state molecular structure of $W_3(\mu_3\text{-}CMe)(\mu_2\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$ which is schematically shown in IV.



IV

The ^1H NMR spectrum of the ethylidyne compound is shown in Figure 4. Note the methylene protons appear as an AB quartet and a singlet indicative of the terminal and bridging μ-ONp ligands, respectively. The resonances for the *tert*-butyl protons are in the ratio 2:1 (terminal:

Table VI. Selected Bond Angles (deg) for the $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$ Molecule

W(2)	W(1)	O(9)	106.7 (7)
W(2)	W(1)	O(15)	105.5 (6)
W(2)	W(1)	O(21)	134.92 (19)
W(2)	W(1)	O(27)	50.85 (17)
W(2)	W(1)	C(5)	48.4 (4)
W(2)	W(1)	C(6)	52.5 (3)
O(9)	W(1)	O(15)	129.5 (3)
O(9)	W(1)	O(21)	95.4 (7)
O(9)	W(1)	O(27)	89.9 (7)
O(9)	W(1)	C(5)	89.8 (7)
O(9)	W(1)	C(6)	125.6 (7)
O(15)	W(1)	O(21)	88.4 (6)
O(15)	W(1)	O(27)	81.3 (6)
O(15)	W(1)	C(5)	140.3 (7)
O(15)	W(1)	C(6)	104.9 (6)
O(21)	W(1)	O(27)	169.6 (5)
O(21)	W(1)	C(5)	94.2 (4)
O(21)	W(1)	C(6)	82.6 (4)
O(27)	W(1)	C(5)	94.8 (4)
O(27)	W(1)	C(6)	101.6 (4)
C(5)	W(1)	C(6)	36.8 (6)
W(1)	W(2)	O(27)	53.11 (18)
W(1)	W(2)	O(33)	111.3 (3)
W(1)	W(2)	O(39)	115.4 (3)
W(1)	W(2)	N(45)	139.07 (23)
W(1)	W(2)	C(5)	58.6 (4)
W(1)	W(2)	C(6)	52.4 (3)
O(27)	W(2)	O(33)	95.6 (5)
O(27)	W(2)	O(39)	85.1 (5)
O(27)	W(2)	N(45)	165.3 (4)
O(27)	W(2)	C(5)	106.2 (5)
O(27)	W(2)	C(6)	103.6 (4)
O(33)	W(2)	O(39)	120.7 (4)
O(33)	W(2)	N(45)	86.6 (5)
O(33)	W(2)	C(5)	84.8 (5)
O(33)	W(2)	C(6)	124.1 (4)
O(39)	W(2)	N(45)	81.3 (5)
O(39)	W(2)	C(5)	151.6 (5)
O(39)	W(2)	C(6)	112.9 (4)
N(45)	W(2)	C(5)	88.5 (5)
N(45)	W(2)	C(6)	86.9 (4)
C(5)	W(2)	C(6)	39.7 (6)
W(1)	O(9)	C(10)	144.8 (17)
W(1)	O(15)	C(16)	136.9 (14)
W(1)	O(21)	C(22)	115.7 (6)
W(1)	O(27)	W(2)	76.04 (22)
W(1)	O(27)	C(28)	128.4 (9)
W(2)	O(27)	C(28)	125.6 (8)
W(2)	O(33)	C(34)	139.7 (10)
W(2)	O(39)	C(40)	132.2 (9)
W(2)	N(45)	C(46)	114.4 (7)
W(2)	N(45)	C(50)	128.4 (8)
C(46)	N(45)	C(50)	117.1 (10)
C(3)	C(4)	C(5)	113.8 (15)
W(1)	C(5)	W(2)	73.0 (5)
W(1)	C(5)	C(4)	130.8 (10)
W(1)	C(5)	C(6)	64.2 (7)
W(2)	C(5)	C(4)	145.8 (12)
W(2)	C(5)	C(6)	74.0 (9)
C(4)	C(5)	C(6)	135.0 (13)
W(1)	C(6)	W(2)	75.1 (4)
W(1)	C(6)	C(5)	78.9 (8)
W(1)	C(6)	C(7)	127.1 (9)
W(2)	C(6)	C(5)	66.3 (8)
W(2)	C(6)	C(7)	148.5 (10)
C(5)	C(6)	C(7)	133.4 (13)
C(6)	C(7)	C(8)	114.9 (14)

bridging) and the capping alkylidyne methyl resonance shows the expected satallite pattern for a $W_3(\mu_3\text{-}CR)$ moiety. The pyridine proton resonances are suggestive of a temperature-dependent reversible ligation.

