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Reactions of the 12-Electron Alkoxide-Supported Tungsten Clusters $W_4(OR)_{12}$ (R = CH_2-i-Pr, CH_2-c-Pen) with Isocyanides, Nitriles, Nitric Oxide, and Alkynes. Comparison with the Reactivity of $W_2(OR)_6$ Compounds

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The reactions between $W_4(OR)_{12}$ compounds, where R = CH_2-i-Pr and CH_2-c-Pen, and the isonitriles RNC, where R = t-Bu, $PhCH_2$, and mesityl (2,4,6-$C_6H_2Me_3$), in hydrocarbon solvents at 22 °C yield the previously characterized μ_4-carbido clusters $W_4(\mu_4\text{-}C)(OR)_{14}$ by cleavage of the $C\equiv N$ bond. Under similar conditions, the $W_4(OR)_{12}$ clusters are inert to the nitriles $MeC\equiv N$ and $NC(CH_2)_5CN$ and to the internal alkynes $MeC\equiv CMe$ and $EtC\equiv CEt$. The reaction between $W_4(OR)_{12}$ compounds and nitric oxide in hydrocarbon solutions at 22 °C yields $[W(OR)_3(NO)(py)]_2$ compounds in the presence of pyridine. The latter compound, where R = CH_2-i-Pr, was characterized by an X-ray diffraction study. Crystal data for $[W(OCH_2\text{-i-Pr})_3(NO)(py)]_2\cdot 2CH_2Cl_2$ at −168 °C: $a = 9.559$ (2) Å, $b = 14.293$ (4) Å, $c = 17.435$ (4) Å, $\beta = 93.75$ (1)°, $Z = 8$, $d_{calcd} = 1.669$ g cm^{-3}, space group = $P2_1/c$. The molecule is centrosymmetric, and each tungsten atom is in an octahedral coordination environment. A pair of μ-OR bridges span a nonbonding W-to-W distance of 3.406 (1) Å. The W–N–O moiety is linear and the W–NO distance is short, 1.75 (1) Å, which together with the low value of ν(NO), 1568 cm^{-1}, are indicative of extensive W d_π-to-NO π^* back-bonding. These findings are compared with related reactions involving the dinuclear compounds $W_2(OR)_6$ ($M\equiv M$) where R = i-Pr, t-Bu, and $SiMe_2$(t-Bu).

Introduction

The dinuclear metal–metal triply-bonded compounds of formula $M_2(OR)_6$, where M = Mo or W and R = a bulky alkyl group (e.g., t-Bu or i-Pr)[1] or trialkylsilyl group (e.g., $SiMe_2$(t-Bu))[2] have proved to be versatile templates for the activation of unsaturated organic molecules. In their reactions with $C\equiv C$ and $C\equiv N$ functionalities, metathetic reactions have been observed leading to the formation of $(RO)_3W\equiv CR'$ and $(RO)_3W\equiv N$ compounds.[3] With $C\equiv O$ and $C\equiv NR'$, bridged compounds of formula $W_2(O\text{-t-Bu})_6(\mu\text{-CX})$ have been isolated (X = O, NR').[4]

The addition of the less sterically demanding alcohols, for example RCH_2OH, where R = i-Pr and c-Pen (Pen = pentyl), to $W_2(O\text{-t-Bu})_6$ leads to the formation of the tetranuclear butterfly clusters $W_4(OCH_2R)_{12}$.[5] It is of obvious interest to compare the reactivity of these 12-electron W_4^{12+}-containing clusters with their dinuclear $(W\equiv W)^{6+}$-containing counterparts. We have recently described the reactions between $W_4(OCH_2R)_{12}$ compounds and carbon monoxide which may lead to $W_4(\mu\text{-}C)^{14+}$-containing clusters by cleavage of the carbonyl C—O bond.[6] Competitive with $C\equiv O$ cleavage is the formation of spike-triangular clusters $W_4(\mu_4\text{-}CO)(CO)_2(OCH_2R)_{12}$.[7] Herein we report our studies of the reactivity of the 12-electron $W_4(OCH_2R)_{12}$ clusters (R = i-Pr, c-Pen) with isocyanides, nitriles, alkynes and nitric oxide.

