

New Routes to Transition Metal-Carbido Species: Synthesis and Characterization of the Carbon-Centered Trigonal Prismatic Clusters $[\text{W}_6\text{CCl}_{18}]^{n-}$ ($n = 1, 2, 3$)

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Transition metal-carbon clusters have long been of interest as fragments of refractory metal carbides and models for intermediates in heterogeneous catalysis.¹ In these molecules, carbon typically serves as an interstitial or capping atom within the core of a multinuclear cluster, particularly in early transition metal halide² and late transition metal carbonyl³ clusters. Recently, however, this chemistry has been extended to include a few complexes featuring a carbon atom as a terminal donor ligand.⁴ While exploring new routes to such complexes, our attention was caught by a report of the structure of $\text{W}_2(\mu\text{-CCl})\text{Cl}_7$, an unusual one-dimensional solid containing chlorocarbene-bridged W_2 units.⁵ In an effort to establish a more facile synthesis of the compound, we attempted to produce it using bismuth metal⁶ to reduce WCl_6 in the presence of a stoichiometric amount of CCl_4 . Herein, we report that this indeed provides an effective means of incorporating carbon into a tungsten chloride cluster, giving rise not to the intended W_2 species, but rather to a carbon-centered trigonal prismatic cluster, $[\text{W}_6\text{CCl}_{18}]^{2-}$, exhibiting extensive redox chemistry.

The new cluster is extracted from a solid precursor produced at high temperature. Under a nitrogen atmosphere, WCl_6 (1.29 g, 3.26 mmol), CCl_4 (0.251 g, 1.63 mmol), and Bi (0.908 g, 4.35 mmol) were sealed in an evacuated Pyrex ampule, and then heated in a tube furnace at 400 °C for 3 days. Colorless BiCl_3 was sublimed away at 360 °C to leave a black solid. The solid was removed from the ampule in air and stirred in 120 mL of 1% HCl for 30 min to give a dark green solution. Addition of $(\text{Bu}_4\text{N})\text{Cl}$ (0.50 g, 1.8 mmol) induced formation of a dark green solid, which was recrystallized from acetonitrile to yield 0.388 g (34%) of $(\text{Bu}_4\text{N})_2[\text{W}_6\text{CCl}_{18}]$ (**1**) as black octahedron-shaped crystals.⁷

Presumably, the original cluster-containing solid in the preparation arises according to the following reaction.



The ensuing black powder is amorphous by X-ray diffraction, but likely possesses an extended two-dimensional $[\text{W}_6\text{CCl}_{12}]\text{Cl}^{2-}_4$ connectivity similar to that observed in W_6Cl_{12} .⁸ Possibly because of a reaction with the surface of the Pyrex ampule at high temperature, the use of 3 equiv of CCl_4 in reaction 1 instead of just 1 equiv was found to result in higher yields. Reactions employing 2 equiv gave, upon workup, a mixture of $[\text{W}_6\text{Cl}_{14}]^{2-}$ and $[\text{W}_6\text{CCl}_{18}]^{2-}$, while those employing 4 equiv afforded no soluble product.

X-ray analysis⁹ of a crystal of **1** revealed the carbon-centered $[\text{W}_6\text{CCl}_{18}]^{2-}$ cluster depicted in Figure 1. Therein, the six tungsten atoms are arranged in a regular trigonal prism, instead of the octahedral geometry usually observed for centered hexanuclear clusters of the early transition metals.² Within the triangular faces of the prism, the W-W distance of 2.667(1) Å is slightly longer than the mean W-W single bond distance of 2.607(4) Å observed¹¹ for the face-capped octahedral cluster $[\text{W}_6\text{Cl}_{14}]^{2-}$. In contrast, the longer edges of the rectangular faces of the prism exhibit a W-W