Concluding Remarks

Alkyne adducts of formula $W_2(ONp)_6(py)_n(\mu\text{-}C_2R_2)$ have been isolated for R = H and Me and $n = 2$ and for R = Et and Ph for $n = 1$. This contrasts with $W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)$ which is the only isolable crystalline alkyne adduct formed in reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and alkynes, $RC{\equiv}CR$, in the presence of pyridine. As the steric bulk of the alkyne group is increased, there are changes in structure involving the coordination environment of the metal. The structural type III is found for $W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)$ and $W_2(ONp)_6(py)(\mu\text{-}C_2R_2)$ compounds, where R = Et and Ph. The ground-state structures of the compounds $M_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ differ from M = Mo and W with the structural type II being favored for tungsten and that of I favored for molybdenum. The preference for one structure over the other is not presently understood, but a dynamic exchange between I and II is easily envisaged and probably accounts for the fluxional behavior of the compounds in solution. The alkyne adducts $W_2(ONp)_6(py)_n(\mu\text{-}C_2R_2)$, where R = Me and $n = 2$ and R = Et and Ph and $n = 1$, act as sources of reactive alkylidyne species $(NpO)_3W{\equiv}CR$ in the syntheses of the alkylidyne-capped compounds $W_3(\mu_3\text{-}CR)(ONp)_9(py)_x$. These reactions conform to a generalized reaction sequence described by (11).

Experimental Section

Reagent and General Techniques. General procedures and the preparation of $W_2(ONp)_6(py)_2$ have been described.[15] Ethyne was purchased from Matheson, 3-hexyne was purchased from Farchan, and diphenylacetylene was purchased from Aldrich. All were used without purification. Dry and oxygen-free hexane, pentane, and pyridine were used in all preparations. Elemental analyses were performed by Alfred Bernhardt Microanalytisches Laboratorium, West Germany.

^{1}H NMR spectra were recorded on a Nicolet NT-360 360-MHz spectrometer in dry and oxygen-free benzene-d_6 or toluene-d_8. ^{13}C NMR spectra were recorded on the same instrument at 90 MHz or on a Varian XL-300 at 75 MHz in benzene-d_6 or toluene-d_8. The ^{13}C NMR spectrum for $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ was obtained by using labeled ethyne (ethyne-*1,2*-$^{13}C_2$ 92 mol % ^{13}C). The ^{13}C-labeled ethyne was purchased from MSD Isotopes and used without purification. All ^{1}H NMR chemical shifts are in parts per million relative to the C_6D_5H singlet of benzene-d_6 set at δ 7.150 or the methyl protio impurity in toluene-d_8 set at δ 2.090. ^{13}C NMR chemical shifts are in parts per million relative to the C_6D_6 triplet of benzene-d_6 set at δ 128.0 or the methyl–carbon of toluene-d_8 set at δ 20.40. The ^{13}C–^{1}H, ^{13}C–^{13}C, and ^{1}H–^{1}H coupling constants reported for the ethyne adduct were obtained by use of gated ^{1}H-decoupled techniques.

Infrared spectra were obtained on a Perkin-Elmer 282 spectrophotometer at Nujol mulls between CsI plates.

$W_2(ONp)_6(py)(\mu\text{-}C_2Ph_2)$. In a Schlenk reaction flask, $W_2(ONp)_6(py)_2$ (0.50 g, 0.48 mmol) was dissolved in hexane (10 mL) and cooled to 0 °C in an ice water bath. A diphenylacetylene solution (2.08 mL, 0.229 M in hexane, 0.48 mmol) was added via syringe to the dark red solution. The reaction mixture was stirred at 0 °C for ca. 2 h after which time the ice in the bath melted and the water slowly warmed to room temperature. After an additional 4.5 h the color of the solution changed to dark purple. The solvent was stripped and the residue redissolved in 2 mL of pentane. The flask was placed in an ice bath for 1.7 h and then placed in an acetone–ice bath at −14 °C for 39 h. The dark crystalline material which formed on the bottom of the flask was filtered and dried in vacuo (yield 100 mg, 18.1%). Anal. Calcd for $W_2O_6C_{49}H_{81}N$: C, 51.27; H, 7.11; N, 1.22. Found: C, 51.02; H, 6.95; N, 1.35.

^{1}H NMR (22 °C, benzene-d_6): δ (py, ortho) 8.55, d; δ (py, para) 6.52, t; δ (py, meta) 6.25, t; δ (C_2Ph_2, ortho) 7.52, d; δ (C_2Ph_2, meta) 7.33, t; δ (C_2Ph_2, para) 6.70, t, with py/Ph intensity ratio 1:2; δ ($OCH_2\text{-}t\text{-}Bu$) 4.89 and 4.44, singlets, and 3.95 and 3.15, doublets ($^2J_{HH}$ = 10.8 Hz) of an AB quartet, and 3.89 and 3.82, doublets

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(15) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.