Results and Discussion

Reactions with Isocyanides, $R'N\equiv C$, Where R′ = t-Bu, $PhCH_2$, and 2,4,6-$Me_3C_6H_2$ (Mesityl). The reactions between $W_4(OCH_2R)_{12}$ compounds (R = i-Pr, c-Pen) and the isocyanides R′NC (R′ = t-Bu, $PhCH_2$, 2,4,6-$Me_3C_6H_2$) in hydrocarbon solvents at 22 °C yield $W_4(\mu_4\text{-}C)(OCH_2R)_{14}$ compounds. The latter were obtained in ca. 25% yield based on tungsten and were identified by ^1H and ^{13}C NMR spectroscopy. Crystals of the $W_4(\mu_4\text{-}C)$-containing compound where R = c-Pen were examined by X-ray diffractometry and were found to have the same unit cell dimensions as the previously characterized carbido cluster derived from reactions employing carbon monoxide.[6b,c] Rather interestingly, reactions employing >3 equiv of the isocyanide ligand did not yield a $W_4(CNR)_3$-containing compound. No analogue of $W_4(\mu_4\text{-}CO)(CO)_2(OCH_2R)_{12}$ was detected.

Reactions Involving Alkynes and Nitriles. Attempted room-temperature reactions involving $W_4(OCH_2R)_{12}$ compounds (R = i-Pr, c-Pen) and the internal alkynes $MeC\equiv CMe$ and $EtC\equiv CEt$ led only to the recovery of the starting materials. Similarly, MeCN and $NC(CH_2)_5CN$ showed no reactivity toward the clusters $W_4(OCH_2R)_{12}$, even when the nitriles were present in a 5-fold excess. While it is possible that the failure of the reactions involving internal alkynes is due to steric factors, this cannot be the case for the nitriles. In this case, the lack of reactivity is believed to reflect the poorer ligating ability of these substrates. Thus, the ability of tetranuclear clusters to activate small molecules is greatly influenced by the donor properties of the substrates which follow the order isonitriles ≥ carbon monoxide > nitriles.

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(1) (a) Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J.; Hoffman, D. M. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 432. (b) Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Hampden-Smith, M. J.; Huffman, J. C.; Folting, K.; Ellis, P.; Huggins, B. A. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1523. (c) Chisholm, M. H.; Lucas, E. A.; Sousa, A. C.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1991,** 847. (d) Chisholm, M. H.; Lucas, E. A.; Lubkovsky, E. B. *Organometallics* **1991,** *10,* 3424. (e) Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Huffman, J. C. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 1026.

(2) Chisholm, M. H.; Cook, C.; Huffman, J. C.; Streib, W. C. *J. Chem. Soc., Dalton Trans.* **1991,** 929.

(3) (a) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982,** *104,* 4291. (b) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985,** *4,* 74. (c) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Chem. Soc. Rev.* **1984,** *8,* 69.

(4) (a) X = O: Blower, P. J.; Chisholm, M. H.; Clark, D. L.; Eichhorn, B. W. *Organometallics* **1986,** *5,* 2125. (b) X = NR: Chisholm, M. H.; Clark, D. L.; Ho, D.; Huffman, J. C. *Organometallics* **1987,** *6,* 1532.

(5) Chisholm, M. H.; Folting, K.; Hammond, C. E.; Hampden-Smith, M. J.; Moodley, K. G. *J. Am. Chem. Soc.* **1989,** *111,* 5300.

(6) (a) Chisholm, M. H.; Folting, K.; Hampden-Smith, M. J.; Hammond, C. E. *J. Am. Chem. Soc.* **1989,** *111,* 7283. (b) Chisholm, M. H.; Hammond, C. E.; Huffman, J. C.; Johnston, V. J. *J. Organomet. Chem.* **1990,** *394,* C16. (c) Chisholm, M. H.; Hammond, C. E.; Huffman, J. C.; Streib, W. E.; Johnston, V. J. *J. Am. Chem. Soc.*, submitted for publication.

(7) Chisholm, M. H.; Folting, K.; Johnston, V. J.; Hammond, C. E. *J. Organomet. Chem.* **1990,** *394,* 265.

