

## A tricarbonyl, tetranuclear tungsten cluster supported by alkoxide ligands: $W_4(OCH_2Pr^i)_{12}(\eta^2, \mu_4-CO)(CO)_2$ \*

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### Abstract

Hydrocarbon solutions of  $W_4(OCH_2Pr^i)_{12}$  react with carbon monoxide (3–6 equiv.) to give a green, air and moisture sensitive compound  $W_4(CO)_3(OCH_2Pr^i)_{12}$ , which has been characterized by infrared and NMR spectroscopy in solution and by a single crystal X-ray analysis in the solid state. The latter revealed a “spiked triangle” of tungsten atoms with W–W bonding distances ranging from 2.658(2) Å to 2.806(3) Å, all supported by bridging alkoxides. Two carbonyl ligands are *cis* to one another on a tungsten atom contained in the basal  $W_3$  triangle. The  $\eta^2, \mu_4$ -CO ligand is C bonded to each of the three tungsten atoms in the basal triangle and O bonded to the “spiked” W atom. The  $\eta^2, \mu_4$ -CO ligand contains a highly reduced carbon monoxide moiety that may be viewed as a  $\mu_3$ -oxyalkylidyne ligand and provides a model for partial reduction of CO on a metal surface in the steps preceding reductive cleavage to carbide and oxide. The solution NMR data are consistent with expectations based on the solid-state structure. Crystal data for  $W_4(CO)_3(OCH_2Pr^i)_{12}$  at  $-141^\circ C$ :  $a$  13.361(5) Å,  $b$  22.703(11) Å,  $c$  11.627(5) Å,  $\alpha$   $94.46(3)^\circ$ ,  $\beta$   $107.30(2)^\circ$ ,  $\gamma$   $102.79(3)^\circ$ ,  $Z = 2$ ,  $d_{\text{calcd}}$  1.737 g cm $^{-3}$ , space group  $P\bar{1}$ .

### Introduction

The reductive cleavage of carbon monoxide to carbide and oxide on metal surfaces is believed to be a key step in Fischer–Tropsch chemistry [1]. In previous studies we have shown that  $W_2(OR)_6$  complexes form adducts with CO in which the CO ligands are highly reduced [2–4]. Total cleavage of the C–O bond has been shown to occur in the reactions between the 12-electron clusters  $W_4(OCH_2R)_{12}$  (1) ( $R = Pr^i$ , cy-Bu, cy-Pen, cy-Hex) and CO resulting in the carbide clusters,

\* This paper is dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

$W_4(OCH_2R)_{14}(C)$ . Under some reaction conditions there is competitive formation of tricarbonyl adducts,  $W_4(OCH_2R)_{12}(CO)_3$ . Herein we report the results of our investigations into the structural chemistry of one of these derivatives,  $W_4(OCH_2Pr^i)_{12}(\eta^2, \mu_4-CO)(CO)_2$  (**2**), which contains a partially reduced  $\eta^2$ -bound CO ligand [5].

## Experimental

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk and glovebox techniques. Hydrocarbon solvents were distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves. The preparation of  $W_4(OCH_2Pr^i)_{12}$  (**1**) has been previously described [6]. Isobutanol was purchased from Aldrich Chemical Co., and stored over 4 Å molecular sieves prior to use.

NMR spectra were recorded on either a Bruker AM500 or a Varian XL300 spectrometer. Infrared spectra were recorded on a Perkin Elmer 283 spectrometer.

Table 1

Summary of crystal data

Empirical formula	$C_{51}H_{108}O_{15}W_4$
Color of crystal	dark brown/black
Crystal dimensions (mm)	0.14 × 0.28 × 0.24 (max/min ABS: 0.158, 0.381)
Space group	$P\bar{1}$
Cell dimensions	
temperature (°C)	-141
<i>a</i> (Å)	13.361(5)
<i>b</i> (Å)	22.703(11)
<i>c</i> (Å)	11.627(5)
<i>α</i> (deg)	94.46(3)
<i>β</i> (deg)	107.30(2)
<i>γ</i> (deg)	102.79(3)
Z (molecules/cell)	2
Volume (Å <sup>3</sup> )	3244.46
Calculated density (g/cm <sup>3</sup> )	1.737
Wavelength (Å)	0.71069
Molecular weight	1696.81
Linear absorption coefficient (cm <sup>-1</sup> )	72.745
Scan speed (deg/min)	6.0
Scan width (deg + dispersion)	1.8
Individual background (sec)	6
Two-theta range (deg)	6–45
Total number of reflections collected	10272
number of unique intensities	8523
number with <i>F</i> > 0.0	7675
number with <i>F</i> > 3.0σ( <i>F</i> )	5105
<i>R</i> ( <i>F</i> )	0.0786
<i>R</i> <sub>w</sub> ( <i>F</i> )	0.0829
Goodness of fit for the last cycle	3.003
Maximum δ/σ for last cycle	0.55