Table VII. Comparison of Selected Bond Distances (Å) and Bond Angles (deg) in 1:1 μ-Alkyne Adducts of the Hexaalkoxides of Dimolybdenum and Ditungsten

compd	M–M	C–C	M_1–C(av)	M_2–C(av)	M_1–O(b)[a]	M_2–O(b)[a]	M_1–O(t)(av)
$Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}C_2H_2)$	2.544 (1)	1.368 (6)	2.086 (10)	2.090 (5)	2.147 (15)	1.247 (17)	1.936 (8)
$W_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}C_2H_2)$	2.567 (1)	1.394 (19)	2.088 (16)	2.106 (18)	2.145 (19)	2.141 (23)	1.938 (12)
$W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$[b]	2.610 (2)	1.39 (3)	2.16 (3)	2.08 (3)	2.070 (12)	2.012 (12)	1.961 (23)
$W_2(ONp)_6(py)_2(\mu\text{-}C_2Me_2)$[b]	2.602 (1)	1.374 (15)	2.199 (20)	2.064 (19)	2.123 (7)	2.025 (7)	1.954 (13)
$W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$[c]	2.572 (1)	1.402 (22)	2.20 (5)	2.06 (3)	2.120 (6)	2.055 (6)	1.92 (5)
$W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)$[c]	2.665 (1)	1.441 (14)	2.107 (13)	2.092 (10)	2.083 (6)	1.999 (6)	1.938 (13)

compd	M_2–O(t)(av)	M_1–N	M_2–N	M_1–O–C(b)[a]	M_2–O–C(b)[a]	M_1–O–C-(t)(av)	M_2–O–C-(t)(av)	ref.
$Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}C_2H_2)$	1.947 (9)	2.303 (3)	2.321 (3)	125.2 (8)	125.4 (6)	136.4 (11)	134.6 (5)	6
$W_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}C_2H_2)$	1.945 (10)	2.318 (11)	2.306 (10)	124.8 (14)	125.1 (14)	134.9 (13)	134.4 (9)	7
$W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$	1.927 (20)	2.314 (20)	2.274 (17)	133.9 (14)	132.7 (13)	134 (3)	136.2 (25)	this work
$W_2(ONp)_6(py)_2(\mu\text{-}C_2Me_2)$	1.953 (13)	2.322 (9)	2.243 (10)	126.3 (6)	130.3 (6)	138.3 (17)	134.3 (8)	7
$W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$	1.942 (28)		2.237 (9)	128.4 (9)	125.6 (8)	133 (7)	136.0 (22)	this work
$W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)$	1.919 (8)		2.267 (8)	139.6 (5)	138.9 (5)	149.0 (20)	152.4 (8)	7

[a] Averaged where appropriate. [b] M_1 represents the metal in an octahedral environment. M_2 represents the metal in a trigonal-bipyramidal environment. [c] M_2 contains coordinated pyridine.

Table VIII. Summary of Crystallographic Data[a]

	I	II
fw	1074.79	1051.79
space group	$Pc2_1n$	$P2_1$
a, Å	13.711 (6)	11.977 (4)
b, Å	13.843 (6)	17.981 (9)
c, Å	25.414 (12)	11.389 (4)
β, deg		107.49 (2)
Z	4	2
V, Å	4823.63	2339.28
d_{calcd}, g/cm^{-3}	1.480	1.493
cryst size, mm	0.12 × 0.16 × 0.24	0.12 × 0.10 × 0.08
cryst color	black	black
linear abs coeff, cm^{-1}	49.080	50.578
temp, °C	−156	−158
instrument	Picker four-circle diffractometer, locally modified and interfaced	Picker four-circle diffractometer, locally modified and interfaced
takeoff angle, deg	2.0	2.0
scan speed, deg/min	4.0	4.0
scan width, deg	1.6 + 0.692 tan *θ*	2.0 + 0.692 tan *θ*
background counts (s) at end of scan	8	3
2*θ* range, deg	6–45	6–45
data collected	3850	5839
unique data	3317	5553
unique data with $F > 0.0$	3156	5018
unique data with $F > 3\sigma(F)$	2947	3713
$R(F)$	0.0457	0.0336
$R_w(F)$	0.0455	0.0361
goodness of fit	1.084	0.850
max Δ/σ	0.05	0.05

[a] I, $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$; II, $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$.

($^1J_{HH}$ = 10.8 Hz) of an AB quartet; δ ($OCH_2C(CH_3)_3$) 1.49, 1.10, 1.02, and 0.98, singlets, with intensity ratio 1:1:2:2, respectively.