0020-1669/92/1331-4081$03.00/0

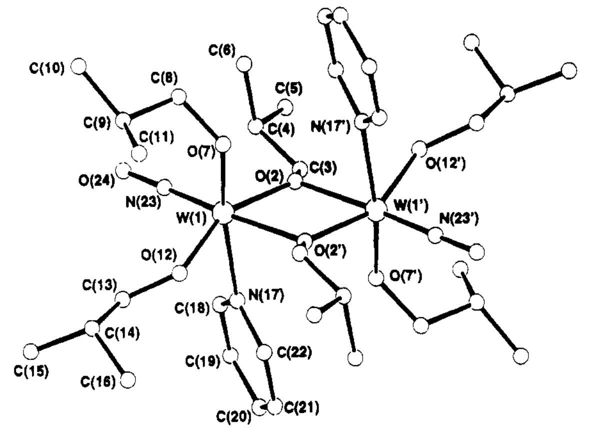

Figure 1. Ball-and-stick drawing of the centrosymmetric $[W(OCH_2$-c-$Pr)_3(NO)(py)]_2$ molecule giving the atom number scheme used in the tables. The disorder for C(4) and C(4)′ is not shown.

The activated nitrile $Me_2NC{\equiv}N$ has been found to react with $W_4(OCH_2R)_{12}$ compounds, but the nature of the adduct (product) has not yet been determined. A parallel may be found in the reactivity of R_2NCN vs RCN with $Mo_2(OR)_6$ compounds.[8] The enhanced nucleophilic character of the former allows for the isolation of the kinetically labile 1:1 adducts [e.g., $Mo_2(OCH_2CMe_3)_6(\mu\text{-}\eta^1,\eta^2\text{-}NCNMe_2)$], while the latter were found to be totally unreactive.

Terminal alkynes do show some reactivity with $W_4(OCH_2R)_{12}$ compounds, but these reactions are complicated by rapid alkyne polymerization. Further studies of these reactions are in progress.

Reactions Involving Nitric Oxide. $W_4(OCH_2$-i-$Pr)_{12}$ and NO (4 equiv) react in hydrocarbon solvents in the presence of pyridine to give the nitrosyl compound $[W(OCH_2$-i-$Pr)_3(NO)(py)]_2$, which has been fully characterized (^1H NMR, $^{13}C\{^1H\}$ NMR, IR, X-ray). When the reaction is carried out in neat pyridine, the uptake of substrate is suppressed, presumably by reversible coordination of pyridine to the cluster. In this case, there is evidence for the formation of an oxotungsten alkoxide as a minor byproduct of the reaction. The exact nature of this compound is not known, but it is apparently the same oxo alkoxide as is formed in the reactions between $W_4(OCH_2R)_{12}$ compounds and CO, Me_2SO, pyO, and O_2 (1 equiv).[6c] The details of this minor reaction remain to be investigated. Suffice it to state that the major product of the reaction in pyridine and the only product when the reaction is carried out in hydrocarbon solvents in the presence of pyridine is the nitrosyl compound, $[W(OCH_2R)_3(py)NO]_2$.

Solid-State and Molecular Structure of $[W(OCH_2$-i-$Pr)_3(NO)(py)]_2$. An ORTEP drawing of the molecule is given in Figure 1 along with the atom number scheme. Atomic coordinates are given in Table I, and a summary of crystal data is given in Table II. Selected bond distances and angles are given in Table III.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for $[W(OCH_2$-i-$Pr)_3(py)(NO)]_2{\cdot}2CH_2Cl_2$