Table 2

Fractional coordinates and isotropic thermal parameters for  $W_4(CO)_3(OCH_2OPr^i)_{12}$ 

Atom	$10^4x$	$10^4y$	$10^4z$	$10B_{iso}$
W(1)	4468(1)	2211(1)	8015(1)	22
W(2)	4720(1)	2596(1)	10462(1)	23
W(3)	2725(1)	2100(1)	8719(1)	20
W(4)	2290(1)	3213(1)	8128(1)	19
C(5)	4075(24)	2942(15)	9142(30)	18(6)
O(6)	3886(15)	3499(10)	8919(20)	17(4)
C(7)	5520(21)	2997(14)	8108(28)	12(5)
O(8)	6157(22)	3411(14)	7869(28)	46(6)
C(9)	3676(31)	2413(19)	6403(40)	36(8)
O(10)	3247(22)	2489(14)	5393(28)	44(6)
O(11)	5244(19)	1929(12)	9694(24)	33(5)
C(12)	6352(25)	1873(16)	10078(32)	22(6)
C(13)	6445(27)	1306(17)	10652(35)	28(7)
C(14)	5854(40)	757(25)	9731(50)	60(12)
C(15)	7566(41)	1279(26)	11019(52)	63(12)
O(16)	3473(16)	1869(10)	10313(20)	20(4)
C(17)	3541(33)	1281(21)	10699(42)	42(9)
C(18)	3975(36)	1364(23)	12070(46)	51(10)
C(19)	3402(38)	1618(24)	12842(48)	55(11)
C(20)	4128(38)	716(24)	12320(48)	56(11)
O(21)	3179(18)	1409(12)	7880(24)	31(5)
C(22)	2565(27)	1055(17)	6717(35)	28(7)
C(23)	2961(34)	530(21)	6461(43)	44(9)
C(24)	2933(41)	83(26)	7211(51)	63(12)
C(25)	2353(42)	206(26)	5108(52)	63(12)
O(26)	1741(17)	2316(11)	7177(21)	24(4)
C(27)	676(28)	1959(18)	6403(36)	30(7)
C(28)	583(26)	1952(17)	5067(34)	25(7)
C(29)	-384(32)	1402(20)	4282(41)	41(9)
C(30)	398(31)	2556(19)	4539(39)	37(8)
O(31)	2109(18)	2730(12)	9543(24)	32(5)
C(32)	1174(29)	2610(18)	9859(37)	33(8)
C(33)	1329(33)	2345(21)	11048(41)	41(9)
C(34)	1944(37)	2811(23)	12138(47)	53(11)
C(35)	189(57)	2039(34)	11054(69)	95(17)
O(36)	5150(19)	1656(12)	7145(24)	33(5)
C(37)	5715(30)	1789(19)	6371(39)	35(8)
C(38)	6474(35)	1376(23)	6446(45)	49(10)
C(39)	5941(37)	731(24)	6178(47)	54(11)
C(40)	7116(41)	1553(25)	5468(51)	61(12)
O(41)	4424(19)	3008(12)	11785(24)	34(5)
C(42)	4910(31)	3524(20)	12642(40)	38(8)
C(43)	5118(27)	3377(17)	13947(35)	29(7)
C(44)	5443(30)	3948(19)	14815(39)	37(8)
C(45)	5915(36)	2993(23)	14204(46)	51(10)
O(46)	6148(17)	3101(11)	11030(21)	24(4)
C(47)	6963(32)	3583(20)	10902(40)	39(8)
C(48)	7929(53)	3782(33)	12032(65)	86(16)
C(49)	8830(63)	4286(38)	11814(75)	108(19)
C(50)	8465(48)	3336(30)	12507(59)	77(15)
O(51)	1398(16)	1480(10)	8635(21)	22(4)
C(52)	1050(36)	851(23)	8656(45)	50(10)
C(53)	-31(43)	507(27)	7936(54)	65(12)

Table 2 (continued)