IR (cm^{-1}): 3040 vw, 1602 vw, 1590 m, 1390 s, 1378 s, 1360 s, 1258 m, 1214 m, 1150 w, 1090 s, 1060 s (br), 1022 s, 1000 s, 945 m, 932 m, 900 w, 800 w, 760 s, 776 s, 719 w, 693 s, 660 s, 614 vw, 6903 vw, 580 w, 560 w, 542 w, 457 m, 400 m, 320 w.

$W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$. In a Schlenk reaction flask, $W_2(ONp)_6(py)_2$ (0.50 g, 0.48 mmol) was dissolved in hexane (6 mL). The dark red solution was stirred rapidly as 3-hexyne (54.5 μL, 0.48 mmol) was slowly added via microsyringe over a 1–2-min period. As the alkyne was added, the color slowly changed from dark red through dark green to dark blue. The solution was stirred at room temperature for 2 h. During this time, small amounts of precipitate formed on the walls of the flask. The volume of the solution was reduced to ca. 2 mL. Slight warming of the solution (45 °C) in a water bath dissolved the precipitate. The solution stood at room temperature for 2 h and then was placed in a freezer at −18 °C for 4.5 h. A dark blue microcrystalline solid was collected by filtration and dried in vacuo (yield 0.17 g, 35%). Anal. Calcd for $W_2O_6NC_{41}H_{81}$: C, 46.82; H, 7.76; N, 1.33. Found: C, 46.51; H, 7.53; N, 1.28.

^{1}H NMR (22 °C, benzene-d_6): δ (py, ortho) 8.40, d; δ (py, para) 6.74, m; δ (py, meta) 6.53, m; δ (OCH_2-*t*-Bu) 4.51 and 4.47, singlets, and 4.32 and 4.07, doublets (J_{HH} = 10.4 Hz) of an AB quartet, and 3.80 and 3.20, doublets (J_{HH} = 10.4 Hz) of an AB quartet; δ ($OCH_2C(CH_3)_3$ 1.53, 1.36, 1.14, and 1.02, singlets, with intensity ratio 1:1:2:2, respectively; δ ($C_2(CH_2CH_3)_2$) 5.14, m; δ ($C_2(CH_2CH_3)_2$) 1.52, t (J_{HH} = 7.38 Hz).

$^{13}C\{^1H\}$ NMR (22 °C, benzene-d_6): δ (py, ortho) 151.96; δ (py, para) 136.33; δ (py, meta) 123.74; δ (OCH_2-*t*-Bu + OCH_2-*t*-Bu, 3 C) 82.41; δ (OCH_2-*t*-Bu, 2 C) 83.93; δ (OCH_2-*t*-Bu, 1 C) 85.59; δ ($OCH_2C(CH_3)_3$) 34.65; δ ($OCH_2C(CH_3)_3$, 12 C) 27.23; δ ($OCH_2C(CH_3)_3$, 6 C) 27.91; δ ($C_2(CH_2CH_3)_2$) 18.29; δ ($C_2(CH_2CH_3)_2$) 27.71; δ (C_2Et_2) 160.88.

IR (cm^{-1}): 1600 w, 1485 vw, 1478 vw, 1390 m, 1360 m, 1307 w, 1211 w, 1150 w, 1060 s, 1020 s, 930 w, 900 w, 755 m, 695 m, 680 2, 660 m, 650 m, 600 w, 457 w, 400 w, 345 vw, 329 vw, 320 vw, 304 vw, 300 vw.

$W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$. In a Schlenk reaction flask, $W_2(ONp)_6(py)_2$ (0.50 g, 0.48 mmol) was dissolved in hexane/pyridine (10 mL/1 mL). The dark red solution was frozen at −196 °C, and ethyne (0.48 mmol) was condensed into the flask by use of a calibrated vacuum manifold. The frozen mixture was warmed to 0 °C and stirred for $^1/_2$ h, during which time the color became green. The volume of the solution was reduced. Slight warming (40–50 °C) of the solution redissolved the precipitate. The flask was placed in a freezer at −15 °C overnight. A dark green microcrystalline solid was collected by filtration and dried in vacuo (yield 253 mg, 49%). Anal. Calcd for $W_2O_6C_{42}N_2H_{78}$: C, 46.94; H, 7.32; N, 2.61. Found: C, 46.77; H, 7.21; N, 2.60.

^{1}H NMR (−65 °C, toluene-d_8): δ (py, ortho) 9.74, 9.41, 9.16, doublets; δ (py, meta and para) 6.84, 6.62, 6.41, and 6.21, multiplets; δ (C_2H_2) 6.51, s; δ (OCH_2-*t*-Bu) 4.71 and 4.69, singlets, and 4.52 and 4.18, doublets ($^2J_{HH}$ = 10.47 Hz) of an AB quartet, and 4.18 and 2.69, doublets ($^2J_{HH}$ = 10.47 Hz) of an AB quartet; δ ($OCH_2C(CH_3)_3$) 1.49, 1.30, 1.12, and 1.01, singlets, with integral intensity ratio 1:1:2:2:, respectively.

