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Structural characterization of a tetranuclear tungsten carbide cluster formed by the reductive cleavage of carbon monoxide: $W_4(\mu_4\text{-}C)(OCH_2\text{-c-}C_5H_9)_{14}$ *

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Abstract

From the reaction between $W_4(OCH_2\text{-c-}C_5H_9)_{12}$ and CO (1 equiv.) in hydrocarbon solvents at room temperature, the tetranuclear carbido cluster $W_4(\mu_4\text{-}C)(OCH_2\text{-c-}C_5H_9)_{14}$ has been isolated and structurally characterized. There is a central $W_4(\mu_4\text{-}C)$ moiety typical of that seen in carbonyl supported $M_4(\mu_4\text{-}C)$ containing compounds. Five W–W distances span the range 2.78 to 2.86 Å and the carbido–tungsten distances fall into two groups: 1.92 and 1.98 Å to the wingtip tungsten atoms and 2.27 and 2.28 Å to the backbone W atoms. The presence of 14 supporting alkoxide ligands allows three of the four tungsten atoms to attain a pseudo-octahedral geometry while the fourth tungsten atom is in a square pyramidal environment. The use of ^{13}CO in the preparation of $W_4(\mu_4\text{-}C)(OCH_2\text{-c-}C_5H_9)_{14}$ reliably establishes that the carbido carbon atom originates from carbon monoxide. The fate of the carbonyl oxygen atom is unknown.

Prior work has shown that carbon monoxide can be activated in reactions with $M_2(OR)_6$ (M≡M) compounds to give inorganic analogues of cyclopropenones, $M_2(OR)_6(\mu\text{-}CO)$ [1,2]. The latter show remarkably low values of $\nu(CO)$, e.g. 1570 cm^{-1} for $M = W$ and $R = Bu^t$ [2]. In a further reaction between $W_2(OR)_6$ and $W_2(OR)_6(\mu\text{-}CO)$ there is evidence that the C–O bond of the carbonyl ligand is cleaved and a $W_4(\mu\text{-}C)$ containing compound is formed [3]. The latter reaction is complicated by competing dimerization reactions which give $W_4(OR)_{12}$ and $W_4(\mu_3\text{-}CO)_2(OR)_{12}$. As an alternative synthetic approach we have studied reactions wherein a preformed tetranuclear alkoxide cluster, $W_4(OR)_{12}$, is allowed to react with CO