Atom	$10^4x$	$10^4y$	$10^4z$	$10B_{iso}$
C(54)	-911(34)	821(22)	8136(44)	46(10)
C(55)	-244(39)	-157(25)	8138(49)	57(11)
O(56)	830(17)	3144(11)	7414(22)	25(5)
C(57)	315(27)	3654(17)	7198(34)	27(7)
C(58)	-948(35)	3501(22)	6987(44)	47(10)
C(59)	-1333(42)	4030(26)	6526(52)	62(12)
C(60)	-1079(30)	3251(19)	7880(38)	35(8)
O(61)	2531(19)	3532(12)	6781(24)	34(5)
C(62)	3376(30)	3885(19)	6389(39)	37(8)
C(63)	3187(35)	4480(22)	6028(45)	47(10)
C(64)	3067(49)	4830(30)	7010(62)	80(15)
C(65)	2187(54)	4361(33)	4885(66)	89(17)
O(66)	2367(18)	3931(11)	9128(23)	29(5)
C(67)	3030(33)	4162(21)	10367(42)	43(9)
C(68)	2695(36)	4715(22)	10856(46)	49(10)
C(69)	1567(50)	4546(31)	10880(62)	82(15)
C(70)	3458(46)	4967(29)	12118(58)	73(14)

*Preparation of  $W_4(OCH_2Pr^i)_{12}(\eta^2, \mu_4-CO)(CO)_2$  (2)*

A 100 mL round bottom flask was charged with **1** (140 mg, 0.087 mmol) and hexane (10 mL). The dark purple solution was degassed by three freeze-pump-thaw cycles. CO ( $\approx 0.4$  mmol) was admitted to the flask, and the solution stirred at room temperature for 24 h. At this point the solvent was removed on the vacuum line to afford  $W_4(OCH_2Pr^i)_{12}(\eta^2, \mu_4-CO)(CO)_2$  (**2**) as a dark green solid.

$^1H$  NMR (500.13 MHz, toluene- $d_8$ , 25 °C)  $\delta$ : methylene,  $CH_2$ : d  $\times$  d;  $H_a^1$  5.50,  $H_a^2$  5.37,  $H_a^3$  5.18,  $H_a^4$  5.00,  $H_a^5$  5.00,  $H_a^6$  4.93,  $H_a^7$  4.90,  $H_a^8$  4.87,  $H_a^9$  4.81,  $H_a^{10}$  4.76,  $H_a^{11}$  4.73,  $H_a^{12}$  4.71,  $H_a^{13}$  4.69,  $H_a^{14}$  4.66,  $H_a^{15}$  4.63,  $H_a^{16}$  4.50,  $H_a^{17}$  4.40,  $H_a^{18}$  4.35,  $H_a^{19}$  4.31,  $H_a^{20}$  4.25,  $H_a^{21}$  3.83,  $H_a^{22}$  3.80,  $H_a^{23}$  3.75,  $H_a^{24}$  3.51,

$^{13}C$  NMR (125.76 MHz, toluene- $d_8$ , 25 °C)  $\delta$ : Carbonyls, CO: 259.47,  $^2J(^{13}C-^{13}C) = 1.6$  Hz,  $^2J(^{13}C) = 4.3$  Hz,  $J(^{183}W-^{13}C) = 169.8$  Hz, 10%,  $J(^{183}W-^{13}C) = 60.4$  Hz, 11%,  $J(^{183}W-^{13}C) = 54.4$  Hz, 11%; 225.96,  $^2J(^{13}C-^{13}C) = 1.6$  Hz,  $^2J(^{13}C-^{13}C) = 3.3$  Hz,  $J(^{183}W-^{13}C) = 177.0$  Hz, 13%; 219.64,  $^2J(^{13}W-^{13}C) = 3.3$  Hz,  $^2J(^{13}C-^{13}C) = 4.3$  Hz,  $J(^{183}W-^{13}C) = 159.6$  Hz, 14%.

Methylenes,  $CH_2$ : 87.64, 87.21, 86.48, 55.56, 83.63, 83.22, 82.61, 81.88, 81.73, 81.63, 78.36, 77.57; methines, CH: 34.91, 35.53, 32.92, 32.83, 32.40, 32.15, 32.10, 31.72, 31.29, 30.46, 28.73; methyls,  $CH_3$ : 22 to 18.

IR (hexane,  $cm^{-1}$ )  $\nu(CO)$  1965 s, 1883 s; (Nujol mull, green,  $cm^{-1}$ ): 1969 s, 1921 m, 1885 s, 1365 s, 1293 w, 1264 w, 1068 vs, 1030 vs, 959 w, 944 w, 905 vw, 822 w, 795 w, 656 m/brd, 624 m/brd.

