J. Am. Chem. Soc. 1992, 114, 7056-7065

Reductive Cleavage of Carbon Monoxide to Carbide and Oxide by Ditungsten and Tetratungsten Alkoxides. Crystal and Molecular Structures of $W_4(\mu_4\text{-}C)(OCH_2\text{-c-Pen})_{14}$, $W_4(\mu_4\text{-}C)(O)(OCH_2\text{-}t\text{-Bu})_{12}$, and $W_4(\mu_4\text{-}C)(O)(O\text{-}i\text{-Pr})_{12}$[1]

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Abstract: Two synthetic strategies for the reductive cleavage of $C\equiv O$ to carbide and oxide ligands have been explored. Both were successful but both had competing side reactions. (1) Addition of CO (1-3 equiv) to $W_4(OCH_2\text{-c-Pen})_{12}$, where Pen = pentyl, leads to the formation of three carbonyl derived products, $W_4(\mu_4\text{-}C)(OCH_2\text{-c-Pen})_{14}$ (I), $W_4(\mu_4\text{-}CO)(CO)_2(OCH_2\text{-c-Pen})_{12}$ (II), and an oxo–tungsten alkoxide. The formation of I occurs by C–O bond cleavage even at −30 °C in toluene-d_8. Reactions employing labeled CO indicate the C–O bond cleavage occurs prior to oxo/alkoxide exchange in the formation of I. The formation of II is favored in the presence of an excess of CO, and the isobutoxide analogue, $W_4(\mu_4\text{-}CO)(CO)_2(OCH_2\text{-}i\text{-Pr})_{12}$, has been structurally characterized and shown to contain a bridging carbonyl ligand that is carbon bonded to three tungsten atoms and oxygen bonded to one. Compounds II (R = CH_2-c-Pen, CH_2-*i*-Pr) are not directly involved in the formation of carbides such as I. (2) The reaction between $W_2(\mu\text{-}CO)(O\text{-}t\text{-Bu})_6$ and $W_2(O\text{-}t\text{-Bu})_6$ in the presence of an excess of alcohol yields $W_4(\mu_4\text{-}C)(O)(OR)_{12}$ where R = CH_2-*t*-Bu (III) and *i*-Pr (IV). Competing with the formation of the carbido compounds, III and IV, are reactions leading to $W_4(\mu\text{-}CO)_2(OR)_{12}$ and $W_4(OR)_{12}$. The compounds I, III, and IV have been characterized by single-crystal X-ray crystallography and are closely related in having a common $W_4(\mu_4\text{-}C)^{14+}$ template. The structures differ only in the identity of R and the position of the μ_2-oxo group or its replacement by a pair of OR ligands. These reactions are the first examples of the cleavage of carbon monoxide to carbide and oxide ligands in a molecular system. These findings are compared to other reactions that are known to yield products derived from cleavage of $C\equiv O$ and, in particular, to the cleavage of $C\equiv O$ on certain metal surfaces that generates surface bound carbide and oxide as in the Fischer–Tropsch reaction.

Introduction

Reactions requiring multielectron redox processes would seem well suited to dinuclear or polynuclear complexes. For example, the reductive cleavage of $C\equiv C$, $C\equiv N$, or $C\equiv O$ surely cannot be achieved by one metal alone, but two or more metal atoms working in concert can have greater success. The work of Wolczanski and co-workers[2] showed that the early transition metal d^2-Ta(3+) complex $(\text{silox})_3Ta$, where silox = $(t\text{-Bu})_3SiO$, reacts with $C\equiv O$ to give $(\text{silox})_3TaO$ and $(\text{silox})_3TaCCTa(\text{silox})_3$ by a circuitous route. All the available evidence suggests that C–C bond formation occurs prior to C–O bond cleavage and that bimolecular pathways involving tantalum are involved for the reaction stoichiometry shown in eq 1.

$$4[(\text{silox})_3Ta] + 2CO \rightarrow 2[(\text{silox})_3TaO] + [(\text{silox})_3TaCCTa(\text{silox})_3] \tag{1}$$

In our development of the dinuclear chemistry of molybdenum and tungsten, we have found that $C\equiv O$ adds to a $(M\equiv M)^{6+}$ center to form $M_2(\mu\text{-}CO)$ containing compounds that have very low $\nu(CO)$ values, ca. 1570 (M = W) and 1640 cm^{-1} (M = Mo).[3] The compounds may be viewed as inorganic analogues of cyclopropenones. Since aldehydes and ketones are known to react with $W_2(OR)_6$ compounds to give alkylidene–oxo ditungsten complexes,[4] an obvious synthetic strategy leading to the stepwise reductive cleavage of $C\equiv O$ is shown in reaction sequence 2.

$$M\equiv M + C\equiv O \rightarrow M{=}M(\mu\text{-}C{=}O) \tag{2a}$$

$$M\equiv M + M{=}M(\mu\text{-}C{=}O) \rightarrow M_4(C)(O) \tag{2b}$$

An alternative approach is to start with a tetranuclear alkoxide cluster, one that is formed from the coupling of two $(W\equiv W)^{6+}$ units,[5] and offer the cluster *one* equivalent of $C\equiv O$, eq 3.

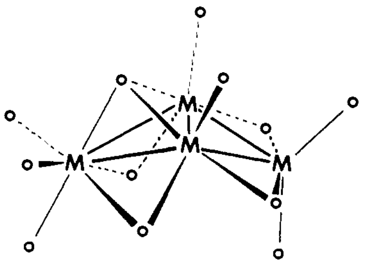
$$2[M\equiv M] \rightarrow M_4 \tag{3i}$$

$$M_4 + C\equiv O \rightarrow M_4(C)(O) \tag{3ii}$$

We report here our findings based on these considerations. Preliminary reports of certain aspects of this work have appeared.[6]

Results and Discussion

Synthesis. (a) $W_4(OR)_{12}$ + CO. The reactions between $W_4(OR)_{12}$ compounds and CO have been studied where R = CH_2-*i*-Pr, CH_2-c-Pr, CH_2-c-Bu, CH_2-c-Pen (Pen = pentyl), and CH_2-c-Hex (Hex = hexyl). This grouping of $W_4(OR)_{12}$ compounds share a common W_4O_{12} skeleton shown in A.[5]



A

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These reactions have been studied by ^{13}C NMR spectroscopy in NMR tubes employing ^{13}CO and mixtures of ^{13}CO and $^{13}C^{18}O$. Qualitatively, these reactions proceed similarly, but only for the alkoxides CH_2-c-Pen and CH_2-*i*-Pr have these reactions been studied in a quantitative manner.

The addition of C≡O (1 equiv) to $W_4(OCH_2\text{-c-Pen})_{12}$ in neat pyridine at room temperature yields the carbido cluster $W_4(\mu_4\text{-C})(OCH_2\text{-c-Pen})_{14}$ (I) as dark green crystals. The isolated yield of I is close to 50% based on tungsten. Related carbido tungsten clusters have been isolated for the alkoxides OCH_2-*i*-Bu, OCH_2-*i*-Pr, and OCH_2-c-Hex. These compounds are air-sensitive and hydrocarbon-soluble but less soluble in pyridine and methylene chloride.

If the addition of C≡O to $W_4(OR)_{12}$ compounds is carried out at room temperature in a hydrocarbon solvent, specifically hexane, benzene, or toluene, the compounds $W_4(\mu_4\text{-C})(OR)_{14}$ are formed, but in competition with the tricarbonyl compounds $W_4(\eta^2,\mu_4\text{-CO})(CO)_2(OR)_{12}$. This necessitates fractional crystallizations, and the isolation of either compound in a pure form is achieved laboriously. Inspection of the structure of the $W_4(OR)_{12}$ clusters with the W_4O_{12} skeleton shown in A indicates that *three* tungsten atoms are coordinatively unsaturated and the structure of the related compound $Mo_4(OCH_2\text{-c-Bu})_{12}(HOCH_2\text{-c-Bu})$[5] confirms the ability of neutral ligands to gain access to the metal atoms. We suggest that the use of pyridine as a solvent suppresses the uptake of CO at the W_4 center by reversible ligation, and thus favors the formation of $W_4(\mu_4\text{-C})(OR)_{14}$ over $W_4(\eta^2,\mu_4\text{-CO})(CO)_2(OR)_{12}$.

The optimum condition for the preparation of the tricarbonyl compounds involves the reaction between the $W_4(OR)_{12}$ compounds and CO (3–4 equiv) at 0 °C in hexane or toluene. This reaction has been observed to be virtually quantitative for R = CH_2-*i*-Pr and CH_2-c-Pen. The compounds $W_4(\eta^2,\mu_4\text{-CO})(CO)_2(OR)_{12}$ (II), are also dark-green, extremely hydrocarbon-soluble, air-sensitive materials.[7] They are thermally unstable in solution over a period of 2–3 days at room temperature, and on decomposition the only carbonyl-containing product that is formed (as determined by ^{13}C NMR spectroscopy) is $W(CO)_6$.[8] The compounds II are not involved in the synthesis of the carbido clusters I but rather are formed in competition with I by facile uptake of CO.

The formation of I in the reaction between $W_4(OR)_{12}$ and CO raises the question of the fate of the carbonyl oxygen atom. After crystallization of dark green I from pyridine or methylene chloride solutions, the filtrate is red-brown. Further crystallization from this mother liquor has only yielded smaller quantities of I. When the solvent is removed from the mother liquor a red-brown solid is obtained. The ^1H and $^{13}C\{^1H\}$ NMR spectra of this residue show the presence of one type of OR group. When $C^{17}O$ was employed, we observed by ^{17}O NMR spectroscopy a signal at δ 762 (relative to $H_2{}^{17}O$) assignable to an oxo tungsten moiety.[9] The line width, $W_{1/2}$ = 170 Hz, precluded the measurement of $J_{^{183}W-^{17}O}$. We propose the residue to be an oxo alkoxide of tungsten of, as yet, unknown formula. Repeated attempts to crystallize this compound have been unsuccessful. However, an equivalent ^{17}O signal can be seen in the ^{17}O NMR spectra of reactions between $W_4(OCH_2\text{-c-Pen})_{12}$ and $^{17}O_2$ (1 equiv) in pyridine at room temperature.