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

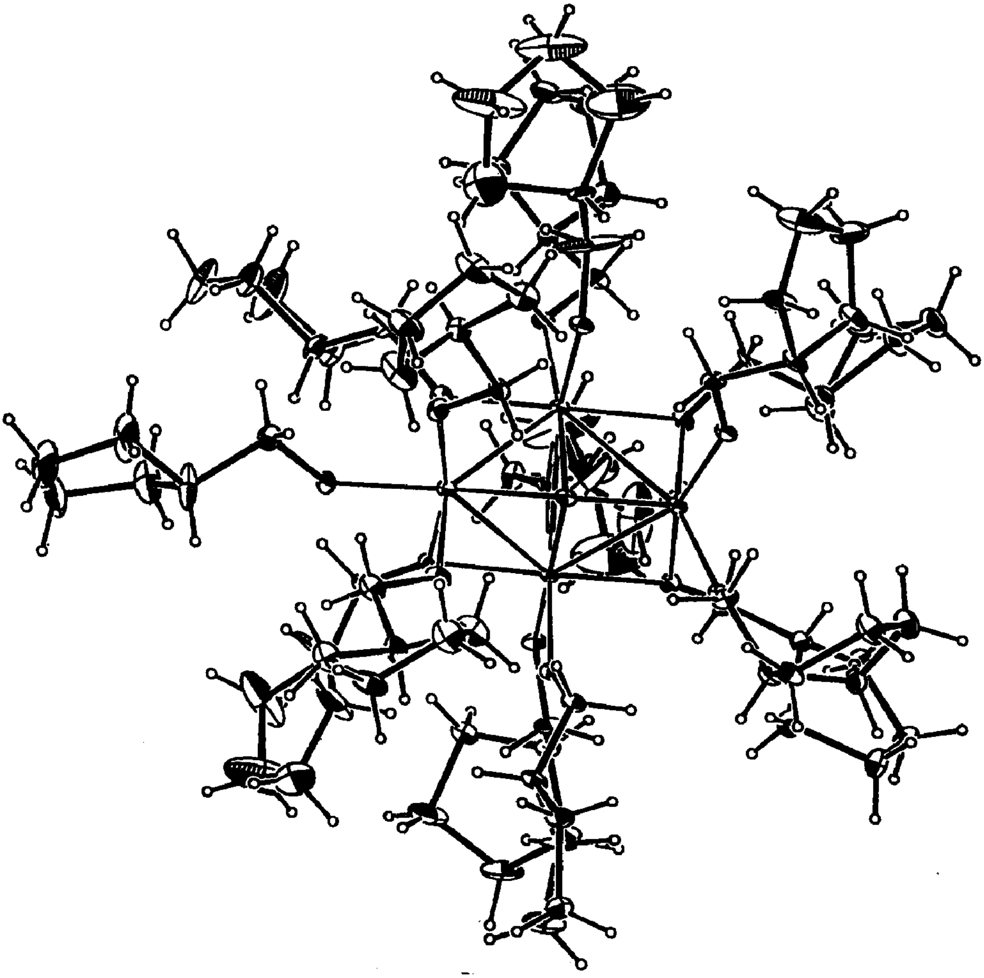

Fig. 1. Molecular structure of $W_4(\mu_4\text{-}C)(OCH_2\text{-}c\text{-}C_5H_9)_{14}$.

[4]. Again there is evidence for the formation of a $W_4(\mu\text{-}C)$ containing compound but here the reaction is complicated by the competitive formation of a tricarbonyl cluster $W_4(\eta^2,\mu_4\text{-}CO)(CO)_2(OR)_{12}$ [5]. We report here the structural characterization of $W_4(\mu_4\text{-}C)(OCH_2\text{-}c\text{-}C_5H_9)_{14}$.

The reaction between $W_4(OCH_2\text{-}c\text{-}C_5H_9)_{12}$ [6] and CO (1 equiv.) in hexane at 0 °C proceeds to give a mixture of products as determined by NMR spectroscopy. When ^{13}CO is employed, only two compounds containing the labelled ^{13}C carbon are observed by ^{13}C NMR: $W_4(\eta^2,\mu_4\text{-}^{13}CO)(^{13}CO)_2(OCH_2\text{-}c\text{-}C_5H_9)_{12}$ and a $W_4(\mu_4\text{-}^{13}C)$ containing compound. The latter is present as the major component and we have been able to isolate it in a pure crystalline form by slow evaporation of a methylene chloride solution.

The molecular structure of $W_4(\mu_4\text{-}C)(OCH_2\text{-}c\text{-}C_5H_9)_{14}$ has been determined by X-ray crystallography and is given in Fig. 1 [7*]. A view of the central $W_4(C)(O)_{14}$ core is presented in Fig. 2, where a comparison is made with $W_4(\mu_4\text{-}$

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* Reference number with asterisk indicates a note in the list of references.