*X-Ray crystallographic analysis of 2*

General procedures for data collection and structure refinement have been previously reported [7]. Additional details are given below and in Table 1.

A few small crystals suitable for X-ray diffraction were grown from toluene solution at -20 °C. Intensity data were collected at -141 °C. The decay of the four standard reflections indicated that the sample was decomposing. The crystal also appeared to fracture and therefore it was remounted approximately midway through

Table 3

Selected bond distances (Å) and angles (°) for  $W_4(OCH_2\text{-}i\text{-Pr})_{12}(CO)_3$ 

## a. Bond distances

A	B	Distance	A	B	Distance
W(1)	W(2)	2.8085(26)	W(3)	O(21)	2.078(25)
W(1)	W(3)	2.6583(21)	W(3)	O(26)	2.050(22)
W(1)	O(11)	2.140(26)	W(3)	O(31)	2.102(25)
W(1)	O(21)	2.171(25)	W(3)	O(51)	1.976(21)
W(1)	O(36)	2.073(25)	W(3)	C(5)	2.23(3)
W(1)	C(5)	2.28(3)	W(4)	O(6)	1.987(19)
W(1)	C(7)	1.98(3)	W(4)	O(26)	2.101(24)
W(1)	C(9)	2.00(4)	W(4)	O(31)	2.088(26)
W(2)	W(3)	2.7537(23)	W(4)	O(56)	1.844(21)
W(2)	O(11)	2.053(26)	W(4)	O(61)	1.860(26)
W(2)	O(16)	2.024(21)	W(4)	O(66)	1.893(25)
W(2)	O(41)	1.924(27)	W(4)	C(5)	2.56(3)
W(2)	O(46)	1.885(21)	O(6)	C(5)	1.37(4)
W(2)	C(5)	1.85(3)	O(8)	C(7)	1.23(4)
W(3)	W(4)	2.8058(24)	O(10)	C(9)	1.19(5)
W(3)	O(16)	1.997(22)			

## b. Bond angles

A	B	C	Angle	A	B	C	Angle
W(2)	W(1)	W(3)	60.42(6)	O(26)	W(4)	O(31)	80.2(10)
O(11)	W(1)	O(21)	83.0(9)	O(26)	W(4)	O(56)	78.2(9)
O(11)	W(1)	O(36)	88.5(10)	O(26)	W(4)	O(61)	92.0(10)
O(11)	W(1)	C(5)	87.5(11)	O(26)	W(4)	O(66)	161.0(9)
O(11)	W(1)	C(7)	100.8(11)	O(26)	W(4)	C(5)	86.3(9)
O(11)	W(1)	C(9)	175.9(14)	O(31)	W(4)	O(56)	95.4(10)
O(21)	W(1)	O(36)	88.2(9)	O(31)	W(4)	O(61)	170.3(10)
O(21)	W(1)	C(5)	102.3(10)	O(31)	W(4)	O(66)	88.0(10)
O(21)	W(1)	C(7)	173.5(10)	O(31)	W(4)	C(5)	71.7(10)
O(21)	W(1)	C(9)	93.1(13)	O(56)	W(4)	O(61)	88.6(10)
O(36)	W(1)	C(5)	168.2(10)	O(56)	W(4)	O(66)	88.2(10)
O(36)	W(1)	C(7)	97.0(11)	O(56)	W(4)	C(5)	161.4(10)
O(36)	W(1)	C(9)	89.9(14)	O(61)	W(4)	O(66)	100.9(11)
C(5)	W(1)	C(7)	72.9(11)	O(61)	W(4)	C(5)	102.2(10)
C(5)	W(1)	C(9)	94.8(14)	O(66)	W(4)	C(5)	104.2(10)
C(7)	W(1)	C(9)	83.1(14)	W(4)	O(6)	C(5)	97.5(17)
W(1)	W(2)	W(3)	57.09(6)	W(1)	O(11)	W(2)	84.1(9)
O(11)	W(2)	O(16)	81.1(9)	W(1)	O(11)	C(12)	124.8(21)
O(11)	W(2)	O(41)	153.2(11)	W(2)	O(11)	C(12)	124.6(21)
O(11)	W(2)	O(46)	90.0(10)	W(2)	O(16)	W(3)	86.5(9)
O(11)	W(2)	C(5)	103.2(13)	W(2)	O(16)	C(17)	127.2(20)
O(16)	W(2)	O(41)	90.0(10)	W(2)	O(16)	C(17)	132.3(23)
O(16)	W(2)	O(46)	158.0(9)	W(1)	O(21)	W(3)	77.4(9)
O(16)	W(2)	C(5)	99.4(11)	W(1)	O(21)	C(22)	119.5(21)
O(41)	W(2)	O(46)	89.1(10)	W(3)	O(21)	C(22)	124.7(20)
O(41)	W(2)	C(5)	103.1(13)	W(3)	O(26)	W(4)	85.0(9)
O(46)	W(2)	C(5)	102.2(12)	W(3)	O(26)	C(27)	127.7(21)
W(1)	W(3)	W(2)	62.49(6)	W(4)	O(26)	C(27)	131.9(20)
W(1)	W(3)	W(4)	97.07(7)	W(3)	O(31)	W(4)	84.1(9)
W(2)	W(3)	W(4)	96.57(7)	W(3)	O(31)	C(32)	127.3(23)
O(16)	W(3)	O(21)	87.5(9)	W(4)	O(31)	C(32)	123.5(22)
O(16)	W(3)	O(26)	170.7(8)	W(1)	O(36)	C(37)	129.3(24)