(b) $W_2(\mu\text{-CO})(OR)_6$ + $W_2(OR)_6$. When R = *i*-Pr, a tetranuclear $W_4(OR)_{12}$ compound is known to be in equilibrium with $W_2(O\text{-}i\text{-Pr})_6$.[10] For R = CH_2-*t*-Bu the dinuclear compound $W_2(OCH_2\text{-}t\text{-Bu})_6$ is known, which slowly and apparently irreversibly dimerizes to $W_4(OR)_{12}$, a compound of unknown structure.[5,11] These tetranuclear compounds (R = *i*-Pr and CH_2-*t*-Bu) behave differently in their reactions with CO from those described above. We do observe some cleavage of C≡O in reactions involving the neopentoxide cluster, but this does not give a high yield of a tetranuclear carbido compound. For the isopropoxide derivative we cannot be sure whether or not the reactions involve the cluster or the dinuclear compound because of the aforementioned equilibrium.

The optimum preparation of $W_4(\mu_4\text{-C})(O)(O\text{-}i\text{-Pr})_{12}$ (IV) involves the slow addition of a solution of $W_2(\mu\text{-CO})(O\text{-}t\text{-Bu})_6$ to a hydrocarbon solution of $W_2(O\text{-}i\text{-Pr})_6/W_4(O\text{-}i\text{-Pr})_{12}$ at room temperature in the presence of an excess of *i*-PrOH. Thus as the $W_2(\mu\text{-CO})(O\text{-}t\text{-Bu})_6$ enters the reaction vessel it is both alcoholyzed and allowed to react with the reactive $W_2(O\text{-}i\text{-Pr})_6$ molecule. This suppresses the dimerization of $W_2(\mu\text{-CO})(O\text{-}i\text{-Pr})_6$ that gives $W_4(\mu\text{-CO})_2(O\text{-}i\text{-Pr})_{12}$.[3c]

The preparation of $W_4(\mu_4\text{-C})(O)(OCH_2\text{-}t\text{-Bu})_{12}$ (III) may be achieved in a one-pot reaction involving a hydrocarbon solution of $W_2(O\text{-}t\text{-Bu})_6$, excess neopentanol, and $^1/_2$ equiv of CO. Here the formation of $W_4(OCH_2\text{-}t\text{-Bu})_{12}$ and $W_4(\mu\text{-CO})_2(OCH_2\text{-}t\text{-Bu})_{12}$[3c] compete, and compound III is obtained by fractional crystallization. This process has allowed separation of III from $W_4(\mu\text{-CO})_2(OCH_2\text{-}t\text{-Bu})_{12}$, but some $W_4(OCH_2\text{-}t\text{-Bu})_{12}$ is always present in our bulk samples of III.

Compounds III and IV are green, hydrocarbon-soluble, air-sensitive, and crystalline.

Compound I, where R = CH_2-c-Pen, can be prepared in a similar manner, namely by the addition of $^1/_2$ equiv of CO to a hydrocarbon solution of $W_2(O\text{-}t\text{-Bu})_6$ followed by addition of excess c-PenCH_2OH.

^{13}C NMR Studies. The formation of compounds I in the reactions between CO and $W_4(OR)_{12}$ raises the following question: At what time in the reaction does carbonyl C–O bond cleavage occur? Specifically, does C–O bond cleavage precede the intermolecular reaction whereby alkoxide/oxygen atom exchange occurs? Fortunately, ^{13}C NMR spectroscopy is of great assistance here. Firstly, the use of ^{13}CO allows the preparation of carbides that are enriched exclusively at the carbido carbon atom and this allows for easy identification of what might otherwise be a difficult signal to detect. Second, at 98% enrichment from ^{13}CO, we can observe the satellite spectra due to the presence of ^{183}W, $I = {}^1/_2$, 14.5% natural abundance. This provides information concerning the symmetry of the cluster. Representative ^{13}C signals for the carbido carbon atoms in I, III, and IV are shown in Figure 1. It is interesting to note that for the oxo–carbido compounds III and IV, the chemical shift of the carbido group is at ca. δ 350, whereas for compounds I the signal appears in the range δ 366–368. In any event, the signals arising from the carbido carbon atoms are downfield from those associated with carbonyl ligands—although for the compounds $W_4(\mu\text{-CO})_2(OR)_{12}$, where R = *i*-Pr and CH_2-*t*-Bu, the signals for the μ-CO ligand are extremely deshielded (δ 313 for R = CH_2-*t*-Bu).[3c]

In an attempt to follow the course of the C–O cleavage reaction, we have monitored NMR tube reactions containing toluene-d_8 solutions of the cluster $W_4(OCH_2\text{-c-Pen})_{12}$ and 1 equiv of ^{13}CO. At −78 °C there was no evidence of any reaction over a period of 24 h. (There was no evidence of ^{13}CO in solution either, which indicates the low concentration of ^{13}CO present in solution.) When the sample was warmed to −30 °C, the first appearance of a ^{13}C signal derived from the added ^{13}CO was at δ 350. This signal was observed in a matter of minutes (ca. 30 min). Upon slowly warming the sample to room temperature over a 12-h period, the signal at δ 366 assignable to I (R = CH_2-c-Pen) grew in at the expense of the initially formed signal at δ 350. In addition, the formation of II was observed as indicated by carbonyl signals at δ 258, 226, and 220.

In a separate reaction involving $W_4(OCH_2\text{-c-Pen})_{12}$ and ^{13}CO (1 equiv) in a benzene-d_6/pyridine solution carried out a room

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

(8) δ 192, $^1J_{^{183}W-^{13}C}$ = 126 Hz: Gansow, O. A.; Kimura, B. Y.; Dobson, G. R.; Brown, R. A. *J. Am. Chem. Soc.* **1971**, *93*, 5922. Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1973**, 2012.

(9) For polyoxotungstates a signal at δ 762 would be indicative of a terminal oxo moiety. (The ^{17}O data for oxo tungsten alkoxides are, however, extremely limited.) Kintzinger, J. P. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; 1983; Vol. 2, Chapter 4.

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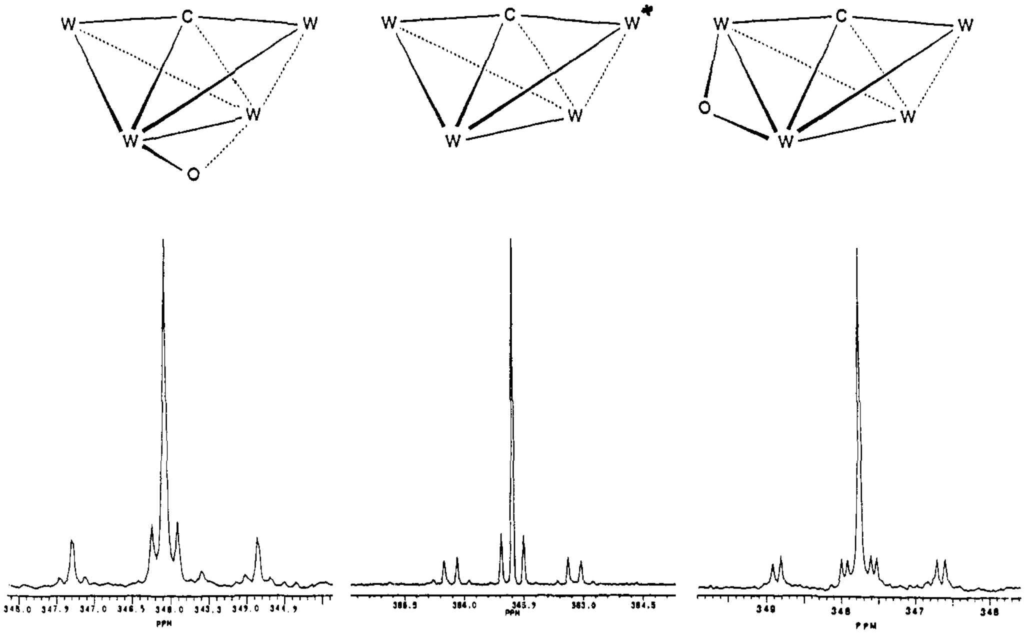

Figure 1. The ^{13}C NMR signals due to the carbido ligands in $W_4(^{13}C)(OCH_2\text{-}t\text{-}Bu)_{12}$ (left), $W_4(^{13}C)(OCH_2\text{-c-Pen})_{14}$ (center), and $W_4(^{13}C)(O)(O\text{-}i\text{-}Pr)_{12}$ (right) showing the satellites that result from $^{13}C-^{183}W$ coupling (^{183}W, $I = ^1/_2$, 14% natural abundance).

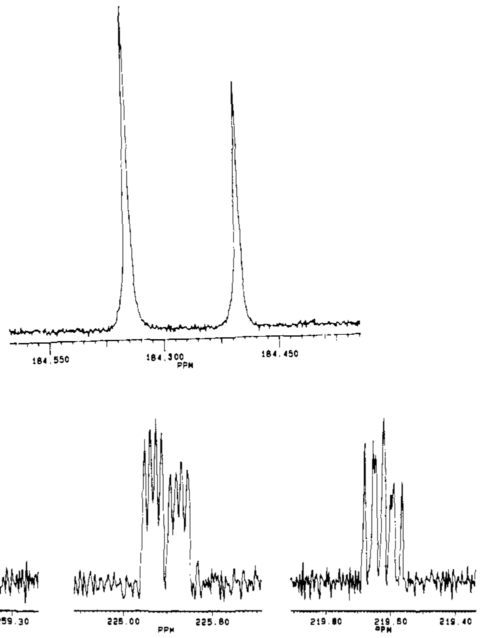

Figure 2. ^{13}C NMR spectra of a 60:40 mixture of $^{13}C^{16}O/^{13}C^{18}O$ (top) and of $W_4(\eta^2,\mu_4\text{-}CO)(CO)_2(OCH_2\text{-}i\text{-}Pr)_{12}$ prepared from $^{13}C^{16}O/^{13}C^{18}O$ (bottom) demonstrating the effect of isotopic substitution at oxygen on the chemical shift of the carbon nuclei. The resonances due to the carbonyl ligands in $W_4(\eta^2,\mu_4\text{-}CO)(CO)_2(OCH_2\text{-}i\text{-}Pr)_{12}$ also exhibit $^{13}C-^{13}C$ coupling and thus appear as doublets of doublets.

temperature, we have observed the appearance and growth of the signal at δ 350 followed by its decrease with the growth of the signal attributable to I (R = CH_2-c-Pen). We can conclude that there is an intermediate of some kinetic persistence in the formation of $W_4(\mu_4\text{-}C)(OCH_2\text{-c-Pen})_{14}$.