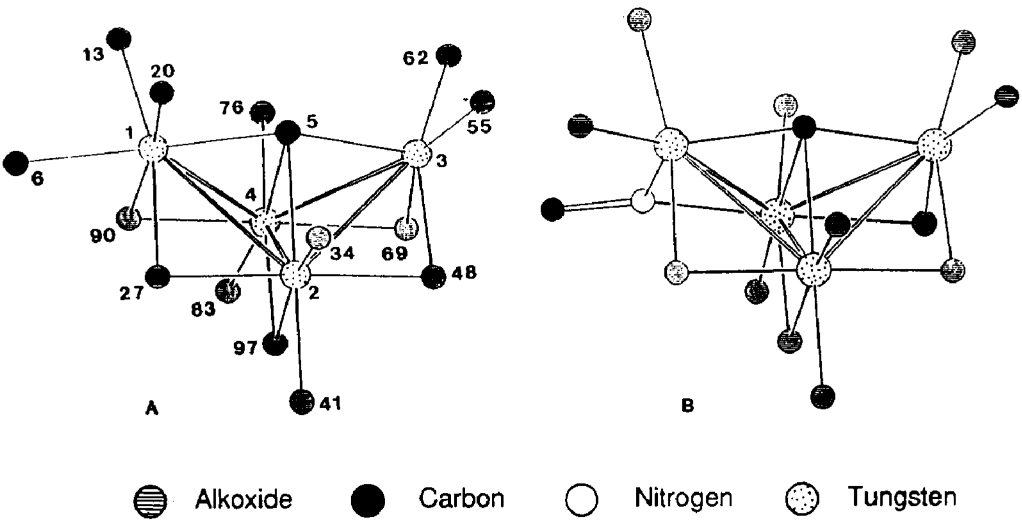
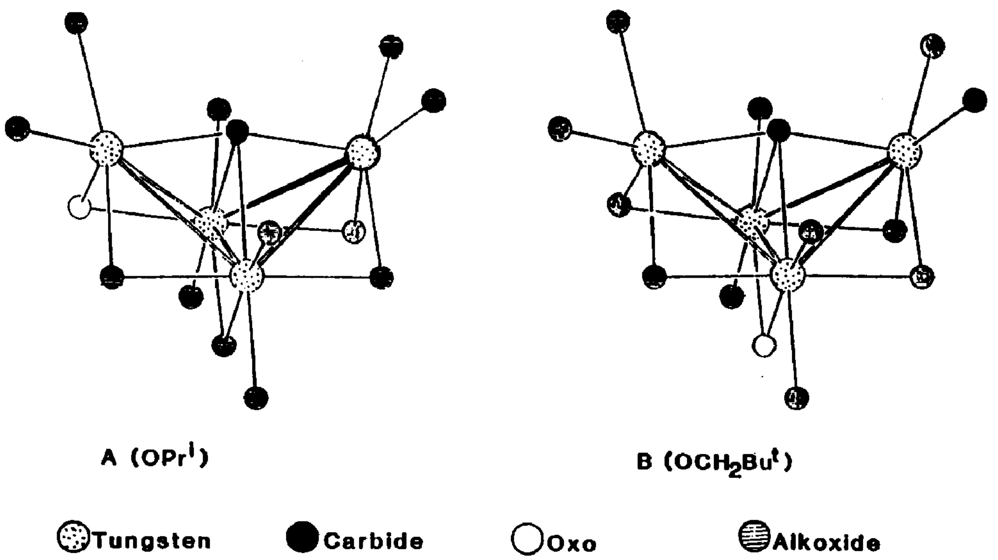


Fig. 2. A. A view of the $W_4(\mu_4\text{-C})(O)_{14}$ core of $W_4(\mu_4\text{-C})(OCH_2\text{-c-}C_5H_9)_{14}$ showing the atomic numbering scheme. B. A view of the $W_4(\mu_4\text{-C})(NMe)(O)_{12}$ core of $W_4(\mu_4\text{-C})(NMe)(OPr^i)_{12}$.

$C)(NMe)(OPr^i)_{12}$, the only other structurally characterized tungsten carbido cluster. The tungsten atoms adopt a butterfly configuration with 5 W–W distances spanning the range 2.78 to 2.86 Å, and the carbido carbon is more strongly bound to the wingtip W atoms (W(1)–C(5) = 1.98(1) Å and W(3)–C(5) = 1.92(1) Å) than to the backbone W atoms (W(2)–C(5) = 2.27(1) Å and W(4)–C(5) = 2.28(1) Å) as judged by W–C distances. The angles subtended by the carbido carbon atom are 162.3(6)° and 75.3(3)° between wingtip and backbone W atoms, respectively. The salient features of the $W_4(\mu_4\text{-C})$ core are similar to those of carbonyl supported $M_4(\mu_4\text{-C})$ clusters, e.g. $Fe_4(\mu_4\text{-C})(CO)_{12}{}^{2-}$ [8]. Ignoring W–W bonds, three of the tungsten atoms are in pseudo-octahedral environments while one of the wingtip W atoms is in a square-based pyramidal environment with the carbido ligand at the apex.

