Octahydrotriborotetracarbonyl Metallates of Chromium, Molybdenum, and Tungsten

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THE $B_3H_8^-$ ion reacts smoothly with the hexacarbonyls of chromium, molybdenum, and tungsten, displacing two moles of carbon monoxide:

$$M(CO)_6 + B_3H_8^- \rightarrow (OC)_4MB_3H_8^- + 2CO$$

Tetra-alkylammonium salts of the resulting anions $(OC)_4MB_3H_8^-$ have been isolated as air-stable, yellow crystals (70% yield).

The infrared spectra of the salts (in KBr discs and in tetrahydrofuran solution) show two regions of B–H absorption, at 2489 and 2435 cm.$^{-1}$, and at 2134 and 2109 cm.$^{-1}$, respectively. The latter pair of bands is less intense than the former. There are also four strong CO bands at 2020, 1905, 1882, and 1848 cm.$^{-1}$. The ^{11}B n.m.r. spectra at 19·3 Mc./sec. consist of two moderately broadened peaks at 23·0 and 61·3 p.p.m.† which sharpen independently of each other into singlets upon

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† MeCN solution. Chemical shifts are relative to $B(OMe)_3$ as external standard. The free $B_3H_8^-$ ion shows an apparent nonet at 48·5 p.p.m. with J(B–H) = 35 c./sec.

superposition of a 60 Mc./sec. ^1H field. The integrated intensity of the two signals is 1 : 2. The highfield signal can be unambiguously assigned to the two boron atoms in proximity to the respective metal atom, whereas the low-field resonance of relative intensity one must be due to the third boron atom further away from the metal atom.

The ^1H n.m.r. spectra exhibit a broad peak at τ 17·3, sharpening upon double irradiation at 60 and 19·3 Mc./sec., which we assign to the two hydrogen atoms in M–H–B bridging positions.

The crystal and molecular structures of tetramethylammonium octahydrotriborotetracarbonyl chromate have been determined by a three-dimensional *X*-ray diffraction investigation. Crystals of $[Me_4N][Cr(CO)_4B_3H_8]$ are monoclinic with $a = 11{\cdot}07 \pm 0{\cdot}01$, $b = 8{\cdot}94 \pm 0{\cdot}01$, $c = 7{\cdot}78 \pm 0{\cdot}01$ Å, and $\beta = 98{\cdot}1 \pm 0{\cdot}1°$. There are two formula units per cell; the space group from systematic absences is either $P2_1$ or $P2_1/m$. Atom positions were obtained from the Patterson function using superposition techniques. All nonhydrogen atom positions were refined by least-squares in the $P2_1/m$ symmetry group, and the conventional *R* at this point in the refinement is 0·10. The molecular configuration having C_s point symmetry is depicted in the Figure along with some pertinent bond distances and angles. The hydrogen atom positions depicted correspond to peak positions in the electron-density difference synthesis.

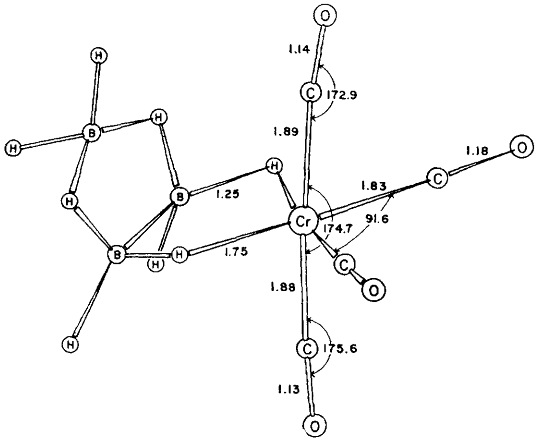

FIGURE. *The molecular configuration of* $Cr(CO)_4B_3H_8^-$.

Crystals of $[Me_4N][Mo(CO)_4B_3H_8]$ and $[Me_4N][W(CO)_4B_3H_8]$ are isomorphous with those of the chromium compound since they crystallize in the same space group with very similar cell sizes and relative intensities as observed on diffraction photographs.

The structural features of $Cr(CO)_4B_3H_8^-$ are noteworthy since an alternative mode of co-ordination of the B_3H_8 moiety has been suggested[1] for the compound $(Ph_3P)_2CuB_3H_8$, which we prepared in 1966. The formation of hydrogen-bridged transition metal complexes of polyhedral borane or heteroborane[2] fragments is quite a general phenomenon for which we have established numerous examples. Apart from $(Ph_3P)_2CuB_3H_8$ and the paramagnetic $(C_5H_5)_2TiB_3H_8$, there exists a complete series of complexes of general stoicheiometry $(Ph_3P)_3M$–L, where M = Cu, Ag, Au, and L = $B_9H_{14}^-$, $B_9H_{12}S^-$, $B_{10}H_{13}^-$, and $B_{11}H_{14}^-$, respectively. Structural studies on representative examples of these are in progress.

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[1] S. J. Lippard and D. Ucko, *Chem. Comm.*, 1967, 983.

[2] W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, 1967, 6, 1696.