We formulate this intermediate as the carbido–oxo compound $W_4(\mu_4\text{-}C)(O)(OCH_2\text{-c-Pen})_{12}$ for two reasons: (1) In reactions involving a 60:40 mixture of $^{13}CO{:}^{13}C^{18}O$ the signal at δ 350 appears as a singlet. We have detected the existence of C–O bonds by the ^{18}O isotopic influence on chemical shift in all examples of carbonyl-containing compounds that we have studied. The chemical shift separation between ^{13}CO and $^{13}C^{18}O$ carbon atoms is small (0.041 (12) ppm) but readily detectable by high-resolution high-field ^{13}C NMR spectroscopy as is shown in Figure 2.[12] Thus,

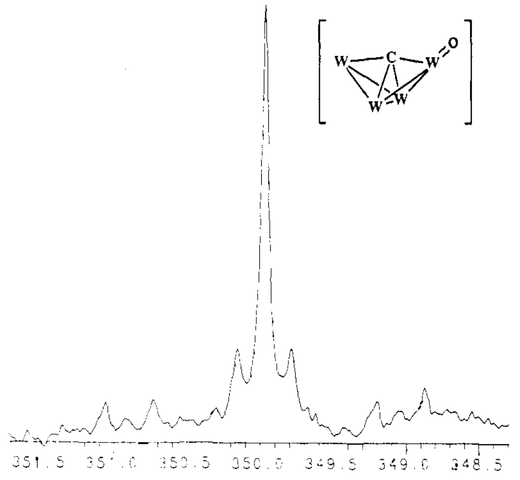

Figure 3. The ^{13}C NMR signal observed for the carbido ligand in the $W_4(^{13}C)(O)(OCH_2\text{-c-Pen})_{12}$ intermediate.

it seems likely that the carbonyl C–O bond has been cleaved upon uptake of CO by the cluster at −30 °C. (By ^{13}C NMR spectroscopy, the ^{13}C signals for the carbido carbon atoms of the isotopically substituted compounds $W_4(\mu_4\text{-}^{13}C)(^{16}O)(OR)_{12}$ and $W_4(\mu_4\text{-}^{13}C)(^{18}O)(OR)_{12}$ would not be expected to be distinguishable.) (2) We have attempted an independent synthesis of $W_4(\mu_4\text{-}^{13}C)(O)(OCH_2\text{-c-Pen})_{12}$ from the addition of c-PenCH$_2$OH (>12 equiv) to $W_4(\mu_4\text{-}^{13}C)(O)(OCH_2\text{-}t\text{-}Bu)_{12}$ (III*, where * represents ^{13}C labeled at the carbide carbon atom). As noted earlier, it has proved impossible to prepare III in bulk quantities free from $W_4(OCH_2\text{-}t\text{-}Bu)_{12}$. The addition of c-PenCH$_2$OH to a sample of III* and $W_4(OCH_2\text{-}t\text{-}Bu)_{12}$ gives rise to the δ 350 resonance in the ^{13}C NMR spectrum, and with time a signal at δ 367 assignable to I* grows in. The ^{13}C signal associated with the carbido carbon atom of the intermediate $W_4(C)(O)(OCH_2\text{-c-Pen})_{12}$ is shown in Figure 3. From the nature and the magnitude of the $^{183}W-^{13}C$ couplings, and the known structures of I, III, and IV, we are able to propose the structure shown in the inset of Figure 3 for $W_4(C)(O)(OCH_2\text{-c-Pen})_{12}$. We favor the structure with a terminal oxo group over one with a face-

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[12] The use of the $^{16}O{:}^{18}O$ isotope chemical shift difference has been extensively used in biochemical systems: Hensen, P. E. *Annu. Rev. N.M.R. Spectrosc.* **1983**, *15*, 105.

Table I. Summary of Crystal Data[a]

	I	III·CH_2Cl_2	IV
empirical formula	$C_{85}H_{154}O_{14}W_4$	$C_{61}H_{132}O_{13}W_4{\cdot}CH_2Cl_2$	$C_{37}H_{84}O_{13}W_4$
color of crystal	black	black	black
crystal dimens (mm)	0.25 × 0.25 × 0.25	0.16 × 0.20 × 0.32	0.24 × 0.36 × 0.36
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
temp (°C)	−155	−181	−170
cell dimens			
a (Å)	14.228 (5)	14.551 (3)	12.248 (2)
b (Å)	23.062 (9)	19.854 (4)	20.536 (3)
c (Å)	14.725 (6)	27.347 (6)	20.010 (3)
α (deg)	81.44 (1)		
β (deg)	67.17 (2)	95.22 (1)	103.60 (1)
γ (deg)	74.82 (2)		
Z (molecules/cell)	2	4	4
vol (Å^3)	4291.73	7867.93	4891.82
calcd density (g/cm^3)	1.653	1.599	1.999
wavelength (Å)	0.71069	0.71069	0.71069
mol wt	2135.54	1894.04	1472.46
linear abs coeff (cm^{-1})	55.162	60.728	96.310
detector-to-sample dist (cm)	22.5	22.5	22.5
sample-to-source dist (cm)	23.5	23.5	23.5
av ω scan width at half height	0.25	0.25	0.25
scan speed (deg/min)	8.0	6.0	8.0
scan width (deg + dispersion)	1.6	1.5	1.9
individual background (sec)	4	6	4
aperture size (mm)	3.0 × 4.0	3.0 × 4.0	3.0 × 4.0
2θ range (deg)	6–45	6–45	6–45
total no. of reflcns collected	11588	11771	9449
no. of unique intensities	11188	10343	6413
no. with $F > 0.0$	10380	9357	6122
no. with $F > 2.33\sigma(F)$	9368		
no. with $F = 3.0\sigma(F)$		8585	5929
$R(F)$	0.0388	0.0684	0.0370
$R_w(F)$	0.0415	0.0632	0.0367
goodness of fit for the last cycle	0.957	1.521	1.675
max δ/σ for last cycle	0.35	0.011	0.014

[a] I = $W_4(\mu_4\text{-C})(OCH_2\text{-c-Pen})_{14}$; III = $W_4(\mu_4\text{-C})(O)(OCH_2\text{-}t\text{-Bu})_{12}$; IV = $W_4(\mu_4\text{-C})(O)(O\text{-}i\text{-Pr})_{12}$.

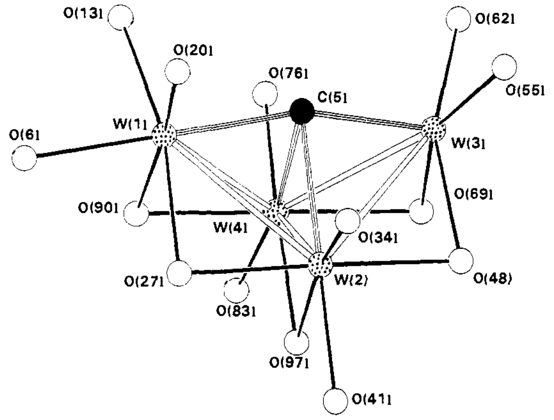

Figure 4. A view of the $W_4(C)(O)_{14}$ core of $W_4(\mu_4\text{-C})(OCH_2\text{-c-Pen})_{14}$ (I).

capping μ_3-O group because it is expected to be more labile toward oxo for RO exchange to yield I.

We conclude that the reaction sequence leading to the cleavage of carbon monoxide proceeds in three steps: (1) uptake of CO by $W_4(OCH_2\text{-c-Pen})_{12}$ which is rate limiting at −30 °C and below; (2) intramolecular C≡O bond cleavage to give a carbido oxo cluster $W_4(\mu_4\text{-C})(O)(OCH_2\text{-c-Pen})_{12}$; and (3) intermolecular oxo-for-alkoxide exchange with the unreacted $W_4(OCH_2\text{-c-Pen})_{12}$ to give I and an as yet uncharacterized oxo–tungsten alkoxide. Although we cannot detect any monocarbonyl compound $W_4(CO)(OCH_2\text{-c-Pen})_{12}$ (because the cleavage of the CO ligand is relatively rapid), we do know that it must have a kinetically significant existence since it is able to react with additional CO to give II. The carbido oxo clusters, once formed, do not react with CO under the mild conditions described here.

Crystal and Molecular Structures. A summary of crystal data is presented in Table I and fractional coordinates and isotropic thermal parameters are provided in the supplementary material along with stereodrawings, complete atom number schemes, and full listings of bond distances and angles. For the sake of brevity we shall discuss only the central cores of the molecular structures of I, II, III, and IV and omit any detailed consideration of the attendant alkyl groups of the OR ligands. We start by considering the structures of the closely related family of μ_4-carbido clusters I, III, and IV.

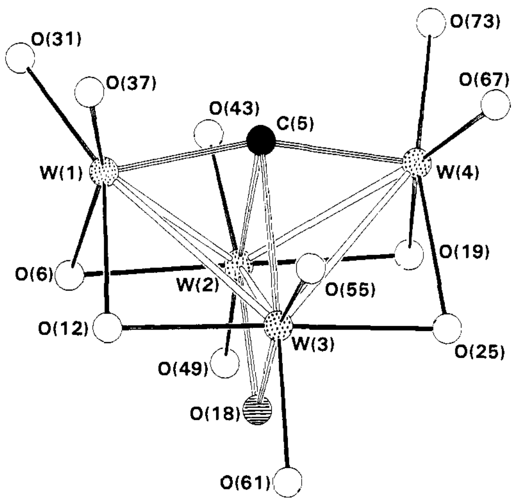

Figure 5. A view of the $W_4(C)(O)_{13}$ core of $W_4(\mu_4\text{-C})(O)(O\text{-}CH_2\text{-}t\text{-Bu})_{12}$ (III). The oxo ligand is labeled O(18).