Table 3 (continued)

b. Bond angles							
A	B	C	Angle	A	B	C	Angle
O(16)	W(3)	O(31)	92.8(9)	W(2)	O(41)	C(42)	137.5(24)
O(16)	W(3)	O(51)	88.6(9)	W(2)	O(46)	C(47)	150.6(24)
O(16)	W(3)	C(5)	88.7(10)	W(3)	O(51)	C(52)	139.7(23)
O(21)	W(3)	O(26)	97.8(9)	W(4)	O(56)	C(57)	126.1(20)
O(21)	W(3)	O(31)	173.9(9)	W(4)	O(61)	C(62)	141.9(24)
O(21)	W(3)	O(51)	87.4(9)	W(4)	O(66)	C(67)	129.1(23)
O(21)	W(3)	C(5)	107.3(10)	W(1)	C(5)	W(2)	85.0(12)
O(26)	W(3)	O(31)	81.1(9)	W(1)	C(5)	W(3)	72.3(10)
O(26)	W(3)	O(51)	84.0(9)	W(1)	C(5)	W(4)	115.5(13)
O(26)	W(3)	C(5)	97.0(10)	W(1)	C(5)	O(6)	132.0(23)
O(31)	W(3)	O(51)	86.5(9)	W(2)	C(5)	W(3)	84.5(13)
O(31)	W(3)	C(5)	78.8(10)	W(2)	C(5)	W(4)	140.2(16)
O(51)	W(3)	C(5)	164.9(11)	W(2)	C(5)	O(6)	137.8(25)
O(6)	W(4)	O(26)	114.6(8)	W(3)	C(5)	W(4)	71.4(8)
O(6)	W(4)	O(31)	92.0(9)	W(3)	C(5)	O(6)	121.7(19)
O(6)	W(4)	O(56)	166.2(9)	W(4)	C(5)	O(6)	50.3(13)
O(6)	W(4)	O(61)	85.9(10)	W(1)	C(7)	O(8)	163.0(27)
O(6)	W(4)	O(66)	80.4(9)	W(1)	C(9)	O(10)	173.(4)
O(6)	W(4)	C(5)	32.1(9)				

the data collection. The two partial data sets were corrected independently for absorption, and then placed on a common scale by use of the standard reflections. The merging  $R$  was 0.083 for the 1586 reflections measured more than once.

The final model included anisotropic thermal parameters for the tungsten atoms, and isotropic thermal parameters for all other atoms. Hydrogen atoms were included as fixed atom contributions at calculated positions ( $d(\text{C}-\text{H}) = 0.96 \text{ \AA}$ ). Fractional coordinates for all non-hydrogen atoms in **2** are listed in Table 2; bond length and selected bond angles data are collected in Table 3.

## Results and discussion

The 12-electron butterfly cluster  $\text{W}_4(\text{OCH}_2\text{Pr}^i)_{12}$  (**1**) rapidly reacts with excess CO at room temperature to afford  $\text{W}_4(\text{OCH}_2\text{Pr}^i)_{12}(\eta^2, \mu_4\text{-CO})(\text{CO})_2$  (**2**). The reaction is essentially quantitative (by NMR) when only a slight excess (3–6 equiv.) of CO is employed. With a greater excess of CO the yields of **2** are lower, and  $\text{W}(\text{CO})_6$  as well as other unidentified products are produced (experiments have shown that **2** reacts with CO to give  $\text{W}(\text{CO})_6$ ). We have previously noted the formation of  $\text{M}(\text{CO})_6$  complexes by the carbonylation of  $\text{M}_2(\text{OR})_6$  clusters ( $\text{M} = \text{Mo}, \text{W}$ ) [2]. Cluster **2** is extremely soluble in hydrocarbon solvents in which it forms dark green solutions. It is air and moisture sensitive both in solution and in the solid.

