SUPPORTING INFORMATION

“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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Experimental Details

Preparation of Compounds. The reagents Et₂O (EM Science), MeCN (EM Science), DMF (EM Science), HCl (EM Science), Bi (-325 mesh, Strem), and (Bu₄N)Cl·xH₂O (Aldrich) were used as purchased. Carbon tetrachloride (Aldrich) was vacuum distilled and dried over 3 Å molecular sieves. Tungsten(VI) chloride was sealed in an evacuated ampule and heated for 24 h with the WCl₆ at 140 °C and the vacant end at room temperature. Red crystals of WOCl₄ formed at the cool end of the tube and were separated from the purple WCl₆ powder. Water was distilled and deionized with a Milli-Q filtering system.

(Bu₄N)₂[W₆CCl₁₈] (1). In a dinitrogen atmosphere glove box, 0.251 g (1.63 mmol) of CCl₄ was charged to a Pyrex capillary that had been sealed at one end. The capillary was then sealed at the other end under partial vacuum and placed in a Pyrex ampule (i.d. × o.d. × l. = 21 × 25 × 260 mm). In a dinitrogen atmosphere, WCl₆ (1.29 g, 3.26 mmol) and Bi (0.908 g, 4.35 mmol) were placed in the same ampule. The ampule was evacuated and sealed with the end containing the reagents cooled with liquid nitrogen. The capillary containing CCl₄ (or 50% enriched ¹³CCl₄) was broken by vigorously shaking the ampule. The tube was situated with the vacant end at the center of the furnace, elevated 45° above the end containing the reactants. The furnace was ramped up 1 °C/min to 400 °C, and maintained at that temperature for 3 d. The furnace was then heated at 360 °C for 16 h with the ampule repositioned with the reactants at the warm end to sublime away colorless BiCl₃. After cooling to room temperature, the ampule was opened in air and the black product was pulverized and stirred in 120 mL of 1% HCl (v/v) for 30 min to give a dark green solution. Addition of 0.50 g (1.8 mmol) of (Bu₄N)Cl induced the formation of a dark green precipitate. The mixture was then heated at reflux for 3 h and filtered while hot; the black solid was washed with three successive 60-mL aliquots of 1% (v/v) HCl and dried in air. The solid was then stirred for 1 h in 60 mL of acetonitrile, causing the solution to become dark green, and the mixture was filtered. The remaining black solid was washed with three successive 30-mL aliquots of acetonitrile, and the dark green filtrates were combined and concentrated. Large, black octahedron-shaped crystals of (Bu₄N)₂[W₆CCl₁₈] (388 mg, 34%) were grown by slow diffusion of diethyl ether vapor into the concentrated acetonitrile solution. ¹³C NMR (MeCN-d₃): δ 280.12 (t, J_{WC} = 25 Hz, [W₆¹³CCl₁₈]²⁻), 59.38 ([Bu₄N]⁺), 24.37 ([Bu₄N]⁺), 20.41 ([Bu₄N]⁺), 13.90 ([Bu₄N]⁺). UV-vis spectrum (MeCN): λ_{max} (ε_M) 217 (56116), 247 (24163), 289 (19918), 313 (15862), 415 (3665), 481 (1967), 608 (1411), 776 (655) nm. ES⁻-MS

(MeCN): m/z 876 ($[\text{W}_6\text{CCl}_{18}]^{2-}$), 1718 ($[\text{W}_6\text{CCl}_{17}]^{1-}$), 1995 ($\{(\text{Bu}_4\text{N})[\text{W}_6\text{CCl}_{18}]\}^-$). Anal. Calcd. for $\text{C}_{33}\text{H}_{72}\text{Cl}_{18}\text{N}_2\text{W}_6$: C, 17.71; H, 3.24; N, 1.25. Found: C, 18.08; H, 3.36; N, 1.07.

(Bu₄N)[W₆CCl₁₈] (2). Under a dinitrogen atmosphere, (NO)(BF₄) (26 mg, 0.22 mmol) was dissolved in 10 mL acetonitrile under dinitrogen atmosphere. Compound **1** (100 mg, 0.044 mmol) was dissolved in 5 mL of MeCN and 2.0 mL of the (NO)(BF₄) solution was added. The solution immediately turned purple and was stirred for 1 min. X-ray quality crystals were obtained directly from the reaction mixture by allowing the solution to stand without agitation for 4 h; the remaining product precipitated upon standing at -40 °C for 10 h. The mother liquor was then decanted and the solid was quickly washed with 3 successive 20-mL aliquots of water. The black solid was recrystallized from acetonitrile at -40 °C, affording 79 mg (0.039 mmol, 87%) of pure, air-stable product. UV-vis spectrum (MeCN): λ_{max} (ϵ_{M}) 309 (19499), 425 (2113), 506 (2344), 730 (2576) nm. $\mu_{\text{eff}} = 2.31 \mu_{\text{B}}$ at 295 K. ES⁻-MS (MeCN): ES⁻-MS (MeCN): m/z 876 ($[\text{W}_6\text{CCl}_{18}]^{2-}$), 1718 ($[\text{W}_6\text{CCl}_{17}]^{1-}$), 1995 ($\{(\text{Bu}_4\text{N})[\text{W}_6\text{CCl}_{18}]\}^-$). Anal. Calcd. for $\text{C}_{17}\text{H}_{36}\text{Cl}_{18}\text{NW}_6$: C, 10.23; H, 1.82; N, 0.70. Found: C, 10.35; H, 1.74; N, 0.73.