$W_4(\mu_4\text{-C})(OCH_2\text{-c-Pen})_{14}$ (I), $W_4(\mu_4\text{-C})(O)(OCH_2\text{-}t\text{-Bu})_{12}$ (III), and $W_4(\mu_4\text{-C})(O)(O\text{-}i\text{-Pr})_{12}$ (IV) share a common $W_4(\mu\text{-C})^{14+}$ core involving a butterfly of tungsten atoms and a carbido ligand that unites them as shown in Figures 4–6. The W–W distances span the range 2.70–2.86 Å, with the shortest distances observed between the oxo bridged W atoms. The W–C distances

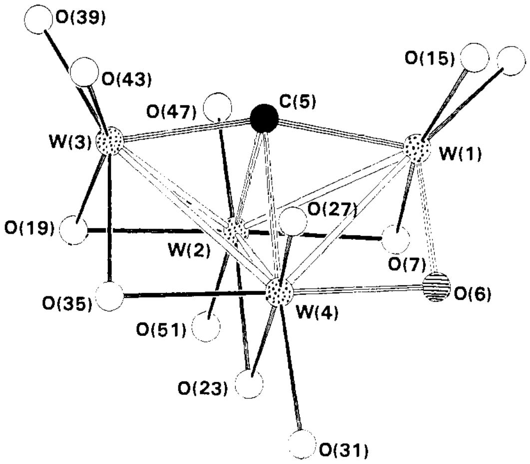

Figure 6. A view of the $W_4(C)(O)_{13}$ core of $W_4(\mu_4\text{-}C)(O)(O\text{-}i\text{-}Pr)_{12}$ (IV). The oxo ligand is labeled O(6).

Table II. Selected Bond Distances (Å) for $W_4(\mu_4\text{-}C)(OCH_2\text{-c-Pen})_{14}$ (I)

A	B	distance	A	B	distance
W(1)	W(2)	2.8306 (15)	W(2)	O(97)	2.048 (8)
W(1)	W(4)	2.8621 (13)	W(2)	C(5)	2.270 (10)
W(1)	O(6)	2.015 (8)	W(3)	W(4)	2.7819 (13)
W(1)	O(13)	1.911 (8)	W(3)	O(48)	2.034 (8)
W(1)	O(20)	1.917 (8)	W(3)	O(55)	1.910 (8)
W(1)	O(27)	2.072 (7)	W(3)	O(62)	1.860 (8)
W(1)	O(90)	2.086 (9)	W(3)	O(69)	2.063 (8)
W(1)	C(5)	1.985 (12)	W(3)	C(5)	1.922 (12)
W(2)	W(3)	2.7794 (13)	W(4)	O(69)	2.062 (8)
W(2)	W(4)	2.7809 (10)	W(4)	O(76)	1.939 (8)
W(2)	O(27)	2.010 (8)	W(4)	O(83)	2.020 (8)
W(2)	O(34)	1.892 (8)	W(4)	O(90)	2.005 (8)
W(2)	O(41)	2.005 (7)	W(4)	O(97)	2.012 (8)
W(2)	O(48)	2.013 (8)	W(4)	C(5)	2.282 (11)

fall into two sets, namely those involving wingtip W atoms, 1.91–1.98 Å, and those involving the backbone W atoms, 2.25–2.30 Å. The W–C–W angles involving the wingtip W atoms are essentially equal with an average value of 161 (1)°. The W–C–W angles involving the backbone W atoms are also very similar: 75.3 (3)° in I, 76.4 (3)° in IV, and 72.0 (4)° in III. The somewhat smaller angle in III arises because the oxo group in III bridges the backbone W atoms giving a slightly shorter W–W distance. Inspection of Figures 5 and 6 reveals that the $W_4(\mu_4\text{-}C)O_{13}$ cores of III and IV are essentially indistinguishable when the identity of the oxo group is not made clear. The $W_4(\mu_4\text{-}C)O_{14}$ core of I (Figure 4) is related to the $W_4(\mu_4\text{-}C)O_{13}$ cores of III and IV by the addition of one OR group to one of the wingtip W atoms, namely W(1), which then becomes octahedrally coordinated. The W–C bond is little perturbed by the presence or absence of the OR group in the trans position.

The tungsten–oxygen distances fall in the expected ranges such that W–μ-oxo lengths range from 1.90 to 1.95 Å and are similar to those of the terminal W–OR distances. The W–μ-*O*R distances are all notably longer, but they are in the range expected for such bonds.

Listings of selected bond distances and angles for I, III, and IV are given in Tables II–VII.

The structure of IV is remarkably similar to that of $W_4(\mu_4\text{-}C)(NMe)(O\text{-}i\text{-}Pr)_{12}$ which was the first example of a molecular carbide of tungsten.[13] The oxo group in IV and the NMe group are isoelectronic, and apparently their location in the carbido clusters is determined by the nature of the alkoxides. Thus the oxo group in IV and the imido group in $W_4(\mu_4\text{-}C)(NMe)(O\text{-}i\text{-}Pr)_{12}$ bridge wingtip and backbone W atoms, whereas in the neopentoxide compound, III, the oxo group bridges two backbone W atoms.

The skeletal remains of these four tetranuclear carbido clusters are shown in Figure 7. One can see that the clusters contain metal atoms that adopt an octahedral coordination or one that is derived from an octahedron by the removal of one ligand if metal–metal bonding is ignored. The structures are also related to a well-known class of octahedral metal clusters of the type $M_6(\mu_6\text{-}E)(\mu_2\text{-}X)_{12}X_6$ by the removal of two cis metals of the octahedral M_6 moiety along with the appropriate number of bridging or terminal X groups. The latter class of materials are common for M = Zr with X = halide and E being a light element such as B, C, or N.[14]

The structure of the tricarbonyl compound II has been described previously and will not be discussed in detail here.[7] A view of the central $W_4(\mu_4\text{-}CO)(CO)_2O_{12}$ moiety is shown in Figure 8. The structural feature most pertinent to the cleavage of a carbonyl ligand is the η^2,μ_4-CO group. This can be viewed as a metalla-oxycarbyne ligand, and as in $W_4(\mu\text{-}CO)_2(O\text{-}i\text{-}Pr)_{12}$, the CO ligand is reduced by both W d_π-to-CO π^* back-bonding and oxygen p_π-to-W d_π bonding (from filled C–O π MO's).[3c,3d]

^{1}H NMR Spectra. The ^{1}H NMR spectra for the carbido tungsten alkoxide clusters I, III, and IV reveal that none of these compounds is fluxional on the NMR time scale. The ^{1}H NMR spectroscopic data generally support the structural conclusions based on X-ray work and on the ^{183}W satellite spectra of the carbido carbon atoms. However, in some cases the spectra do not show the anticipated number of unique resonances because of accidental degeneracy. The ^{1}H NMR spectra are complicated by ^{1}H–^{1}H couplings, and further by second-order spin systems. Illustrative of these general features is the ^{1}H NMR spectrum of the $W_4(\mu_4\text{-}C)(OCH_2\text{-c-Pen})_{14}$ compound shown in Figure 9. Only the region of the methylene protons is shown. In the crystal structure there is a virtual mirror plane of symmetry that contains two of the OR ligands, namely the alkoxide ligands represented by O(6) and O(97) in Figure 4. The other 12 OR ligands lie off this virtual plane of symmetry and are pairwise related by this plane. This leads to the expectation of a 2:2:2:2:2:2:1:1 disposition of OCH_2-c-Pen groups with all those of relative intensity 2 containing diastereotopic methylene protons. Depending upon the chemical shift separation, the diastereotopic methylene protons may give rise to either an AB or an AX spectrum. With this in mind, a careful inspection of the methylene proton signals shown in Figure 9 reveals that all is in order and the two OCH_2-c-Pen groups that lie on the mirror plane, those associated with O(6) and O(97), give rise to doublets at δ 4.76 and 4.48. Of course, an absolute assignment is not possible (at least not with the level of NMR probing presented here) and would not be expected to be particularly enlightening. For the sake of brevity, the listing of NMR data has been transferred from the Experimental Section to the supplementary material.

Speculation on the Reaction Pathway Leading to C–O Bond Cleavage. The W(4) to μ_4-CO carbon distance is 2.56 Å in II, and it is not difficult to imagine that a $W_4(\mu_4\text{-}CO)(OR)_{12}$ molecule similar to II but lacking the additional CO ligands might be a reactive intermediate in the formation of $W_4(\mu_4\text{-}C)(O)(OR)_{12}$. The presence of the two π-acid η^1-CO ligands presumably suppresses the reductive cleavage of the μ_4-CO ligand to carbide, C^{4-}, and oxide, O^{2-}, ligands by removing electron density from W d_π orbitals that would otherwise be available for reduction of the unique carbonyl ligand. The fact that a reactive monocarbonyl complex persists long enough for additional uptake of CO in the formation of II is a reflection of the reorganizational energy involved in the C–O bond cleavage. This intramolecular reaction presumably involves the movement of several OR groups, along with the formation of the μ_4-C and oxo ligands, and has a lower energy of activation than the bimolecular reaction involved in the formation of the monocarbonyl intermediate. The latter is the rate-determining step and does not occur to any significant extent at −78 °C in toluene-d_8.

Analogies with the Activation of Carbon Monoxide on Metal Surfaces. The activation of carbon monoxide upon coordination to clean metal surfaces has been a topic of considerable interest

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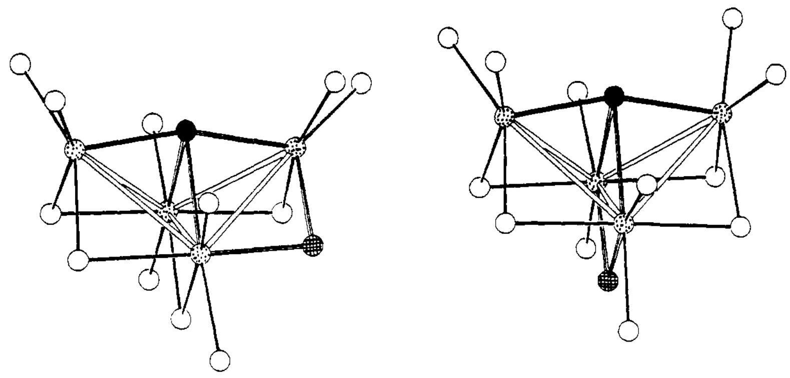
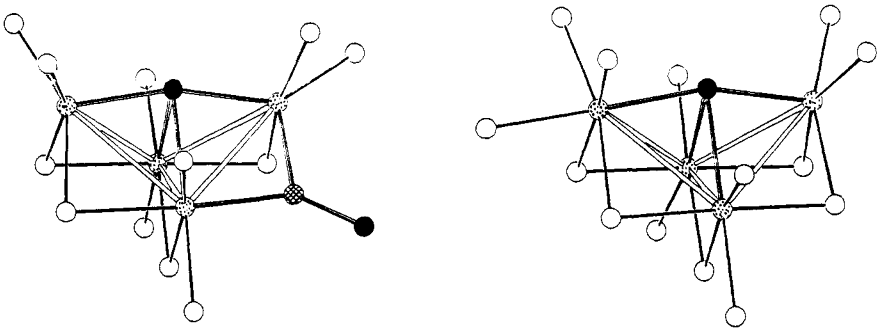


$W_4(C)(O)(O\text{-}i\text{-}Pr)_{12}$ $W_4(C)(O)(OCH_2\text{-}t\text{-}Bu)_{12}$



$W_4(C)(NMe)(O\text{-}i\text{-}Pr)_{12}$ $W_4(C)(OCH_2\text{-}c\text{-}Pen)_{14}$

Figure 7. Central cores of the four $W_4(C)$ clusters discussed in this work.