atom	10^4x	10^4y	10^4z	$10B_{iso}$ (Å^2)
W(1)	3738.4 (4)	3975.2 (3)	4490.5 (2)	13
O(2)	4122 (6)	10053 (4)	5521 (3)	13
C(3)	3157 (10)	10484 (7)	6019 (6)	21 (2)
C(4)	2005 (18)	9910 (13)	6273 (10)	9 (3)
C(4)′	2826 (25)	9910 (7)	6684 (14)	29 (4)
C(5)	1451 (16)	10471 (11)	6996 (9)	54 (3)
C(6)	2383 (11)	8937 (8)	6578 (6)	22 (2)
O(7)	4707 (7)	8256 (5)	4781 (4)	17
C(8)	4150 (12)	7338 (8)	4867 (6)	25
C(9)	3732 (11)	6864 (8)	4118 (6)	25
C(10)	3193 (12)	5878 (8)	4267 (7)	29
C(11)	4949 (13)	6862 (9)	3593 (7)	33
O(12)	3764 (7)	9238 (5)	3399 (4)	17
C(13)	2569 (10)	9135 (7)	2876 (6)	20
C(14)	2924 (11)	8743 (8)	2108 (6)	20
C(15)	1574 (11)	8617 (8)	1605 (6)	23
C(16)	3932 (12)	9345 (9)	1719 (6)	29
N(17)	2979 (8)	10809 (5)	4119 (4)	15
C(18)	1742 (10)	11166 (7)	4297 (6)	22
C(19)	1291 (10)	12038 (8)	4103 (6)	23
C(20)	2117 (11)	12611 (8)	3692 (6)	22
C(21)	3349 (11)	12262 (8)	3462 (6)	22
C(22)	3670 (10)	11370 (7)	3689 (6)	17
N(23)	2016 (9)	8998 (6)	4597 (5)	18
O(24)	787 (7)	8757 (5)	4671 (4)	24
C(25)	−930 (14)	6966 (9)	4001 (7)	38
Cl(26)	−1003 (4)	5983 (2)	4613 (2)	41
Cl(27)	−425 (5)	6653 (3)	3091 (2)	58

Table II. Summary of Crystal Data for $[W(OCH_2$-i-$Pr)_3(py)(NO)]_2{\cdot}2CH_2Cl_2$

empirical formula	$C_{34}H_{64}N_4O_8W_2{\cdot}2CH_2Cl_2$	V(Å^3)	2377.00
		Z	8
space group	$P2_1/c$	d_{calcd} (g/cm^3)	1.669
T (°C)	−168	wavelength (Å)	0.710 69
a (Å)	9.559 (2)	mol wt	597.23
b (Å)	14.293 (4)	μ (cm^{-1})	52.129
c (Å)	17.435 (4)	$R(F_o$ or $F_o^2)$	0.0392
β (deg)	93.75 (1)	$R_w(F_o$ or $F_o^2)$	0.0376

Table III. Selected Bond Distances (Å) and Angles (deg) for the $[W(OCH_2$-i-$Pr)_3(NO)(py)]_2$ Molecule

W(1)–O(2)	2.054 (6)	W(1)–O(12)	1.915 (6)
W(1)–O(2)′	2.204 (6)	W(1)–N(17)	2.255 (8)
W(1)–O(7)	1.900 (7)	W(1)–N(23)	1.753 (9)
O(2)–W(1)–O(2)′	73.78 (26)	O(7)–W(1)–N(23)	99.1 (3)
O(2)′–W(1)–O(7)	83.01 (25)	O(12)–W(1)–N(17)	80.3 (3)
O(2)–W(1)–O(7)	96.20 (26)	O(12)–W(1)–N(23)	98.4 (3)
O(2)′–W(1)–O(12)	87.51 (25)	N(17)–W(1)–N(23)	91.3 (3)
O(2)–W(1)–O(12)	154.81 (27)	W(1)–O(2)–W(1)′	106.22 (26)
O(2)′–W(1)–N(17)	86.67 (25)	W(1)–O(2)–C(3)	130.0 (5)
O(2)–W(1)–N(17)	81.85 (26)	W(1)′–O(2)–C(3)	118.5 (5)
O(2)′–W(1)–N(23)	173.3 (3)	W(1)–O(7)–C(8)	128.6 (6)
O(2)–W(1)–N(23)	99.6 (3)	W(1)–O(12)–C(13)	125.9 (6)
O(7)–W(1)–O(12)	98.12 (28)	W(1)–N(23)–O(24)	178.2 (8)
O(7)–W(1)–N(17)	169.63 (27)		