The structure of **2** has been determined by X-ray crystallography. Although the overall agreement of the model was poor ( $R = 0.079$ ) the gross features of the structure of **2** are believed to be correct.

A view of the molecule is shown in Fig. 1 and four views of the central skeleton (one showing the atom numbering scheme) are given in Fig. 2. The four tungsten atoms adopt a spiked-triangular configuration, with the W(3)–W(4) vector almost

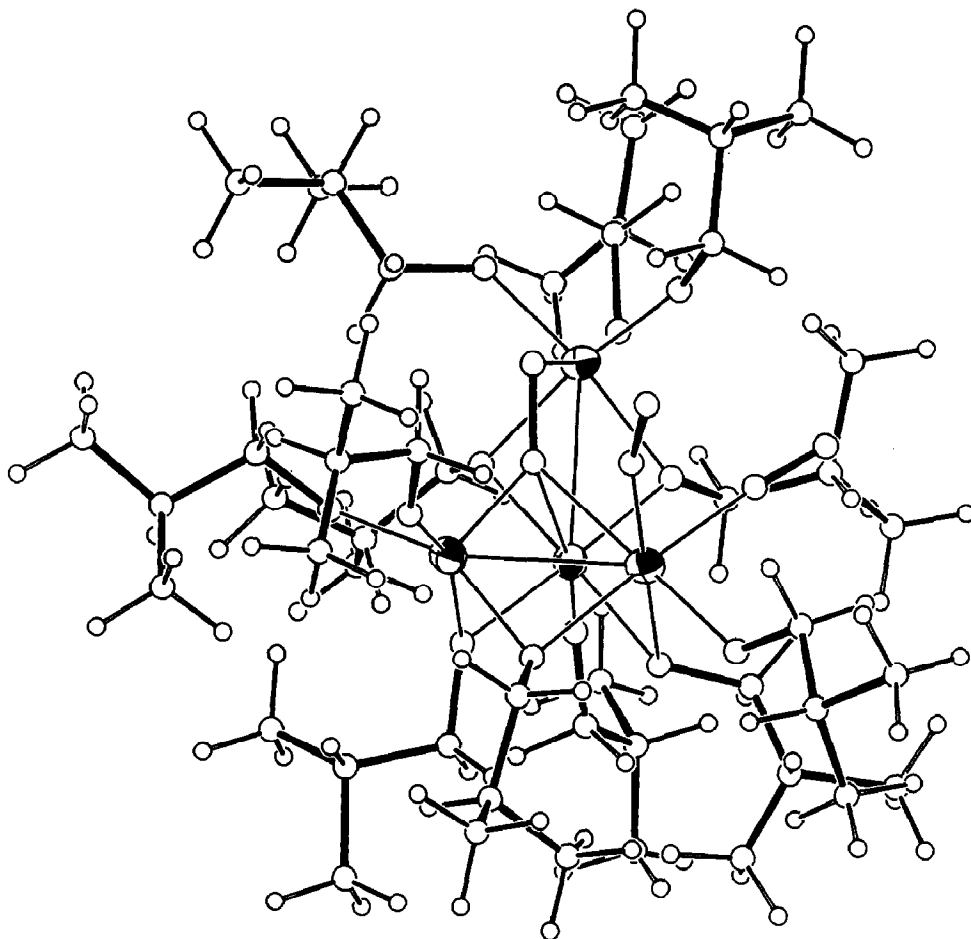


Fig. 1. Molecular structure of  $W_4(OCH_2Pr^i)_{12}(\eta^2, \mu_4-CO)(CO)_2$  (1).

perpendicular to the plane of the W(1)–W(2)–W(3) triangle. All the W–W bonding interactions have bridging alkoxide ligands, and with lengths ranging from 2.658(2) Å to 2.806(3) Å (see Table 3) they may be considered as single bonds. The metals are also linked by the isocarbonyl ligand, which is triply bridging the W(1)–W(2)–W(3) triangle through the carbon atom, and bound to W(4) principally through the oxygen atom (W(4)–O(6) = 1.99(2) Å versus W(4)–C(5) = 2.56(3) Å). The remaining CO groups are both terminally bound to W(1) and they are *cis* to each other.