The ^{13}C NMR spectrum reveals that the carbido ligand derived from ^{13}CO (δ 366.8) is flanked by satellites due to coupling to ^{183}W ($I = 1/2$, 14.5% nat. abund.) of magnitude 23.4 Hz, 117 Hz, and 144 Hz, and relative intensity 2 : 1 : 1, respectively. The smaller coupling of 23.4 Hz must arise from coupling to the two equivalent backbone tungsten atoms [9*].

The present work unequivocally establishes that there are 14 alkoxide ligands and that there is no oxo group present. The similarity in the ^{13}C and ^1H NMR spectra of the compounds $W_4(\mu_4\text{-C})(OCH_2R)_{14}$, where $R = Pr^i$, c-Bu, c-Pen, and c-Hex, strongly suggests that these clusters are related both in structure and formula [10]. In contrast, two other compounds that have a $W_4(\mu_4\text{-C})$ core are different in structure and formula. It seems most likely that all share a closely related $[W_4(\mu_4\text{-C})]^{14+}$ core. We formulate the other clusters as $W_4(\mu_4\text{-C})(O)(OPr^i)_{12}$ [3], and $W_4(\mu_4\text{-C})(O)(OCH_2Bu^t)_{12}$ [4]. It is evident from elemental analysis and NMR spectroscopy that there are 12 alkoxide ligands in these compounds and that the isopropoxide cluster lacks any element of symmetry whereas the neopentoxide has C_{2v} symmetry. The NMR data agree with the skeletal structures shown in A and B. Note that the isopropoxide cluster is a structural analogue of $W_4(\mu_4\text{-C})(NMe)(OPr^i)_{12}$ [3].



A (OPr^i) B (OCH_2Bu^t)

This work also provides a rare example of the reductive cleavage of carbon monoxide by a molecular cluster under mild conditions [11*]. It seems likely that this occurs to carbide and oxide and if so this will be the first such reaction in a homogeneous system [12*]. The fate of the carbonyl oxygen atom remains to be established.

Further studies are in progress.

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References and notes

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7 *Crystal data*: $W_4C_{85}H_{154}O_{14}$, triclinic, $P\bar{1}$, a 14.228(5) Å, b 23.062(9) Å, c 14.725(6) Å, α 81.44(1)°, β 61.17(2)°, γ 74.82(2)°, $Z = 2$. The structure was solved by direct methods and refined to $R = 0.039$ by least squares using 9368 reflections with $F > 2.3\sigma(F)$.

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9 The $^{13}C\{^1H\}$ NMR spectrum of $W_4(\mu_4\text{-}C)(OCH_2\text{-}c\text{-}C_5H_9)_{14}$ consists of seven resonances between δ 85 and δ 75 with relative intensities 4:2:2:2:2:1:1 that are assignable to the methylene carbon atoms of the $OCH_2\text{-}c\text{-}C_5H_9$ ligands. This pattern is consistent with the solid-state structure of $W_4(\mu_4\text{-}C)(OCH_2\text{-}c\text{-}C_5H_9)_{14}$ if the resonance of intensity 4 results from the accidental degeneracy of two resonances of equal intensity. The ^1H NMR spectrum of $W_4(\mu_4\text{-}C)(OCH_2\text{-}c\text{-}C_5H_9)_{14}$ is also

consistent with the structure found in the solid. Full details are given in ref. 10 and will be published in a future report.

10 C.E. Hammond, Ph.D. Dissertation, Indiana University, 1989.

11 In homogenous systems, reductive cleavage of CO is usually accompanied by the formation of new bonds between the carbon or oxygen atoms and other groups such as H^+ and CO. Good reviews of the pertinent literature are given in: D.R. Neithamer, R.E. LaPointe, R.A. Wheeler, D.S. Richeson, G.D. Van Duyne and P.T. Wolczanski, J. Am. Chem. Soc., 111 (1989) 9056, and D.F. Shriver and M.J. Sailor, Acc. Chem. Res., 21 (1988) 374.

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