^{13}C NMR (−20 °C, toluene-d_8): δ (C_2H_2) 133.20, $^1J_{W-C}$ = 44.77 and 32.81 Hz, $^1J_{C-H}$ = 189.7 Hz, $^2J_{C-H}$ = 1.0 Hz, $^1J_{C-C}$ = 19.0 Hz, $^3J_{H-H}$ = 2.9 Hz. The relative signs of $^1J_{C-H}$ and $^2J_{C-H}$ are the same and assumed to be positive. The relative signs of $^1J_{C-C}$ and $^3J_{H-H}$ are not known.

IR (cm^{-1}): 1602 m, 1390 s, 1380 s, 1254 w, 1214 m, 1147 w, 1075 s (br), 1040 s, 1022 s, 942 w, 931 w, 901 w, 800 w, 759 s, 694 s, 660 s, 640 s, 619 m, 600 w, 579 w, 494 w, 447 m, 406 m, 386 w, 334 w, 328 w, 286 w, 276 w, 244 w, 221 w.

$W_3(\mu_3\text{-}CMe)(ONp)_9(py)_x$. Method 1. In an N_2-filled glovebox, $W_2(ONp)_6(py)_2$ (145 mg, 0.138 mmol) was dissolved in hexane (ca. 4–5 mL) in a Schlenk reaction flask. Neopentanol (1 mL, 0.8 M, 0.8 mmol) in hexane was added and thoroughly mixed. To this solution was added $[(t\text{-BuO})_3W{\equiv}CMe]_2$ (60 mg, 0.140 mmol) in hexane (ca. 1 mL) with a disposable pipet. The color of the solution changed from dark red to dark blue to dark green-brown and finally to its original color of dark red within seconds. The solution was stirred for ca. 2.5 h at room temperature. The volume of the solution was reduced under a dynamic vacuum to ca. 1 mL. The flask was placed in a freezer at −15 °C for 4 days. The dark brown crystalline solid was filtered and dried in vacuo (yield 30 mg, 13%). By ^1H NMR the reaction is quantitative.

Method 2. In a Schlenk reaction flask, $W_2(ONp)_6(py)_2$ (200 mg, 0.191 mmol) was dissolved in hexane (10 mL) and frozen at −196 °C. By the use of a calibrated vacuum manifold, 2-butyne (0.0636 mmol) was condensed into the flask. Upon warming, the mixture melted and became bluish green upon approaching room temperature. The solution was stirred at room temperature for 18 h. By ^1H NMR trace amounts of $W_2(\mu_3\text{-CMe})(ONp)_9(py)_x$ could be detected while the major product was $W_2(ONp)_6(py)_2(\mu\text{-}C_2Me_2)$ with some unreacted $W_2(ONp)_6(py)_2$.

Method 3. In an N_2-filled glovebox, $W_2(ONp)_6(py)_2(\mu\text{-}C_2Me_2)$ (20 mg, 0.0181 mmol) and $W_2(ONp)_6(py)_2$ (38 mg, 0.0363 mmol, 2.00 equiv) were dissolved in benzene-d_6 (ca. 0.5 mL) and transferred to an NMR tube. The NMR tube was frozen at −196 °C and sealed under vacuum with a torch. The tube was warmed to room temperature and analyzed by ^1H NMR after 24 h. The ^1H NMR reveals a mixture of $W_3(\mu_3\text{-CMe})(ONp)_9(py)_x$, $W_2(ONp)_6(py)_2$, and $W_2(ONp)_6(py)_2(\mu\text{-}C_2Me_2)$ in a ca. 2:1:1 ratio, respectively.

^1H NMR (21 °C): δ (py, ortho) ca. 9, v br; δ (py, para) 6.95, t; δ (py, meta) 6.75, m; δ (μ_3-CCH_3) 4.41, s, with ^{183}W satellites ($^3J_{^{183}W-^1H}$ = 7.10 Hz); δ (OCH_2-t-Bu) 4.30 and 4.21, doublets of an AB quartet (J_{HH} = 10.44 Hz), and 4.14, s, with an integral intensity ratio of 1:1:1; δ (OCH$_2$C(CH_3)$_3$) 1.13 and 1.11, singlets, with an integral intensity of 2:1, respectively.