If the W–W bonds are ignored, then three of the tungsten atoms can be seen to be in pseudo-octahedral environments while the fourth, W(2), is in a pseudo-square pyramidal environment.

The bond lengths associated with the  $\eta^2, \mu_4-CO$  ligand are: W(1)–C(5) = 2.28(3) Å, W(2)–C(5) = 1.85(3) Å, W(3)–C(5) = 2.23(3) Å, C(5)–O(6) = 1.37(4) Å, and W(4)–O(6) = 1.99(2) Å. The C(5)–O(6) bond length is comparable to the C–O bond lengths in other  $\eta^2$ -bound carbonyl ligands. Thus in the alkoxide clusters  $[W_2(OPr^i)_6(CO)]_2$  [3] and  $[W_2(OPr^i)_6(py)(CO)]_2$  [8] the C–O bond lengths in the isocarbonyl ligands are 1.35(1) Å and 1.33(3) Å, respectively, while those in the carbonyl clusters  $(OC)_9Co_3(\eta^2, \mu_4-CO)MCl(\eta^5-C_5H_5)$  (M = Ti, Zr, Hf) range from 1.22(4) Å for M = Ti to 1.32(3) Å for M = Hf [9,10]. Another example of an

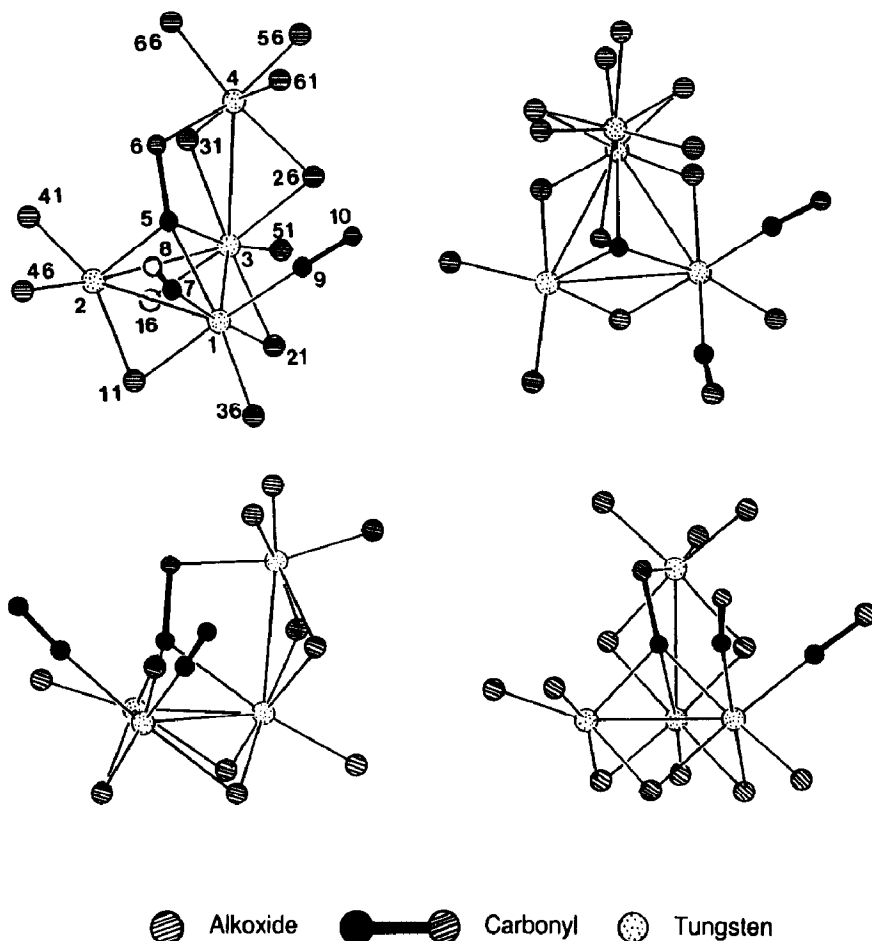


Fig. 2. Four views of the central  $W_4(O)_{12}(CO)_3$  skeleton of the  $W_4(OCH_2Pr^1)_{12}(CO)_3$  molecule giving the atom numbering scheme used in the tables.