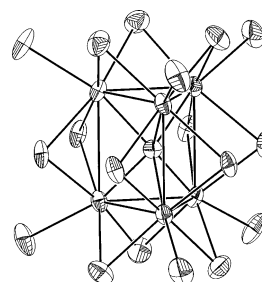


Figure 1. Structure of the carbon-centered trigonal prismatic cluster $[\text{W}_6\text{CCl}_{18}]^{2-}$ in **1**. The lines connecting W atoms are intended to emphasize the W_6 trigonal prism and do not necessarily represent full single bonds (see text). Selected mean interatomic distances (Å) and angles (deg) for the $[\text{W}_6\text{CCl}_{18}]^{n-}$ ($n = 1, 2, 3$) clusters in **2**, **1**, and **3'**, respectively (Δ = triangle edge, | = longer rectangle edge, b = bridging, t = terminal): W-W $^{\Delta}$ 2.74(1), 2.667, 2.71(5), W-W $^{|}$ 2.93(2), 3.028, 2.96(8), W-C 2.157(8), 2.1595, 2.15(3), W-Cl $^{b\Delta}$ 2.389(4), 2.381(5), 2.412(8), W-Cl $^{b|}$ 2.433(6), 2.4585(5), 2.46(1), W-Cl $^{t|}$ 2.41(1), 2.443, 2.47(1), W-C-W $^{\Delta}$ 78.9(5), 76.28, 78(2), W-C-W $^{|}$ 85.7(3), 89.02, 87(4), W-Cl $^{b\Delta}$ -W 70.0(3), 68.14, 68(2), W-Cl $^{b|}$ -W 74.1(4), 76.00, 74(2).

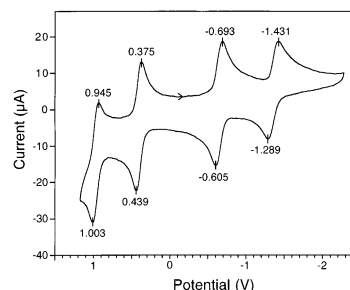


Figure 2. Cyclic voltammogram of compound **1** in DMF, with potentials referenced to $\text{Cp}_2\text{Fe}^{0/1+}$. A scan rate of 1500 mV/s was employed to improve the reversibility of the leftmost couple.

separation of 3.028(1) Å, for which Pauling's empirical relation $D(n) = D(1) - 0.60 \log n$ suggests a W-W bond order of just $n = 0.20$.¹² The W-C distance of 2.1595(6) Å is close to the analogous distance of 2.197 Å in WC, the structure of which indeed features a trigonal prismatic coordination of carbon.¹³ Thus, the central W_6C unit of $[\text{W}_6\text{CCl}_{18}]^{2-}$ can be viewed as a fragment of WC stabilized by 18 surrounding chlorine atoms. These chlorine atoms bridge the edges—with one spanning each triangle edge and two spanning each of the longer rectangle edges—and cap the vertices of the W_6 trigonal prism in a manner that preserves its D_{3h} symmetry. Notably, this cluster geometry has been encountered previously only within the one-dimensional solids $\text{A}_3\text{Nb}_6\text{SBr}_{17}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}, \text{Ti}$).^{10,14,15}

The cyclic voltammogram of compound **1** in DMF (Figure 2) reveals an electrochemistry that is remarkably rich for such a compact cluster. Two reduction processes are apparent at $E_{1/2} = -0.649$ V ($\Delta E_p = 88$ mV) and $E_{1/2} = -1.360$ V ($\Delta E_p = 142$ mV) versus $\text{Cp}_2\text{Fe}^{0/1+}$, corresponding to $[\text{W}_6\text{CCl}_{18}]^{2-/3-}$ and $[\text{W}_6\text{CCl}_{18}]^{3-/4-}$

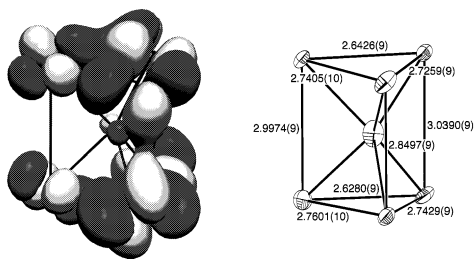


Figure 3. Left: Depiction of the central portion of one of the lowest unoccupied e' orbitals of $[\text{W}_6\text{CCl}_{18}]^{2-}$, as calculated using DFT. Right: Corresponding portion of the structure of the $[\text{W}_6\text{CCl}_{18}]^{3-}$ cluster in **3'**, displaying a Jahn–Teller distortion consistent with population of this orbital; W–W distances are given in Å.

couples, respectively. In addition, two oxidation processes occur at $E_{1/2} = 0.407$ V ($\Delta E_p = 64$ mV) and $E_{1/2} = 0.974$ V ($\Delta E_p = 58$ mV), corresponding to $[\text{W}_6\text{CCl}_{18}]^{2-/-}$ and $[\text{W}_6\text{CCl}_{18}]^{1-/0}$ couples, respectively. The reversibility of the latter couple is improved significantly at higher scan rates, suggesting a reduced solubility for $[\text{W}_6\text{CCl}_{18}]^0$. Potentially, all five redox states of the cluster will be chemically accessible.