The molecule is centrosymmetric, and each tungsten atom is in a distorted octahedral environment. The halves of the molecule are united by a pair of bridging ligands that span a nonbonding W-to-W distance of 3.4 Å. The $W_2(\mu\text{-}O)_2$ moiety has asymmetric bridges, W–O = 2.20 (1) and 2.05 (1) Å, corresponding to the bonds that are trans to nitrosyl and alkoxide ligands, respectively. The difference in M–μ-O distance reflects the differing trans influence[9] of the ligands: NO > OR. The W–OR(terminal) distances are 1.90 (1) and 1.915 (6) Å, typical of terminal W–OR distances.[10] The W–N(nitrosyl) distance of 1.75 (1) Å is short and, taken together with the value of $\bar{\nu}(NO) = 1568\ cm^{-1}$, provides evidence of extensive W d_π-to-NO π^* back-bonding and a significant contribution from the valence bond description $W{\equiv}N{\rightarrow}O$. In all aspects, the structure is similar to that previously reported for $[Mo(O$-i-$Pr)_3(NO)(HNMe_2)]_2$.[11]

Solution Behavior of $[W(OCH_2$-i-$Pr)_3(NO)(py)]_2$. At room temperature in CD_2Cl_2, the compound is fluxional and only broad unresolved resonances are observed in the 300-MHz ^1H NMR spectrum. At −50 °C, however, the exchange process is slow relative to the ^1H NMR time scale, and the spectrum obtained is consistent with expectations based on the centrosymmetric structure found in the solid state. There are, however, several other signals present (<2% total) that may arise from other isomeric species. A plausible interpretation of the dynamic behavior may involve an equilibrium of the type

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(8) Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. *Organometallics* **1987**, *6*, 1073.

(9) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1972**, *10*, 352.

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

(11) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *Inorg. Chem.* **1980**, *19*, 2762.

The mononuclear $W(OCH_2\text{-i-Pr})_3(NO)(py)$ compound would be an analogue of $W(O\text{-t-Bu})_3(NO)(py)$.[12]

Concluding Remarks

The dinuclear compounds $W_2(OR)_6$ ($M{\equiv}M$) and their dimers, the 12-electron clusters $W_4(OR)_{12}$, show remarkably different, though in some ways complementary, chemistry. (1) With carbon monoxide and isocyanide, the dinuclear compounds form 1:1 adducts wherein the substrate bridges the two metal atoms. The tetranuclear compounds form 1:1 adducts of transient persistence being labile to cleavage of the $C{\equiv}X$ bond (X = O or NR). (2) With alkynes and nitriles, the $W_2(OR)_6$ compounds often yield products of $W{\equiv}W$ and RÇ$\equiv$X (X = N, CR) metathesis. In contrast, the $W_4(OR)_{12}$ compounds are notably unreactive toward nitriles and internal alkynes. It appears that the tungsten atoms in the $W_4(OR)_{12}$ compounds are less Lewis acidic, and for this reason (and perhaps for steric reasons as well) they are less reactive than their $W_2(OR)_6$ counterparts toward weakly basic substrates such as nitriles and internal alkynes. (3) With nitric oxide, both $W_2(OR)_6$ and $W_4(OR)_{12}$ compounds react as $W(OR)_3$ sources in the formation of $W(OR)_3(NO)(py)$ compounds. We discount the possibility that $W_4(OCH_2R)_{12}$ compounds (R = c-Pen, i-Pr) are in equilibrium with $W_2(OCH_2R)_6$ compounds (as is seen for $W_4(O\text{-i-Pr})_{12}$ and $W_2(O\text{-i-Pr})_6$)[13] because $W_4(OCH_2R)_{12}$ compounds do not react with $Me_2PCH_2PMe_2$ to give $W_2(OCH_2R)_6(Me_2PCH_2PMe_2)$. The latter are rapidly formed in reactions between $W_2(OCH_2R)_6$ and $Me_2PCH_2PMe_2$ and are kinetically inert with respect to formation of $W_4(OCH_2R)_{12}$.

Further studies of the reactivity of $W_4(OR)_{12}$ compounds are in progress.

Experimental Section

All manipulations were carried out using standrd Schlenk or inert-atmosphere drybox techniques. Hexane and toluene were distilled over sodium benzophenone ketyl and stored under nitrogen prior to use. Anhydrous pyridine was purchased from Aldrich and used as received. $W_4(OCH_2\text{-c-Pen})_{12}$ (**1**) and $W_4(OCH_2\text{-i-Pr})_{12}$ (**2**) were prepared by the published method.[5]

NMR spectra were recorded on a Varian XL-300 spectrometer. Infrared spectra were recorded on a Nicolet 510P FT-IR instrument. Microanalyses were performed by Oneida Research Services.