$\eta^2$ -bound carbonyl is found in the cluster  $[Co_2Mo_2(\mu-CO)_3(\eta^2, \mu_4-CO)(\eta^5-C_5H_5)_2(\eta^5-C_5Me_5)_2]$  (3) [11]. This cluster has a structure that is very similar to that of 2 with a triangular  $Co_2Mo$  fragment attached to the second molybdenum atom by a  $Mo=Mo$  double bond. The isocarbonyl ligand bridges the four metal atoms in a similar manner as found in 2. However, while the isocarbonyl ligand in 3 should be considered as a  $\pi$ -bound CO, that in 2 is only  $\sigma$ -bound through the oxygen. This difference probably results from the different electronic requirements of the metals.

The  $W(4)-O(6)$  and  $C(5)-O(6)$  bond lengths are within the range of the  $W-O$  (alkoxide) and  $O-C$  (alkoxide) bond lengths found in 2. Thus this group may be viewed as an metallo-alkoxide, or, alternatively as a  $\mu_3$ -oxyalkylidyne (i.e.,  $W_3C-O-W$ ). Alternatively, given the inequivalence of the  $W-C(5)$  bond lengths (see below), this ligand may also be viewed as a  $(RO)_3W\equiv C-O-W$  fragment  $\pi$ -bonded to the two remaining tungsten atoms.

In solution, NMR and infrared data suggest that 2 has essentially the same structure as found in the solid. The  $^{13}C\{^1H\}$  NMR spectrum of 2 in toluene- $d_8$  solution at ambient temperature consists of 12 resonances between  $\delta$  77 and  $\delta$  88



that can be assigned to the methylene carbon atoms of the 12 inequivalent  $\text{OCH}_2\text{Pr}^i$  ligands. The  $^1\text{H}$  NMR spectrum contains 24 doublets of doublets assignable to the methylene protons, which indicates that the 12 alkoxide ligands do not lie on planes of symmetry.

Three resonances are observed in the carbonyl region of the  $^{13}\text{C}$  NMR spectrum. The pattern of  $^{13}\text{C}$ - $^{13}\text{C}$  and  $^{13}\text{C}$ - $^{183}\text{W}$  coupling indicates that all three carbonyl groups are attached to the same tungsten atom, and that two of these groups are bound through carbon to a single tungsten atom while the third is bound through carbon to three chemically different tungsten atoms. On this basis the resonance at  $\delta$  259.5 can be assigned to the carbon atom of the isocarbonyl ligand. The magnitudes of the  $^{13}\text{C}$ - $^{183}\text{W}$  couplings for this resonance (54.4 Hz, 60.4 Hz, and 169.8 Hz) are consistent with the asymmetry in the W-C bond lengths found in the solid (see Table 3).

The infrared spectrum of **2** in hexane contains two bands in the terminal CO stretching region at  $1965\text{ cm}^{-1}$  and  $1883\text{ cm}^{-1}$  consistent with a *cis*-W(CO)<sub>2</sub> grouping. The relative intensities of these bands indicate a OC-W-CO angle of about  $80^\circ$  [12], in excellent agreement with that found in the solid ( $83(1)^\circ$ ). Attempts to assign the  $\nu(\text{CO})$  of the isocarbonyl group were unsuccessful. The infrared spectra of **2** and **2'** (made with  $^{13}\text{CO}$ ) showed the expected shifts in the terminal CO-stretching region, but were the same from  $1600$  to  $600\text{ cm}^{-1}$ . It is possible that the band due to the  $\eta^2, \mu_4$ -CO is weak, or it could be obscured by the intense, broad absorptions at  $1068$  and  $1030\text{ cm}^{-1}$ .

In our original communication we commented on the apparent competitive formation of **2** and the carbide cluster,  $\text{W}_4(\text{OCH}_2\text{Pr}^i)_{14}(\text{C})$  (**4**), by the reaction of **1** with CO. Recent evidence suggests that this is indeed the case. The relative amounts of **2** and **4** formed are dependent on the reaction conditions, with, for example, **2** being favored in noncoordinating solvents. Further studies are in progress to uncover the details of the formation of **4**, but the partial reduction of CO to the isocarbonyl ligand in **2** is indicative of one possible route. It may be that the presence of the two terminal CO groups in **2** prevents the complete reduction of the  $\eta^2, \mu_4$ -CO ligand to carbide and oxide.

Finally, we note that the addition of three CO groups to **1** results in the cleavage of one wingtip-hinge W-W bond of the metal core. This is in contrast to the behavior of butterfly clusters supported by carbonyl ligands, for which one metal-metal bond is cleaved for each two-electron donor ligand added [13]. The difference probably reflects the greater  $\pi$ -buffering capabilities of alkoxide ligands as compared to that of CO ligands [14].

## Acknowledgment

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