(Cp₂Co)(Bu₄N)₂[W₆CCl₁₈] (3). In a dinitrogen atmosphere, cobaltocene (21 mg, 0.22 mmol) was dissolved in 5.0 mL of MeCN. A concentrated solution of **1** (100 mg, 0.044 mmol) in 5 mL of MeCN was prepared. To this solution, 2.0 mL of the cobaltocene solution was added. The resulting solution was stirred for 5 h, slowly becoming brown-green. Diethyl ether (40 mL) was then added to the solution to precipitate an olive green powder. The mother liquor was decanted and the solid was washed with three successive 20-mL aliquots of diethyl ether and dried under vacuum, affording 100 mg (0.043 mmol, 95%) of compound **3**. UV-vis spectrum (MeCN): λ_{max} (ϵ_{M}) 262 (81200), 299 (16700), 442 (4180), 645 (2020), 801 (1290), 1002 (1130). $\mu_{\text{eff}} = 3.05 \mu_{\text{B}}$ at 295 K. ES⁻-MS (MeCN): m/z 876 ($[\text{W}_6\text{CCl}_{18}]^{2-}$), 1718 ($[\text{W}_6\text{CCl}_{17}]^{1-}$), 1995 ($\{(\text{Bu}_4\text{N})[\text{W}_6\text{CCl}_{18}]\}^-$). Anal. Calcd. for $\text{C}_{43}\text{H}_{82}\text{Cl}_{18}\text{N}_2\text{CoW}_6$: C, 21.28; H, 3.41; N, 1.15. Found: C, 21.08; H, 3.53; N, 1.11. X-ray quality crystals of (Ph₄P)₃[W₆CCl₁₈]·MeCN·Et₂O (**3'**) were prepared by slow diffusion of diethyl ether into a concentrated acetonitrile solution of 100 mg of **3** and 50 mg of (Ph₄P)Cl.

X-ray Structure Determinations. Crystals were coated in Paratone-N oil, attached to quartz fibers, transferred to a Siemens SMART diffractometer, and cooled in a dinitrogen stream. Lattice parameters were initially determined from a least-squares analysis of more than 100 centered reflections; these parameters were later refined against all data. None of the crystals showed significant decay during data collection. The raw intensity data were converted (including corrections for background, Lorentz, and polarization effects) to structure factor

amplitudes and their esd's using the SAINT 4.15 program. An empirical absorption correction was applied to each data set using SADABS. Space group assignments were based on systematic absences, E-statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of difference Fourier maps and were refined against all data using the SHELXTL 5.0 software package. In all structures, hydrogen atoms were inserted at idealized positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens). Thermal parameters for all non-hydrogen atoms were refined anisotropically, except for the atoms in the $(\text{Bu}_4\text{N})^+$ cations in the structure of **1** and the carbon atoms of the $(\text{Bu}_4\text{N})^+$ cation in the structure of **2**, as these cations were disordered.

Other Physical Measurements. Electronic absorption spectra were obtained using a Hewlett-Packard 8453 spectrophotometer. Electro-chemical measurements were conducted with a Bioanalytical Systems CV-50 potentiostat with platinum-disk working, platinum-wire auxiliary, and silver-wire reference electrodes. Samples were measured at a scan rate of 1500 mV/s in 0.1 M $(\text{Bu}_4\text{N})(\text{BF}_4)$ supporting electrolyte, and ferrocene was added after each measurement as an internal reference. Mass spectrometric measurements were performed in the negative ion mode on a Brüker Apex II 7 T actively shielded FT-ICR mass spectrometer equipped with an analytical electrospray ion source instrument. Magnetic moments were measured on a Quantum Design MPMS2 SQUID magnetometer.

Density Functional Theory (DFT) Calculations

Calculations of the electronic structure of the $[\text{W}_6\text{CCl}_{18}]^n$ clusters were performed with NWChem 4.5¹ using the HCTH/407² density functional and the LANL2DZ³ basis set + ECP. The basis was augmented with diffuse and polarization functions (LANL2DZdp⁴ for C, Cl; d-exp = 0.03397, f-exp = 0.823⁵ for W). The charge density was fit using the basis set of Ahlrichs.⁶ Convergence problems were alleviated by uncontracting the d-functions on tungsten. Cluster geometries were optimized under D_{3h} symmetry for $n = 0, 1$, and 2.

For the 3- cluster, the unpaired electron could reasonably occupy either the e'' or e' set of low-lying unoccupied MO's, which should lead to a Jahn-Teller distortion. The crystal structure of the 3- cluster shows a significant distortion away from D_{3h} -symmetry, with one of the long W-W distances shortened and the W_3 faces taking on an isosceles arrangement. Optimizing the geometry in C_{2v} with the a_1 orbital (one of the LUMO+1 e'' in D_{3h}) occupied results in a geometry with the same character of distortion. The calculated distortion is noticeably stronger than that in the crystal structure, suggesting that the distortions resulting from populating some of the other three frontier orbitals also contribute to the average solid-state geometry.

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Figure S1. Energy level diagram for the frontier orbitals of the carbon-centered trigonal prismatic cluster $[\text{W}_6\text{CCl}_{18}]^{2-}$, as calculated using DFT. Electrons fill up through the $2a_2''$ orbital.

Figure S2. Selected frontier orbitals of the carbon-centered trigonal prismatic cluster $[W_6CCl_{18}]^{2-}$, as calculated using DFT. See Figure S1 for relative orbital energies.