IR (cm^{-1}): 2685 w, 1610 m, 1497 m, 1492 s, 1481 s, 1220 m, 1180 m, 1070 2, 1020 s, 980 m, 930 s, 900 w, 816 s, 770 m, 756 m, 672 s, 650 s, 582 w, 498 w, 450 w, 400 w, 300 w.

$W_3(\mu_3\text{-CEt})(ONp)_9(py)$. Method 1. $W_3(\mu_3\text{-CEt})(ONp)_9(py)$ was prepared from $W_2(ONp)_6(py)_2$ and $[(t\text{-BuO})_3W{\equiv}CEt]_2$ in a manner similar to $W_3(\mu_3\text{-CMe})(ONp)_9(py)_x$. The yield is quantitative by ^1H NMR.

Method 2. $W_3(\mu_3\text{-CEt})(ONp)_9(py)$ was prepared in a Schlenk flask from a hexane solution of $W_2(ONp)_6(py)_2$ by the addition of $^1/_3$ equiv of EtC≡CEt from a syringe. Treatment of the solution as described in method 2 above for $W_3(\mu_3\text{-CMe})(ONp)_9(py)_x$ provided a crystalline yield of 19%. However by ^1H NMR the yield was virtually quantitative.

Method 3. In a Schlenk reaction flask, $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$ (80 mg, 0.0761 mmol) was dissolved in hexane (5 mL) to give a blue solution. In a second Schlenk flask, $W_2(ONp)_6(py)_6$ (160 mg, 0.153 mmol) was dissolved in hexane (5 mL) yielding a red solution. The second solution was transferred to the first by use of a cannula to give a green solution. The solution was stirred at room temperature for 1 day resulting in a brown solution. The volume of the solution was reduced to ca. 1 mL, and the solution was warmed in a water bath (ca. 50 °C) to dissolve any solid on the sides of the flask. The solution was allowed to cool to room temperature for 30 min and then placed in a freezer at −15 °C for 2 days. The black solid was filtered and dried in vacuo (yield 35 mg, 16%). Anal. Calcd for $W_3O_9C_{53}H_{109}N_1$: C, 43.72; H, 7.55; N, 0.96. Found: C, 43.48; H, 7.41; N, 0.96. By ^1H NMR the reaction was virtually quantitative.

^1H NMR (21 °C): δ (py, ortho) 8.64, br m; δ (py, para) 6.95, br m; δ (py, meta) 6.68, br m; δ (OCH_2-t-Bu) 4.34 and 4.23, doublets of an AB quartet (J_{HH} = 10.6 Hz), and 4.10, s, with an integral intensity ratio of 1:1:1; δ (OCH$_2$C(CH_3)$_3$) 1.15 and 1.11, singlets, with an intensity ratio of 2:1, respectively; δ (μ_3-CCH_2CH$_3$) 4.56, q, with ^{183}W satellites (J_{HH} = 7.47 Hz, J_{WH} = 6.89 Hz); δ (μ_3-CCH$_2$CH_3) 1.66, t (J_{HH} = 7.47 Hz).

IR (cm^{-1}): 1390 m, 1363 m, 1075 s, 1058 m, 1039 m, 1022 s, 932 w, 753 w, 658 m, 637 m, 454 w, 400 w, 320 w.

$W_3(\mu_3\text{-CPh})(ONp)_9(py)_x$. Method 1. Addition of $(t\text{-BuO})_3W{\equiv}CPh$ to $W_2(ONp)_6(py)_2$ solutions failed to produce $W_3(\mu_3\text{-CPh})(ONp)_9(py)_x$.

Method 2. In a Schlenk reaction flask, $W_2(ONp)_6(py)_2$ (200 mg, 0.191 mmol) was dissolved in hexane (10 mL). Diphenylacetylene (11.5 mg, 0.0645 mmol) was added as a solid by use of an addition tube to the stirring dark red solution. The solution was stirred at room temperature for 1.5 days, reduced in volume, and placed in a freezer at −15 °C for 4 days. The precipitated solid was not pure. By ^1H NMR the yield was estimated to be ca. 75%.

Method 3. $W_3(\mu_3\text{-CPh})(ONp)_9(py)_x$ was prepared from $W_2(ONp)_6(py)(\mu\text{-}C_2Ph_2)$ and $W_2(ONp)_6(py)_2$ as described above for $W_3(\mu_3\text{-CEt})(ONp)_9(py)_x$. The yield is virtually quantitative by ^1H NMR.