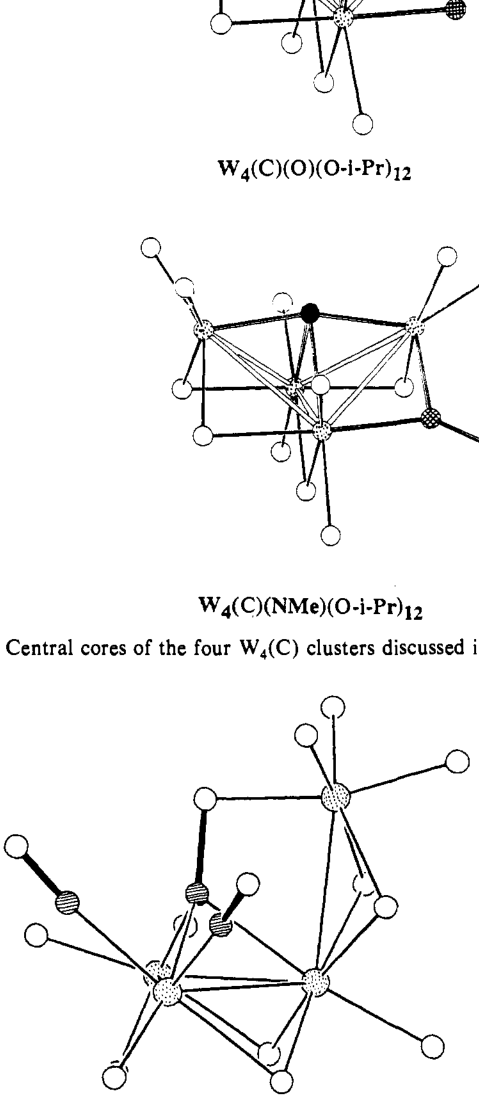


Figure 8. A view of the $W_4(CO)_3(O)_{12}$ core of $W_4(\eta^2,\mu_4\text{-}CO)(CO)_2(OCH_2\text{-}i\text{-}Pr)_{12}$.

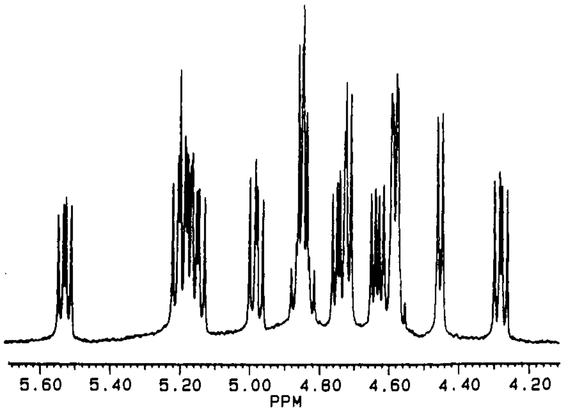


Figure 9. The methylene region of the ^1H NMR spectrum of $W_4(\mu_4\text{-}C)(OCH_2\text{-}c\text{-}Pen)_{14}$ in toluene-d_8 at room temperature.

to surface scientists.[15] CO is well known to bind in an upright manner, perpendicular to the metal surface, and may occupy a 1-fold site as on Pt(111), a 2-fold bridging site as on Pd(100), or a 3-fold site as on Pd(111).[15b] In analogy with the molecular chemistry of the carbonyl ligand, these represent examples of terminal and μ_2- and μ_3-coordination modes. The preference for the site on a metal surface is determined by the relative energy of the d band of the metal. The higher the energy of the d band, the greater the degree of metal-to-CO π^* back-bonding which favors bridging coordination. For a given metal surface, the type of CO binding can be modified by (i) the extent of CO loading, (ii) co-adsorbed ions, e.g. Cs or K, and (iii) cathodic charging. Theoretical treatments of CO on surfaces bear a close analogy to the simple MO pictures that are now familiar to all molecular organometallic chemists.[15b]

More recently it has been observed that metals with partially filled d bands can also accommodate side-on carbon monoxide. Examples now include CO on Cr,[16] Fe,[17] and Ru[18] surfaces. Here the d band behaves both as an electron donor to the C≡O π^* MO's and as an acceptor from the filled π MO of carbon monoxide. The latter involves oxygen-to-metal π-bonding and is favored for the middle and early transition metals.[15b] In side-on CO coordinations the C–O bond is stretched and weakened, and cleavage is generally observed to be facile at around 300 K. With a later transition metal such as Ni, side-on bonding is never seen, but presumably can occur to some degree and is responsible for

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[15] For general features of the coordination of CO to metal surfaces and the theory of bonding see: (a) Albert, M. R.; Yates, J. T. In *A Surface Scientists Guide to Organometallic Chemistry*; American Chemical Society: Washington, DC, 1987. (b) Anderson, A. B. In *Theoretical Aspects of Heterogeneous Catalysis*; Moffat, J. B., Ed.; Van Nostrand Reingold: New York, 1990; Chapter 10.

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Table III. Selected Bond Angles (deg) for $W_4(\mu_4\text{-}C)(OCH_2\text{-c-Pen})_{14}$ (I)

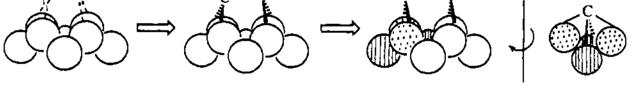
A	B	C	angle	A	B	C	angle	A	B	C	angle
W(2)	W(1)	W(4)	58.480 (25)	O(27)	W(2)	O(97)	88.1 (3)	O(62)	W(3)	C(5)	102.9 (4)
O(6)	W(1)	O(13)	84.9 (3)	O(27)	W(2)	C(5)	91.1 (4)	O(69)	W(3)	C(5)	101.8 (4)
O(6)	W(1)	O(20)	88.0 (4)	O(34)	W(2)	O(41)	85.9 (3)	W(1)	W(4)	W(2)	60.19 (3)
O(6)	W(1)	O(27)	82.4 (3)	O(34)	W(2)	O(48)	90.1 (3)	W(1)	W(4)	W(3)	86.29 (4)
O(6)	W(1)	O(90)	85.3 (3)	O(34)	W(2)	O(97)	167.3 (3)	W(2)	W(4)	W(3)	59.95 (3)
O(6)	W(1)	C(5)	178.1 (4)	O(34)	W(2)	C(5)	93.9 (4)	O(69)	W(4)	O(76)	88.1 (3)
O(13)	W(1)	O(20)	93.0 (3)	O(41)	W(2)	O(48)	90.3 (3)	O(69)	W(4)	O(83)	96.2 (3)
O(13)	W(1)	O(27)	166.0 (3)	O(41)	W(2)	O(97)	81.4 (3)	O(69)	W(4)	O(90)	178.8 (3)
O(13)	W(1)	O(90)	89.7 (3)	O(41)	W(2)	C(5)	179.6 (4)	O(69)	W(4)	O(97)	87.6 (3)
O(13)	W(1)	C(5)	94.9 (4)	O(48)	W(2)	O(97)	88.8 (3)	O(69)	W(4)	C(5)	90.7 (4)
O(20)	W(1)	O(27)	92.6 (3)	O(48)	W(2)	C(5)	90.0 (4)	O(76)	W(4)	O(83)	88.5 (3)
O(20)	W(1)	O(90)	172.6 (3)	O(97)	W(2)	C(5)	98.8 (4)	O(76)	W(4)	O(90)	92.9 (3)
O(20)	W(1)	C(5)	90.1 (4)	W(2)	W(3)	W(4)	60.01 (3)	O(76)	W(4)	O(97)	172.1 (3)
O(27)	W(1)	O(90)	83.3 (3)	O(48)	W(3)	O(55)	88.6 (3)	O(76)	W(4)	C(5)	87.2 (4)
O(27)	W(1)	C(5)	97.9 (4)	O(48)	W(3)	O(62)	156.6 (3)	O(83)	W(4)	O(90)	83.2 (3)
O(90)	W(1)	C(5)	96.5 (4)	O(48)	W(3)	O(69)	83.6 (3)	O(83)	W(4)	O(97)	85.4 (3)
W(1)	W(2)	W(3)	86.95 (3)	O(48)	W(3)	C(5)	100.1 (4)	O(83)	W(4)	C(5)	171.8 (4)
W(1)	W(2)	W(4)	61.33 (3)	O(55)	W(3)	O(62)	89.5 (3)	O(90)	W(4)	O(97)	91.3 (3)
W(3)	W(2)	W(4)	60.04 (3)	O(55)	W(3)	O(69)	154.1 (3)	O(90)	W(4)	C(5)	90.1 (4)
O(27)	W(2)	O(34)	92.8 (3)	O(55)	W(3)	C(5)	103.9 (4)	O(97)	W(4)	C(5)	99.5 (3)
O(27)	W(2)	O(41)	88.6 (3)	O(62)	W(3)	O(69)	88.0 (3)	W(1)	C(5)	W(3)	162.3 (6)
O(27)	W(2)	O(48)	176.9 (3)					W(2)	C(5)	W(4)	75.3 (3)

Table IV. Selected Bond Distances (Å) for $W_4(\mu_4\text{-}C)(O)(OCH_2\text{-}t\text{-}Bu)_{12}\cdot CH_2Cl_2$ ($III\cdot CH_2Cl_2$)

A	B	distance	A	B	distance
W(1)	W(2)	2.7852 (11)	W(2)	C(5)	2.298 (15)
W(1)	W(3)	2.7887 (10)	W(3)	W(4)	2.7774 (10)
W(1)	O(6)	2.134 (10)	W(4)	O(12)	2.068 (11)
W(1)	O(12)	2.055 (10)	W(3)	O(18)	1.933 (11)
W(1)	O(31)	1.865 (11)	W(3)	O(25)	2.044 (11)
W(1)	O(37)	1.892 (11)	W(3)	O(55)	1.958 (10)
W(1)	C(5)	1.914 (15)	W(3)	O(61)	2.010 (11)
W(2)	W(3)	2.7038 (10)	W(3)	C(5)	2.301 (14)
W(2)	W(4)	2.7984 (11)	W(4)	O(19)	2.055 (11)
W(2)	O(6)	2.040 (10)	W(4)	O(25)	2.100 (11)
W(2)	O(18)	1.926 (10)	W(4)	O(67)	1.903 (12)
W(2)	O(19)	2.079 (11)	W(4)	O(73)	1.870 (12)
W(2)	O(43)	1.967 (10)	W(4)	C(5)	1.924 (15)
W(2)	O(49)	2.020 (11)			

the formation of surface bound carbide and oxide at elevated temperatures (450–600 K).[19] This carbide is transformed to methane in the presence of hydrogen. The oxygen on the nickel surface is readily removed as water in the presence of H_2 and in the absence of H_2 by CO as CO_2. The disproportionation of CO to C and CO_2 on a metal surface is called the Boudouard reaction and has some parallels in metal carbonyl cluster chemistry where, upon pyrolysis, CO_2 is evolved and carbide ligands are generated. For this to occur, CO ligands are initially lost, thereby opening up coordination sites that are required for activation of a CO ligand in a side-on manner. Some nice examples of this are seen in work of Lewis and co-workers in the synthesis of higher nuclearity osmium clusters.[20]

In a theoretical treatment of the cleavage of CO on an iron surface, Blyholder[21] concluded that the minimum energy pathway involved a 4-fold site as shown below.