Reaction of $W_4(OCH_2\text{-c-Pen})_{12}$ with $CNCH_2C_6H_5$. $W_4(OCH_2\text{-c-Pen})_{12}$ (140 mg, 0.073 mmol) and pyridine (15 mL) were placed in a small Schlenk flask. Benzyl isocyanide (10 μL, 0.07 mmol) was added with a syringe and the solution stirred at room temperature for about 18 h. At this point a significant amount of fine, dark-green precipitate was observed on the walls of the flask. About half of the solvent was removed in vacuo, and the flask was cooled to −20 °C for 2 h. The solution was filtered through a glass frit, and the green precipitate was collected and recrystallized from CH_2Cl_2. It was identified as $W_4(C)(OCH_2\text{-c-Pen})_{14}$ (25%) on the basis of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In addition, the unit cell of a crystal matched that found for $W_4(C)(OCH_2\text{-c-Pen})_{14}$ prepared from **1** and CO. Similar results were obtained for experiments employing t-BuNC and 2,4,6-$Me_3C_6H_2NC$ and **2**.

Attempted Reactions of 2 with Internal Alkynes and Nitriles. A solution of **2** (155 mg, 0.096 mmol) in pyridine (20 mL) was degassed by three freeze–pump–thaw cycles. 2-Butyne (≥1 equiv) was condensed into the flask from a calibrated manifold. The solution was warmed to room temperature and stirred for 24 h. At this point, the volatiles were removed in vacuo and the residue was taken up in C_6D_6. The ^1H and $^{13}C\{^1H\}$ NMR spectra contained only the resonances due to **2**. Similar results were obtained for $EtC{\equiv}CEt$, $t\text{-BuC}{\equiv}CMe$, MeCN, and $NC(CH_2)_5CN$.

Reaction of 2 with NO. **2** (210 mg, 0.130 mmol) was placed in a Schlenk flask. Hexane (20 mL) and pyridine (5 mL) were added, and the solution was degassed by two freeze–pump–thaw cycles. NO (0.52 mmol) was introduced from a calibrated manifold, and the solution was warmed to room temperature and stirred. The color of the solution changed from dark purple to pale orange-yellow over about 1 h. After about 20 h, the volatiles were removed on the vacuum line to leave a yellow oil. Crystallization from CH_2Cl_2 afforded $[W(NO)(OCH_2\text{-i-Pr})_3(py)]_2$ (183 mg, 0.20 mmol, 77%). Anal. Calcd for $W_2C_{34}H_{54}N_2O_8$: C, 41.40; H, 5.48; N, 5.68. Found: C, 38.67; H, 5.69; N, 5.63.

^1H NMR (−50 °C, CD_2Cl_2), (δ: OCH_2CHMe_2 4.87 (2 H, d × d, J_{H-H} = 9 and 6 Hz), 4.47 (2 H, d × d, J_{H-H} = 7 and 11 Hz), 4.39 (2 H, d × d, J_{H-H} = 7 and 11 Hz), 4.15 (2 H, t, J_{H-H} = 9 Hz), 3.75 (2 H, d × d, J_{H-H} = 8 and 11 Hz), 3.59 (2 H, d × d, J_{H-H} = 6 and 10 Hz); OCH_2CHMe_2 2.44 (2 H, m), 1.35 (4 H, m); OCH_2CHMe_2 1.11 (6 H, d, J_{H-H} = 6 Hz), 0.94 (6 H, d, J_{H-H} = 6 Hz), 0.61 (6 H, d, J_{H-H} = 8 Hz), 0.58 (6 H, d, J_{H-H} = 6 Hz), 0.56 (6 H, d, J_{H-H} = 6 Hz), 0.49 (6 H, d, J_{H-H} = 7 Hz); C_5H_5N 8.73 (4 H, m), 7.94 (2 H, m), 7.52 (4 H, m).