^1H NMR (21 °C): δ (py, ortho) 9.15, v br m; δ (py, para) 6.93, m; δ (py, meta) 6.76, m; δ (C_6H_5, ortho) 7.67, d (J_{HH} = 7.56 Hz); δ (C_6H_5, meta) 7.30, t (J_{HH} = 7.92 Hz); δ (C_5H_6, para) 6.89, multiplet overlapping with the para proton resonances of py; δ (OCH_2-t-Bu) 4.20 and 4.092, doublets of an AB quartet (J_{HH} = 10.8 Hz), and 4.12, s, with an integral intensity ratio of 1:1:1; δ (OCH$_2$C(CH_3)$_3$) 1.14 and 1.11, singlets, with an integral intensity ratio of 1:2, respectively.

Reaction of $W_2(ONp)_6(py)_2(\mu\text{-}{}^*C_2H_2)$ and $W_2(ONp)_6(py)_2(\mu\text{-}C_2D_2)$. $W_2(ONp)_6(py)_2(\mu\text{-}{}^*C_2H_2)$ and $W_2(ONp)_6(py)_2(\mu\text{-}C_2D_2)$ (30 mg each) were dissolved in benzene-d_6 (ca. 0.5 mL) and placed in an NMR tube. The solution was frozen at −196 °C. The tube was evacuated and sealed with a torch. The solution was allowed to warm to room temperature. The $^{13}C\{^1H\}$ NMR spectrum was recorded after 1 and 2 weeks. Only resonances assignable to the $W_2(\mu\text{-}{}^*C_2H_2)$ moiety were observed. These observations are to be contrasted with those previously described[7] for $W_2(O\text{-}t\text{-Bu})_6(py)(\mu\text{-}{}^*C_2H_2)$ and $W_2(O\text{-}t\text{-Bu})_6(py)(\mu\text{-}C_2D_2)$ which show the formation of the μ-H*CCD containing compound.

Observance of the Two Isomers of $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$. A variable-temperature $^{13}C\{^1H\}$NMR experiment was performed on a sample of $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ in toluene-d_8. At 20 °C only one resonance was observed at δ 137.42. Upon lowering the temperature to −35 °C, two resonances appear, representing the minor isomer, δ 167.38 with $^1J_{^{183}W-^{13}C}$ = 42.8 Hz, and the major isomer, δ 133.02 with $^1J_{^{183}W-^{13}C}$ = 46.1 Hz and $^1J_{^{183}W-^{13}C}$ = 33.4 Hz in an approximate ratio of 1:10. Returning to a temperature of 20 °C gives a time-average resonance at δ 137.42.

Crystallographic Studies. General operating facilities and listings of programs have been given previously.[16] Crystal data for the two compounds studied in this work are given in Table VIII.

$W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$. A small crystal fragment was selected and transferred to the goniostat by using standard inert-atmosphere handling techniques. The crystal was cooled to −156 °C. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibit orthorhombic symmetry and systematic extinctions consistent with the space group *Pcmn* or *Pc*2$_1$*n*. The choice of the noncentrosymmetric space group *Pc*2$_1$*n* was confirmed by the successful solution and refinement of the structure.

The structure was solved by the standard heavy-atom method. The two W atoms were located by means of direct methods, and the remaining atoms were located by means of a difference Fourier phased with the heavy atoms. Hydrogen atoms were introduced in calculated positions. Refinement of the structure was carried out by full-matrix least squares, using anisotropic thermal parameters for the two tungsten atoms and isotropic parameters for all other atoms. The chirality of the crystal studied was determined by refinement in the two possible settings before the introduction of the hydrogen atoms. Residuals for the two possible settings were 0.051 and 0.048, and the latter setting was used for the remainder of the refinement. The final residual $R(F)$ was 0.046 for 2947 reflections having $F > 3\sigma(F)$. A final difference Fourier was essentially featureless, the largest peaks were located close to the W atoms. Psi scans of several reflections indicated no absorption correction was necessary.

$W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$. A fragment was cleaved from a larger sample and transfered to the goniostat by using standard inert-atmosphere handling techniques. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima which were of monoclinic symmetry and appear to have only $0k0$, $k = 2n + 1$, as a condition for extinction. The apparent

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[16] (a) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755. (b) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

space group would then be either $P2_1/m$ or $P2_1$.

Data were collected for the entire copper sphere ($2\theta = 55°$). Direct methods (MULTAN 78) were first attempted in the centric space group, and a solution was obtained with the two W atoms lying in a mirror plane. The two peaks were also located in a Patterson syntheses. Refinement and Fourier techniques progressed normally, with all atoms in the pyridine and five neopentoxy ligands being easily located (with one apparently disordered OC_2CMe_3).