B

The surface bound carbide group that results from the cleavage of the CO ligand would be the equivalent of a μ_4-C ligand in a butterfly arrangement of iron atoms. The backbone atoms of the butterfly are provided by the layer of metal atoms below the surface layer.

The cleavage of CO in our studies has many obvious parallels with CO cleavage on a surface, but it also has one important difference. Uptake of CO by a metal surface is *always* more facile than the C–O bond cleavage reaction. This is presumably because the surface atoms of a metal surface are more unsaturated and receptive to ligand (Lewis base) uptake. In our unsaturated $W_4(OR)_{12}$ clusters, there are probably a number of significant rearrangements (reactions) that have to occur prior to Lewis base uptake as evidenced by the lack of reactivity with CO at −78 °C in toluene-d_8. Since we have no knowledge of the structure of a $W_4(OR)_{12}(CO)$ intermediate, we can only speculate that the CO may initially bind to one of the backbone W atoms as does the alcohol ligand in $Mo_4(OCH_2\text{-c-Bu})_{12}(HOCH_2\text{-c-Bu})$.[5] Once the CO ligand adopts a bridging position in which the carbon and oxygen atoms are bonded to tungsten atoms, the C–O bond cleavage is nothing more than a skeletal rearrangement of a $W_4O_{13}C$ containing cluster.

Comments on Bonding. We previously described[22] in detail our studies of the bonding in $W_4(\mu_4\text{-}C)(NMe)(O\text{-}i\text{-}Pr)_{12}$, a compound that is formed in very small quantities, ca. 5% on the basis of W, in the reaction between $W_2(NMe_2)_6$ and i-PrOH (≥6 equiv). The origin of the carbide ligand in that reaction can reasonably be traced to the degradation of a NMe_2 ligand at a dinuclear center probably by way of a μ-CH_2NMe ligand as seen in other work.[23] In describing the bonding in $W_4(\mu_4\text{-}C)(NMe)(O\text{-}i\text{-}Pr)_{12}$ we employed the Fenske–Hall method[24] and used as our model the hypothetical species $W_4(\mu\text{-}C)(OH)_{13}^+$. [With the isolation of $W_4(\mu_4\text{-}C)(O)(O\text{-}i\text{-}Pr)_{12}$, this model formulation seems even more appropriate.] Given the isolation of four structurally or substitutionally different $W_4(\mu_4\text{-}C)^{14+}$ containing compounds (as shown in Figure 7), we can conclude that the essential features of the bonding in the W_4C core are little perturbed by the exact number or disposition of the ligands, OR vs oxo or imido or alkylidyne. The coordination about the tungsten atoms is always either pseudooctahedral or square-based pyramidal, with the carbido group in the apical position.

In our earlier discussions of bonding, we have drawn on the isolobal analogies that exist for early transition metal alkoxide clusters and carbonyl clusters of the later transition series, i.e.

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Table V. Selected Bond Angles (deg) for $W_4(\mu_4\text{-}C)(O)(OCH_2\text{-}t\text{-}Bu)_{12}\cdot CH_2Cl_2$ ($III\cdot CH_2Cl_2$)

A	B	C	angle	A	B	C	angle	A	B	C	angle
W(2)	W(1)	W(3)	58.035 (26)	O(18)	W(2)	O(43)	168.9 (4)	O(25)	W(3)	O(55)	87.9 (4)
O(6)	W(1)	O(12)	83.2 (4)	O(18)	W(2)	O(49)	85.4 (4)	O(25)	W(3)	O(61)	90.8 (4)
O(6)	W(1)	O(31)	85.6 (4)	O(18)	W(2)	C(5)	99.7 (5)	O(25)	W(3)	C(5)	91.9 (5)
O(6)	W(1)	O(37)	163.5 (4)	O(19)	W(2)	O(43)	90.7 (5)	O(55)	W(3)	O(61)	85.6 (4)
O(6)	W(1)	C(5)	101.3 (5)	O(19)	W(2)	O(49)	87.7 (5)	O(55)	W(3)	C(5)	90.3 (5)
O(12)	W(1)	O(31)	151.8 (4)	O(19)	W(2)	C(5)	89.5 (5)	O(61)	W(3)	C(5)	175.0 (5)
O(12)	W(1)	O(37)	90.1 (5)	O(43)	W(2)	O(49)	84.0 (4)	W(2)	W(4)	W(3)	58.013 (24)
O(12)	W(1)	C(5)	101.9 (5)	O(43)	W(2)	C(5)	91.1 (5)	O(19)	W(4)	O(25)	83.1 (4)
O(31)	W(1)	O(37)	93.5 (5)	O(49)	W(2)	C(5)	174.3 (5)	O(19)	W(4)	O(67)	148.9 (5)
O(31)	W(1)	C(5)	105.6 (5)	W(1)	W(3)	W(2)	60.917 (26)	O(19)	W(4)	O(73)	91.3 (5)
O(37)	W(1)	C(5)	94.8 (6)	W(1)	W(3)	W(4)	85.63 (3)	O(19)	W(4)	C(5)	101.6 (6)
W(1)	W(2)	W(3)	61.048 (26)	W(2)	W(3)	W(4)	61.38 (3)	O(25)	W(4)	O(67)	84.3 (4)
W(1)	W(2)	W(4)	85.296 (26)	O(12)	W(3)	O(18)	91.6 (4)	O(25)	W(4)	O(73)	162.3 (4)
W(3)	W(2)	W(4)	60.605 (25)	O(12)	W(3)	O(25)	178.2 (4)	O(25)	W(4)	C(5)	102.0 (5)
O(6)	W(2)	O(18)	88.7 (4)	O(12)	W(3)	O(55)	91.1 (4)	O(67)	W(4)	O(73)	92.1 (5)
O(6)	W(2)	O(19)	178.0 (4)	O(12)	W(3)	O(61)	87.6 (4)	O(67)	W(4)	C(5)	108.8 (6)
O(6)	W(2)	O(43)	88.3 (4)	O(12)	W(3)	C(5)	89.6 (5)	O(73)	W(4)	C(5)	95.6 (5)
O(6)	W(2)	O(49)	90.4 (4)	O(18)	W(3)	O(25)	89.0 (4)	W(2)	O(18)	W(3)	89.0 (4)
O(6)	W(2)	C(5)	92.3 (5)	O(18)	W(3)	O(55)	170.0 (4)	W(2)	C(5)	W(3)	72.0 (4)
O(18)	W(2)	O(19)	91.9 (5)	O(18)	W(3)	O(61)	84.9 (4)	W(2)	C(5)	W(4)	82.5 (5)
				O(18)	W(3)	C(5)	99.3 (5)				

Table VI. Selected Bond Distances (Å) for $W_4(\mu_4\text{-}C)(O)(O\text{-}i\text{-}Pr)_{12}$ (IV)

A	B	distance	A	B	distance
W(1)	O(6)	1.897 (7)	W(3)	O(43)	1.875 (7)
W(1)	O(7)	2.073 (6)	W(3)	C(5)	1.929 (11)
W(1)	O(11)	1.895 (7)	W(4)	O(6)	1.956 (7)
W(1)	O(15)	1.943 (6)	W(4)	O(23)	2.029 (7)
W(1)	C(5)	1.941 (11)	W(4)	O(35)	2.102 (6)
W(2)	O(7)	1.999 (6)	W(4)	O(47)	1.958 (7)
W(2)	O(19)	2.012 (6)	W(4)	O(51)	2.017 (7)
W(2)	O(23)	2.055 (6)	W(4)	C(5)	2.253 (11)
W(2)	O(27)	1.901 (7)	W(1)	W(2)	2.810 (1)
W(2)	O(31)	2.013 (7)	W(1)	W(3)	3.818 (1)
W(2)	C(5)	2.267 (10)	W(1)	W(4)	2.709 (1)
W(3)	O(19)	2.040 (6)	W(2)	W(3)	2.815 (1)
W(3)	O(35)	2.058 (7)	W(2)	W(4)	2.796 (1)
W(3)	O(39)	1.902 (7)	W(3)	W(4)	2.801 (1)

$d^3\text{-}W(OR)_3 \leftrightarrow Fe(CO)_3^-$ or $Co(CO)_3$.[22,25] Furthermore, we have emphasized the complementary nature of alkoxide and carbonyl ligands in their role as π-buffers.[25,26] The bonding in these $W_4(\mu_4\text{-}C)^{14+}$ containing clusters is thus qualitatively similar to the bonding in $M_4(\mu_4\text{-}C)$ carbonyl supported clusters, where M = Fe or Ru.[27,28] One difference that the calculations suggested was the degree of carbon 2s orbital participation. In the $M_4(\mu_4\text{-}C)$ carbonyl compounds of iron and ruthenium, the carbon atom uses its 2p atomic orbitals almost exclusively; there is little contribution to M–C bonding from carbon 2s.[27,28] For tungsten, the orbital energy match favors much greater participation of the carbon 2s orbital.