Consistent with its electrochemistry, DFT calculations¹⁶ performed on the diamagnetic $[\text{W}_6\text{CCl}_{18}]^{2-}$ cluster revealed many closely spaced energy levels in the frontier orbital region.¹⁷ The seven highest-energy occupied orbitals are primarily W–W bonding in character. Situated 0.86 eV above an a_1' orbital, the a_2'' HOMO exhibits W–W bonding character within the W_3 triangles, but W–W antibonding character between opposing W_3 triangles. Unoccupied e'' and e' orbitals lie 0.61 and 0.71 eV above the HOMO, respectively, and also feature a mixture of W–W bonding and antibonding character. Given their comparable energies, it is difficult to predict just which of these orbitals would be occupied upon reduction of the cluster.

Addition of a single equivalent of (NO)(BF₄) to an acetonitrile solution of **1** prompts a color change from green to purple, signaling formation of the one-electron oxidized species $[\text{W}_6\text{CCl}_{18}]^{1-}$. Cooling the solution to -40 °C permitted isolation of (Bu₄N)[$[\text{W}_6\text{CCl}_{18}]$] (**2**) in 87% yield as a black precipitate.¹⁸ X-ray analysis⁹ of a black, irregularly shaped crystal of **2** obtained directly from the reaction solution confirmed retention of the trigonal prismatic cluster geometry. Showing no significant deviations from D_{3h} symmetry, the monoanion differs from the dianion most notably in its W–W distances, which are longer along the triangular edges and shorter along the other three edges of the trigonal prism (see Figure 1 legend). These differences are consistent with removal of an electron from the a_2'' HOMO calculated for $[\text{W}_6\text{CCl}_{18}]^{2-}$.

The one-electron reduced cluster $[\text{W}_6\text{CCl}_{18}]^{3-}$ was generated by adding 1 equivalent of cobaltocene to an acetonitrile solution of **1**. Addition of ether to the ensuing green-brown solution precipitated (Cp₂Co)(Bu₄N)₂[$[\text{W}_6\text{CCl}_{18}]$] (**3**) in 95% yield.¹⁹ Crystals of **3** exhibited extensive disorder; however, metathesis with (Ph₄P)Cl led to black rectangular plate-shaped crystals of (Ph₄P)₃[$[\text{W}_6\text{CCl}_{18}]$]·MeCN·Et₂O (**3'**) suitable for X-ray analysis.⁹ Therein, the trianionic cluster displays a significant distortion away from D_{3h} symmetry, as shown at the right in Figure 3. Relative to the structure of the dianion in Figure 1, the distortion mainly involves pinching the two foremost W atoms together to give a shorter W–W distance of 2.8497(9) Å, while simultaneously pulling these same two atoms forward (away from the rear-most W_4 rectangle) to give four longer W–W distances in the range 2.7405(10)–2.7601(10) Å. These changes are fully consistent with a Jahn–Teller distortion arising from population of one of the low-lying unoccupied e' orbitals (see Figure 3, left) calculated for $[\text{W}_6\text{CCl}_{18}]^{2-}$. Similar, albeit much less

dramatic, Jahn–Teller distortions have been observed previously in octahedral Mo₆ and Re₆ clusters.²⁰

Future work will attempt to extend this new method for incorporating carbon into clusters, will probe the generality of the centered trigonal prismatic cluster geometry, and will employ these cluster units in the synthesis of microporous coordination solids with noncubic symmetry.

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Supporting Information Available: Full experimental details on the preparations of **1–3**, and results from the DFT calculations performed on $[\text{W}_6\text{CCl}_{18}]^{2-}$ (PDF). X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- See ref 14b for another analysis of the bonding in this structure type.
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- Characterization of **3**: UV–vis spectrum (MeCN) λ_{max} (ϵ_M) 262 (81 200), 299 (16 700), 442 (4180), 645 (2020), 801 (1290), 1002 (1130) nm. ES–MS (MeCN): m/z 876 ($[\text{W}_6\text{CCl}_{18}]^{2-}$), 1718 ($[\text{W}_6\text{CCl}_{17}]^{1-}$), 1995 ($\{(\text{Bu}_4\text{N})[\text{W}_6\text{CCl}_{18}]^{2-}\}^-$). $\mu_{\text{eff}} = 3.05 \mu_B$ at 295 K. Anal. Calcd for C₄₃H₈₂Cl₁₈·CoN₂W₆: C, 21.28; H, 3.41; N, 1.15. Found: C, 21.08; H, 3.53; N, 1.11.
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