At this point it was noted that there was also an apparent disorder in the acetylenic ligand and also that several of the atoms did not "settle down" as would be expected. Since the Patterson map is consistent with either $P2_1$ or $P2_1/m$, an attempt was made to refine the structure in the noncentric setting. This proved to be the correct space group as the residuals rapidly decreased and the apparent disorder in the acetylenic ligand and bridging neopentoxy ligand were no longer present. In spite of resolving the disorder, it was difficult to obtain convergence because of the large correlations between similar atoms on either side of the molecular plane. It is to be noted in the tables provided in the supplementary material that several of the carbon atoms lie at unrealistic distances [the extreme being 1.80 for C(34)–C(35)]. While convergence may indeed have been obtainable at some stage, it was felt the increased precision would not justify the expense since the molecular parameters of interest were not shifting significantly. Although some of the hydrogen atoms were visible in a difference Fourier, no attempt was made to locate or refine them, instead using idealized fixed hydrogen contributions. Psi scans indicated no absorption correction was necessary.

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Registry No. $W_2(ONp)_6(py)_2$, 88608-50-8; $W_2(ONp)_6(py)(\mu$-$C_2Ph_2)$, 104872-65-3; $PhC{\equiv}CPh$, 501-65-5; $W_2(ONp)_6(py)(\mu$-$C_2Et_2)$, 104872-66-4; $EtC{\equiv}CEt$, 928-49-4; $W_2(ONp)_6(Py)_2(\mu$-$C_2H_2)$, 104779-53-5; $HC{\equiv}CH$, 74-86-2; $[(t$-$BuO)_3W{\equiv}CMe]_2$, 86669-24-1; $MeC{\equiv}CMe$, 503-17-3; $W_2(ONp)_6(py)_2(\mu$-$C_2Me_2)$, 104870-71-5; $W_3(\mu_3$-$CEt)(ONp)_9(py)$, 104779-54-6; $[(t$-$BuO)_3W{\equiv}CEt]_2$, 104779-55-7; $(t$-$BuO)_3W{\equiv}CPh$, 82228-87-3.

Supplementary Material Available: VERSORT and ORTEP drawings and complete listings of atomic positional parameters, anisotropic thermal parameters, bond distances, and bond angles (19 pages); listings of F_o and F_c values (42 pages). Ordering information is given on any current masthead page. The complete structural reports are available in microfiche form only from the Indiana University Library at 2.50 per copy. Request MSC Report No. 84040 for $W_2(ONp)_6(py)_2(\mu$-$C_2H_2)$ and 84029 for W_2-$(ONp)_6(py)(\mu$-$C_2Et_2)$.

Diamagnetic Isocyanide Complexes of Titanium, Zirconium, and Hafnium

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Isocyanide complexes of the type $Cp_2M(CO)(L)$ (Cp = η^5-cyclopentadienyl, L = *tert*-butyl isocyanide, M = Ti, Zr, Hf; L = 2,6-dimethylphenyl isocyanide, M = Ti, Zr; L = methyl isocyanide, M = Ti) and $(Ind)_2Ti(CO)(L)$ (Ind = η^5-indenyl, L = *tert*-butyl isocyanide) were prepared and characterized by their IR, ^1H and ^{13}C NMR, and mass spectra. These are the first examples of diamagnetic isocyanide complexes of group 4 elements. The crystal structure of $Cp_2Ti(CO)(CN$-t-$Bu)$ (1) was determined by X-ray diffraction using 1414 reflections that were refined to a final R index of 0.077. The crystals were monoclinic, space group $P2_1/c$, with unit cell parameters $a = 6.559$ (2) Å, $b = 14.236$ (3) Å, and $c = 16.631$ (4) Å, $\beta = 100.81$ (3)°, and $Z = 4$. The molecular structure is typical of compounds of the type Cp_2TiXY, with pseudotetrahedral geometry.

Introduction

Numerous examples of transition-metal isocyanide complexes now exist.[2] Surprisingly, however, no diamagnetic isocyanide complexes of group 4 metals are known.[3] This may be due to the tendency of isocyanide ligands to form polymeric or polynuclear products when treated with low-valent early transition-metal complexes. As part of our continuing program to synthesize and study the chemistry of low-valent group 4 metallocene derivatives, we have undertaken the development of synthetic routes to diamagnetic group 4 metallocene isonitrile complexes. In this paper we report on the synthesis and spectral properties of the first diamagnetic isocyanide complexes of group 4 metals and on the crystal structure of $Cp_2Ti(CO)(CN$-t-$Bu)$ (1).

Results and Discussion

When *tert*-butyl isocyanide was added to THF solutions of $Cp_2M(CO)_2$ (M = Ti, Zr and Hf)[4] at −78 °C and the solutions then allowed to slowly warm to ambient temperature, the isocyanide complexes 1–3 were obtained as pure, crystalline solids.

The crude reaction products (before crystallization) contained small amounts of the dicarbonyl starting materials. Experiments run in pentane or at higher tem-

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