We see evidence for the participation of the carbon 2s orbital in the magnitude of the $^{183}W\text{-}^{13}C$ coupling constants. The coupling constants to the wingtip tungsten atoms are large, 120–140 Hz, in the range typically seen for bridging (μ_2) alkylidynes. Coupling involving the backbone W atoms and the carbide carbon atoms is much smaller, 20–30 Hz, as expected from considerations of the longer distances and of the bonding in the $W_4(\mu\text{-}C)^{14+}$ core. For comparison, we list some values of $^1J_{^{183}W\text{-}^{13}C}$ for a varirty of W–C containing compounds in Table VIII. If we accept that the Fermi contact term[29] dominates the magnitude of $^1J_{^{183}W\text{-}^{13}C}$ values, then the coupling constants provide us with a measure of C 2s bonding to tungsten. Thus, in the $W_4(\mu_4\text{-}C)^{14+}$ containing compounds, there is extensive use of the C 2s orbital in bonding to the wingtip tungsten atoms.

Concluding Remarks. Several aspects of the present work are worthy of emphasis.

1. The synthetic strategies reported here for the cleavage of C≡O to carbide and oxide ligands have been successful in generating a new class of carbido clusters containing a central $W_4(\mu_4\text{-}C)^{14+}$ core. These are the first molecular carbides of tungsten, and given the substitutional lability of OR ligands,[30] we imagine that this class of $W_4(\mu_4\text{-}C)^{14+}$ containing compounds will be quite extensive.

2. This work provides the first example of the cleavage of carbon monoxide to carbido, C^{4-}, and oxo, O^{2-}, ligands in a molecular system. This reaction involves a formal 6-electron reduction of CO and is easily achieved by 12-electron W_4^{12+} containing clusters. The electrons in the M–M bonds in $W_4(OR)_{12}$ can be accessed in the same way that the d-band of a metal surface is accessed by adsorbed CO. The key feature for the reductive cleavage of C≡O to carbide and oxide is the ability of the metal atoms, either within the cluster or on the metal surface, to behave as d_π-donors to the CO π* MO's and as d_π-acceptors from the filled CO π MO via O p_π-to-M d_π donation. This aspect of the chemistry of CO has been emphasized before by others in terms of metal surface C–O cleavage[15] and by us in our discussion of the bonding in $W_4(\mu_3\text{-}CO)_2(O\text{-}i\text{-}Pr)_{12}$.[31]

3. There are other examples in molecular chemistry in which the C—O bond of carbon monoxide is cleaved. In all of these, however, there is C—X and/or O—Y bond formation. For example, in the activation of C≡O by early transition metal elements, C—C bond formation is common, as in the work of Wolczanski[2] noted earlier. Alternatively, the oxygen atom may be transferred to a good leaving group. This is seen in the formation of carbido carbonyl clusters where CO_2 is evolved,[20] or in the protonation of carbonyl ligands in clusters where water is formed.[32] In these reactions where C—X and/or O—Y bonds are formed, it is possible to cleave the C≡O triple bond without a six-electron reduction, e.g. eq 1 could be written as the following redox reaction: $4e^- + C{\equiv}O \rightarrow {}^1/_2[C_2^{4-}] + O^{2-}$. In the reaction between $X_4W_2(\mu\text{-}CSiMe_3)_2(M\text{-}M)$ and C≡O that yields $X_4W_2(\mu\text{-}CSiMe_3)(\mu\text{-}CCSiMe_3)(O)$,[33] where X = CH_2SiMe_3 or

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Table VII. Selected Bond Angles (deg) for $W_4(\mu_4\text{-}C)(O)(O\text{-}i\text{-}Pr)_{12}$ (IV)

A	B	C	angle	A	B	C	angle	A	B	C	angle
O(6)	W(1)	O(7)	87.49 (27)	O(27)	W(2)	O(31)	85.25 (28)	O(23)	W(4)	C(5)	99.2 (3)
O(6)	W(1)	O(11)	95.6 (3)	O(27)	W(2)	C(5)	92.6 (3)	O(35)	W(4)	O(47)	86.71 (27)
O(6)	W(1)	O(15)	132.3 (3)	O(31)	W(2)	C(5)	177.7 (3)	O(35)	W(4)	O(51)	92.51 (27)
O(6)	W(1)	C(5)	100.8 (4)	O(19)	W(3)	O(35)	83.43 (27)	O(35)	W(4)	C(5)	90.2 (3)
O(7)	W(1)	O(11)	164.43 (26)	O(19)	W(3)	O(39)	85.9 (3)	O(47)	W(4)	O(51)	89.35 (28)
O(7)	W(1)	O(15)	80.89 (26)	O(19)	W(3)	O(43)	157.12 (27)	O(47)	W(4)	C(5)	87.0 (3)
O(7)	W(1)	C(5)	98.3 (3)	O(19)	W(3)	C(5)	98.5 (3)	O(51)	W(4)	C(5)	175.4 (3)
O(11)	W(1)	O(15)	85.81 (28)	O(35)	W(3)	O(39)	152.1 (3)	W(1)	O(6)	W(4)	89.4 (3)
O(11)	W(1)	C(5)	96.1 (4)	O(35)	W(3)	O(43)	90.7 (3)	W(1)	C(5)	W(3)	161.4 (6)
O(15)	W(1)	C(5)	126.5 (4)	O(35)	W(3)	C(5)	101.4 (4)	W(2)	C(5)	W(4)	76.4 (3)
O(7)	W(2)	O(19)	176.77 (27)	O(39)	W(3)	O(43)	89.2 (3)	W(2)	W(1)	W(3)	47.31 (3)
O(7)	W(2)	O(23)	87.40 (25)	O(39)	W(3)	C(5)	105.6 (4)	W(2)	W(1)	W(4)	60.85 (3)
O(7)	W(2)	O(27)	92.22 (27)	O(43)	W(3)	C(5)	104.3 (3)	W(3)	W(1)	W(4)	47.13 (3)
O(7)	W(2)	O(31)	90.28 (27)	O(6)	W(4)	O(23)	92.74 (27)	W(1)	W(2)	W(3)	85.50 (2)
O(7)	W(2)	C(5)	90.6 (3)	O(6)	W(4)	O(35)	179.09 (27)	W(1)	W(2)	W(4)	57.79 (3)
O(19)	W(2)	O(23)	89.47 (26)	O(6)	W(4)	O(47)	93.53 (28)	W(3)	W(2)	W(4)	59.89 (3)
O(19)	W(2)	O(27)	91.00 (28)	O(6)	W(4)	O(51)	88.4 (3)	W(1)	W(3)	W(2)	47.19 (3)
O(19)	W(2)	O(31)	90.17 (26)	O(6)	W(4)	C(5)	89.0 (3)	W(1)	W(3)	W(4)	45.14 (3)
O(19)	W(2)	C(5)	89.1 (3)	O(23)	W(4)	O(35)	87.11 (25)	W(2)	W(3)	W(4)	59.71 (3)
O(23)	W(2)	O(27)	169.47 (27)	O(23)	W(4)	O(47)	171.26 (25)	W(1)	W(4)	W(2)	61.36 (3)
O(23)	W(2)	O(31)	84.23 (27)	O(23)	W(4)	O(51)	84.76 (26)	W(1)	W(4)	W(3)	87.73 (2)
O(23)	W(2)	C(5)	98.0 (3)					W(2)	W(4)	W(3)	60.40 (2)

Table VIII. $^{183}W-^{13}C$ Coupling Constants for Some Terminal, μ_2- and μ_3-Alkylidyne Ligands

compd	$J_{^{183}W-^{13}C}$ (Hz)	ref
$(t\text{-BuO})_3W{\equiv}CMe$	302	*a*
$W_2(\mu\text{-CMe})(OCH_2\text{-}t\text{-Bu})_6(O\text{-}t\text{-Bu})$	160	*b*
$HW_2(\mu\text{-CCH}{=}\text{CHMe})(OSi(t\text{-Bu})Me_2)_6$	142	*b*
$W_2(\mu\text{-CSiMe}_3)_2(NMe_2)_4$	156	*c*
$W_3(\mu_3\text{-CCH}_3)(O\text{-}i\text{-Pr})_9$	187	*a*

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i-PrO, there is C≡O bond cleavage, but the tungsten atoms provide only one electron apiece, with the other electrons coming from one of the alkylidyne ligands: $W_2^{10+} + RC^{3-} + C{\equiv}O \rightarrow W_2^{12+} + RCC^- + O^{2-}$. In the present chemistry a six-electron reduction of C≡O to carbide and oxide is achieved by the 12-electron W_4^{12+} alkoxide supported clusters, which supports the hypothesis that clusters of this type may be useful in achieving multielectron redox reactions that cannot be carried out with mononuclear complexes.

4. The successful cleavage of C≡O to carbide and oxide naturally leads us to speculate about the cleavage of N≡N to nitride (2 equiv), a similar six-electron reduction. All the work carried out in this study was performed under an N_2 atmosphere (1 atm). The $W_4(OR)_{12}$ complexes are completely inert to N_2 under these conditions. We propose that this is on kinetic grounds: the N_2 molecule does not bind to $W_4(OR)_{12}$ molecules.

The compounds $[(RO)_3NM]_\infty$[34] are known for both M = Mo and W, as is $Mo_4(O\text{-}i\text{-}Pr)_{12}(N)_2$,[13] and represent likely thermodynamic products in reactions involving $M_2(OR)_6$ or $M_4(OR)_{12}$ compounds with N_2. As we have shown here for the cleavage of C≡O, the uptake of CO by the $M_4(OR)_{12}$ compound is the slow step. Given that N_2 is a weaker Lewis base than CO we suggest that the initial associative step is not operative for N_2. In this regard it is worth noting that the related $Mo_4(OCH_2R)_{12}$ compounds (R = c-Pen or *i*-Pr) do not react with C≡O under mild conditions (1 atm of CO, room temperature). Given the similarity in the $M_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}CO)$ and $M_2(OR)_6(py)_2(\mu\text{-}CO)$ compounds (R = *i*-Pr and CH_2-*t*-Bu) where M = Mo and W,[3] we believe that this too is a kinetic effect reflecting the better initial ligation (W > Mo). This leads us to believe that by an appropriate selection of attendant ligands, 12-electron W_4^{12+} containing clusters will be capable of activating dinitrogen toward a similar cleavage. Further studies are in progress.