IR (KBr pellet), cm^{-1}: 2966 s, 2871 s, 2830 m, 1608 m, 1568 vs, 1489 w, 1468 m, 1458 m, 1444 s, 1385 m, 1362 m, 1262 m, 1221 m, 1065 vs, 1048 vs, 1016 sh, 1009 vs, 822 m, 802 m, 762 m, 700 s, 683 m, 658 m, 640 m, 625 m, 556 m, 496 m.

Preparation of $W_2(OCH_2\text{-i-Pr})_6(dmpm)$. (Dimethylphosphino)methane dmpm, 32 μL, 0.22 mmol) was added to a room-temperature solution of $W_2(O\text{-t-Bu})_6$ (170 mg, 0.211 mmol) in hexane (10 mL). The solution was stirred for 5 min. Excess isobutanol (0.4 mL) was added to the solution, and the reaction mixture was stirred for an additional 5 min. The volatiles were removed on the vacuum line, and the resulting dark-red residue was dissolved in a minimum amount of hexane. The solution was cooled to −20 °C, and crystalline $W_2(OCH_2\text{-i-Pr})_6(dmpm)$ was isolated in 45% yield. Anal. Calcd for $C_{29}H_{68}O_6P_2W_2$: C, 36.96; H, 7.22. Found: C, 36.44; H, 7.05.

^1H NMR (C_6D_6, 22 °C), δ: OCH_2CHMe_2 4.89 (d, J_{H-H} = 5.1 Hz, 4 H), 4.45 (d × d, J_{H-H} = 6.3 and 9.0 Hz, 4 H), 4.38 (d × d, J_{H-H} = 6.3 and 9.6 Hz, 4 H); OCH_2CHMe_2 2.19 (m); OCH_2CHMe_2 and $Me_2PCH_2PMe_2$ overlapping doublets 1.32–1.16; $MePCH_2PMe_2$ 2.37 (t, $J_{^{31}P-^{1}H}$ = 10.2 Hz).

$^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C), δ: OCH_2CHMe_2 81.5 (2 C), 80.4 (4 C); OCH_2CHMe_2 33.1 (2 C), 32.8 (4 C); OCH_2CHMe_2 20.0; $Me_2PCH_2PMe_2$ 41.4 (t, $J_{^{31}P-^{13}C}$ = 99 Hz); $Me_2PCH_2PMe_2$ 14.8.

Attempted Reaction of $W_4(OCH_2\text{-i-Pr})_{12}$ with dmpm. A Schlenk flask was charged with $W_4(OCH_2\text{-i-Pr})_{12}$ (193 mg, 0.12 mmol), hexane (10 mL), and dmpm (20 μL, 0.13 mmol). The solution was stirred at room temperature for 20 h, after which the volatiles were removed in vacuo. The resulting dark purple residue was dissolved in C_6D_6, and the ^1H NMR spectrum revealed only unreacted **2**.

X-ray Crystallographic Analysis of $[W(NO)(OCH_2\text{-i-Pr})_3(py)]_2{\cdot}CH_2Cl_2$. General procedures and descriptions of the equipment and programs used habe been given previously.[14] Specific details are given below and in Table II. Final atomic coordinates are listed in Table I, and complete structural details are included in the supplementary material.

The data were collected at −168 °C and showed no indication of decay. Because of the irregular shape of the crystal, no absorption correction was applied. The $[W(NO)(O\text{-i-Bu})_3(py)]_2$ molecule lies on an inversion center of the space group $P2_1/c$, and the CH_2Cl_2 solvate is in a general position (there are no significant contacts between these groups). The methinic carbon atom of the bridging O-i-Bu ligand suffers from disorder, which was modeled by refining two half-occupancy atoms, namely C(4) and C(4)′. All carbon atoms of this group were refined with isotropic thermal parameters, and all other non-hydrogen atoms were given anisotropic thermal parameters. Hydrogen atoms, except those associated with the disordered ligand, were included as fixed atom contributions at calculated positions.

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Supplementary Material Available: Tables of crystal data collection parameters, anisotropic thermal parameters, and complete non-H bond distances and bond angles and VERSORT drawings (9 pages). Ordering information is given on any current masthead page.

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(12) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 116.

(13) Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 574.

(14) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.