Experimental Section

All manipulations were carried out under an atmosphere of dry nitrogen with standard Schlenk and glovebox techniques. Hydrocarbon solvents were distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves. Anhydrous pyridine was purchased from Aldrich and stored over sieves prior to use. The preparations of $W_2(O\text{-}t\text{-}Bu)_6$,[35] $W_2(\mu\text{-}CO)(O\text{-}t\text{-}Bu)_6$,[36] and $W_4(OCH_2\text{-c-Pen})_{12}$[2] have been previously described. Neopentanol, 2-propanol, and cyclopentanemethanol were obtained from Aldrich. Elemental analyses were performed by Oneida Research Services.

^1H and ^{13}C NMR spectra were recorded on either a Bruker AM500 or a Varian XL300 spectrometer. A Nicolet NT360 instrument was used to obtain the ^{17}O NMR spectra. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer. Isotopically labeled compounds were prepared analogously to their unlabeled isotopomers by use of the appropriately labeled starting material.

Preparation of $W_4(C)(OCH_2\text{-c-Pen})_{14}$ (I). A small Schlenk flask was charged with $W_4(OCH_2\text{-c-Pen})_{12}$ (400 mg, 0.208 mmol) and pyridine (~20 mL). The solution was degassed by 3 freeze–pump–thaw cycles. ^{13}CO (0.21 mmol) was introduced from a calibrated manifold. The flask and contents were warmed quickly to room temperature and the solution was stirred for 2 days. The volatile components were then removed in vacuo, and the dark green residue was dried. Recrystallization from CH_2Cl_2 at −20 °C followed by filtration afforded $W_4(C)(OCH_2\text{-c-Pen})_{14}$ (I) in good yield (225 mg, 51%).

Anal. Calcd for $W_4O_{14}C_{85}H_{154}$: C, 47.31; H, 7.27. Found: C, 47.31; H, 7.17.

^1H NMR (500.12 MHz, C_6D_6, 25 °C): OCH_2-c-C_5H_9 overlapping multiplets between δ 0.4 and 2.2; OCH-c-C_5H_5 listed in supplementary materials.

IR (KBr, cm^{-1}): 2949 (vs), 2864 (vs), 2695 (w), 2361 (w), 2336 (w), 1450 (s), 1362 (s), 1339 (m), 1314 (w), 1260 (w), 1173 (w), 1070 (vs), 941 (s), 901 (m), 804 (w), 656 (s).

An attempt was made to assign the vibrations associated with the carbido ligand by comparing the spectra obtained for I and I* (made with ^{13}CO). However, the spectra of I and I* were found to be identical. Either the vibrations involving the W–C bonds were very weak or they were obscured by the intense, broad absorptions arising from the OR groups.

The filtrate at this point was dark red-brown and contained a mixture of I and an oxo alkoxide of tungsten that has not been fully characterized. An alternate route to the oxo compound follows: $W_4(OCH_2\text{-c-Pen})_{12}$ (465 mg, 0.242 mmol) and pyridine (20 mL) were placed in a Schlenk tube. The solution was degassed by 3 freeze–pump–thaw cycles. O_2 (0.24 mmol) was introduced from a calibrated manifold, and the solution was stirred at room temperature. After 20 h the solution had changed from purple to red, and the volatile components were removed on the

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vacuum line to leave a dark-red solid. Numerous attempts at recrystallization have failed.

^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ OCH_2-c-C_5H_9, 4.76 (d, J_{H-H} = 6.3 Hz); c-C_5H_9, overlapping multiplets between δ 2.4 and δ 1.0. $^{13}C\{^1H\}$ (75 MHz, C_6D_6, 25 °C): δ 8.02 (1 C), 43.2 (1 C), 29.8 (2 C), and 26.1 (2 C).

^{17}O NMR (48.97 MHz, C_6D_6, 25 °C): δ 762. The same signal is observed for samples prepared from $W_4(OCH_2$-c-Pen$)_{12}$ with ^{17}O-enriched O_2 (~30% ^{17}O) or from $W_4(OCH_2$-c-Pen$)_{12}$ and $C^{17}O$ (~20% ^{17}O).

Preparation of $W_4(C)(O)(OCH_2$-*t*-Bu$)_{12}$ (III). $W_2(O$-*t*-Bu$)_6$ (1.00 g, 1.24 mmol) and solid *t*-BuCH_2OH (0.677 h, 7.45 mmol) were placed in a Schlenk flask and placed in a 0 °C bath. Hexane (25 mL) was added and the solution was stirred for 2 h, at which point the volatile components were removed on the vacuum line (at 0 °C). The yellow residue was redissolved in hexane (10 mL) and the solution quickly frozen (−196 °C). The flask was evacuated, and ^{13}CO (0.62 mmol) was introduced from a calibrated manifold. The flask was warmed to room temperature and stirred for 12 h. At this point a fine red precipitate, $W_4(\mu_3$-CO$)_2$-$(OCH_2$-*t*-Bu$)_{12}$, had formed. The flask was placed in the freezer (−20 °C) overnight, and then the solution was filtered through a glass frit. The volatile components were removed in vacuo, and the dark residue was recrystallized from CH_2Cl_2. This procedure produced a mixture of dark-green block-shaped crystals of $W_4(C)(O)(OCH_2$-*t*-Bu$)_{12}$ (III) contaminated with $W_4(OCH_2$-*t*-Bu$)_{12}$ that formed dark needles. While crystals of III obtained in this manner were suitable for X-ray crystallography (see below), a satisfactory elemental analysis has not been obtained.

Preparation of $W_4(C)(O)(O$-*i*-Pr$)_{12}$ (IV). A solution of W_2-$(^{13}CO)(O$-*t*-Bu$)_6$ (277 mg, 0.333 mmol) in hexane (50 mL) was slowly added with stirring to a solution of $W_2(O$-*t*-Bu$)_6$ (260 mg, 0.33 mmol) and HO-*i*-Pr (3 mL) in hexane (10 mL) at room temperature. After about 6 h the addition was complete and the reaction was stirred for another 12 h. The volatile components were removed in vacuo, and the dark residue was dried. Recrystallization from hexane afforded W_4-$(\mu_4$-C$)(O)(O$-*i*-Pr$)_{12}$ (IV) as dark-green crystals. The first crop was analytically pure, but subsequent crops contained visible amounts of red $W_4(\mu_3$-CO$)_2(O$-*i*-Pr$)_{12}$. Washing with a small amount of hexane removed this impurity. The isolated yield of IV was 78 mg (16%).

Anal. Calcd for $W_4O_{13}C_{37}H_{84}$: C, 30.18; H, 5.71. Found: C, 30.23; H, 5.54.

^{13}C NMR Studies. In a typical experiment, a solution of W_4-$(OCH_2$-c-Pen$)_{12}$ (200 mg, 0.104 mmol), $Cr(acac)_3$ (10 mg, 0.03 mmol), pyridine (0.3 mL), and C_6D_6 (0.3 mL) was placed in a 5-mm NMR tube equipped with a J-young valve. The solution was degassed by 3 freeze–pump–thaw cycles and then cooled to −196 °C. ^{13}CO (1 equiv) was added from a calibrated manifold, and the tube was carefully warmed to room temperature. The $^{13}C\{^1H\}$ NMR spectrum was recorded at an operating frequency of 75 MHz with a delay of 0.2 s. The use of $Cr(acac)_3$ as a shiftless relaxation agent allowed for the collection of an adequate spectrum in about 30 min. The course of the reaction was monitored hourly for 4 h and then after ~20 h and again after ~34 h. The initial spectrum had a resonance at δ 350.0 and a smaller one at δ 365.9. Over the course of the reaction, the latter resonance grew in intensity at the expense of the former.

The variable-temperature experiment was performed similarly, but the tube was maintained at the temperatures specified in the discussion section.

In an effort to determine whether or not the carbon atom in the intermediate that gives rise to the signal near δ 350 was bound to oxygen, the above reaction was repeated with $^{13}C^{16}O/^{13}C^{18}O$ (1:1). There was no evidence for an isotopic chemical shift which suggests that there is no direct C–O bonding involving this carbon atom. Free $^{13}C^{16}O/^{13}C^{18}O$ gave rise to two signals at δ 184.38 and 184.34 under similar conditions.

X-ray Crystallographic Studies. The general procedures followed during data collection and structure refinement have been previously described.[36] Additional details are given below and in Table I.

(a) **$W_2(C)(OCH_2$-c-Pen$)_{14}$** (I). X-ray quality crystals were grown from CH_2Cl_2 solution. A sample of roughly equal dimensions (0.25 mm) was selected, mounted on the goniometer, and cooled to −155 °C for characterization and data collection. The successful solution and refinement of the structure confirmed the choice of space group $P\bar{1}$. The hydrogen atoms were included in fixed, calculated positions (d(C–H) = 0.95 Å). All non-hydrogen atoms were refined with anisotropic thermal parameters.

(b) **$W_4(C)(O)(OCH_2$-*t*-Bu$)_{12}\cdot CH_2Cl_2$** (III·CH_2Cl_2). Crystals of III·CH_2Cl_2 were obtained from CH_2Cl_2 at −20 °C, and a sample of dimensions 0.16 × 0.20 × 0.32 mm was selected for the analysis. Data were collected at −181 °C and an absorption correction was applied. There was no evidence for the decay of the standard reflections monitored. The hydrogen atoms were included in fixed, calculated positions. During the final cycles of refinement, the anisotropic thermal parameters of five carbon atoms (C(5), C(7), C(38), C(44), and C(69)) refined poorly and therefore isotropic thermal parameters were used. All other non-hydrogen atoms were refined with anisotropic thermal parameters.

(c) **$W_4(C)(O)(O$-*i*-Pr$)_{12}$** (IV). A large crystal (grown from hexane solution) was cleaved to dimensions 0.24 × 0.36 × 0.36 mm, mounted, and cooled to −170 °C for data collection. The data were corrected for absorption. The structure was solved by direct methods. Hydrogen atoms were included in fixed, calculated positions. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Acknowledgment. We thank the Department of Energy, Office of Basic Science, Chemical Sciences Division for financial support.

Supplementary Material Available: Tables of $^{13}C\{^1H\}$ and ^1H NMR data for I, III, and IV, VERSORT drawings for W_4-$(\mu_4$-C$)(OCH_2$-c-Pen$)_{14}$, $W_4(\mu_4$-C$)(O)(OCH_2$-*t*-Bu$)_{12}$, and W_4-$(\mu_4$-C$)(O)(O$-*i*-Pr$)_{12}$, and listings of isotropic and anisotropic thermal parameters, bond distances, and bond angles (54 pages); listings of F_o and F_c values (64 pages). Ordering information is given on any current masthead page.

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