P. Coutts, and H. Weigold, "Organometallic Chemistry of Titanium, Zirconium and Hafnium," Academic Press, New York, N. Y., 1974.

(2) Many metallocarboranes exist which have no metallocene counterparts, *e.g.*, $[M(C_2B_9H_{11})_2]^{n-}$ (M = Cu, Au; n = 1 or 2), or counterparts that are considerably less stable (M = Ni, Pd, Cr, etc.). For example, see L. F. Warren, Jr., and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 4823 (1968); H. W. Ruhle and M. F. Hawthorne, *Inorg. Chem.*, **7**, 2279 (1968).

(3) (a) D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **95**, 1109 (1973); (b) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *ibid.*, **95**, 4565 (1973).

(4) Satisfactory elemental analyses were obtained for all the new metallocarboranes reported herein.

(5) A detailed study of the temperature dependent nmr spectra of these complexes will appear at a later date.

(6) CH_3CN solution, 0.1 *M* Et_4NPF_6, platinum button or hanging mercury drop electrode, sce reference.

(7) Under nitrogen or *in vacuo*, III initially dissolved and then rapidly decomposed in acetone to yield a colorless solution; thus it was recrystallized from CH_2Cl_2–THF.

(8) D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **96**, 3085 (1974).

(9) Due to coupling of the unpaired electron with ^{51}V ($I = \frac{7}{2}$).

(10) R. J. Wiersema and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **96**, 761 (1974).

(11) For example, the electron-rich metallocarboranes containing d^8 and d^9 metals (formally 20- and 21-electron complexes) adopt a "slipped sandwich" structure (*cf.* R. M. Wing, *J. Amer. Chem. Soc.*, **89**, 5599 (1967); **90**, 4828 (1968)) while the 15-electron Cr(III) complexes adopt a symmetric structure containing relatively long metal-to-ring distances (*cf.* D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **10**, 2587 (1971). Also, recent crystallographic studies in these laboratories on the complex $(\eta^5\text{-}C_5H_5)_2Fe_2C_2B_6H_8$ have revealed the first ten-vertex metallocarborane possessing a geometry which cannot be described as a bicapped Archimedean antiprism (K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, submitted to *J. Amer. Chem. Soc.*). This complex formally contains two 17-electron Fe(III) atoms, thus the entire polyhedron is deficient two electrons.

(12) F. Y. Lo, C. E. Strouse, K. P. Callahan, C. B. Knobler and M. F. Hawthorne, *J. Amer. Chem. Soc.*, following communication.

(13) For instance, Co(IV), Ni(IV), and Cu(III) are among the highest oxidation states obtainable for these metals, and organometallic complexes in these states would be considered rare although many carboranyl complexes exist. On the other hand, the organometallic chemistry of the early transition metals is dominated by the highest obtainable states (+3, +4), Zr(II) and Hf(II) thus being somewhat rare organometallic oxidation states.

(14) The $C_2B_{10}H_{12}^{2-}$ ligand appears to be a formal 6-electron donor, as in $C_5H_5Co^{III}C_2B_{10}H_{12}$ (see ref 3a and M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **13**, 1411 (1974)). Because of the structural similarities between this cobaltacarborane and complex II, we believe it not unlikely that $C_2B_{10}H_{12}^{2-}$ is also a 6-electron donor in these early transition metal complexes.

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Structures of Metallocarboranes. VI. A Titanium Sandwich Complex. Crystal and Molecular Structure of $[(CH_3)_4N]_2\{[1,6\text{-}C_2B_{10}H_{10}(CH_3)_2]_2Ti\}$, Bis(tetramethylammonium) 4,4′-*commo*-Bis(decahydro-1,6-dimethyl-1,6-dicarba-4-titana-*closo*-tridecaborate)(2−) at −160°[1]

Sir:

The preceding communication[2] reported the synthesis and spectral properties of the first metallocarboranes which incorporate group IVa (Ti, Zr) and group Va (V) metals in the polyhedral framework. We wish to report the crystal and molecular structure of one of these compounds, the bis(tetramethylammonium) salt of the commo titanacarborane anion $\{4,4'\text{-}Ti\text{-}[1,6\text{-}C_2B_{10}H_{10}(CH_3)_2]_2\}^{2-}$.

A well-formed dark red crystal of the compound was mounted on a Syntex $P\bar{1}$ automated diffractometer equipped with a locally constructed low-temperature device[3] and cooled to −160°. The complex was found to crystallize in the centrosymmetric triclinic space group $P\bar{1}$ (confirmed by successful refinement) with unit cell dimensions a = 13.412 (3) Å, b = 9.325 (2) Å, c = 16.781 (5) Å, α = 95.21 (2)°, β = 106.15 (2)°, and γ = 81.55 (2)°. The measured density of 1.19 (3) g cm^{-3} at 25° corresponds to a calculated density at −160° of 1.096 g cm^{-3}. The unit cell contains two molecules of the acetone-solvated compound $[(CH_3)_4N]_2\{Ti[C_2B_{10}H_{10}(CH_3)_2]_2\}\cdot 2(CH_3)_2CO$.

Table I. Bond Distances in the Metallocarborane Polyhedra[a]

	D	D'	D_c
M–C1	2.176 (5)	2.185 (5)	2.032 (4)
M–B2	2.408 (6)	2.417 (6)	2.199 (6)
M–B3	2.420 (6)	2.406 (7)	2.203 (4)
M–C6	2.471 (5)	2.466 (5)	2.150 (3)
M–B7	2.433 (6)	2.430 (7)	2.165 (3)
M–B10	2.338 (7)	2.338 (6)	2.093 (3)
C1–CM1	1.518 (7)	1.540 (7)	
C1-B2	1.564 (8)	1.549 (8)	1.429 (10)
C1–B3	1.589 (8)	1.561 (8)	1.527 (6)
C1–B5	1.769 (8)	1.757 (8)	1.775 (6)
B2–B5	1.990 (9)	1.992 (5)	2.081 (10)
B2–C6	1.652 (8)	1.687 (7)	1.694 (7)
B2–B9	1.778 (9)	1.791 (8)	1.818 (7)
B3–B5	1.995 (9)	1.978 (9)	1.947 (6)
B3–B7	1.769 (9)	1.773 (8)	1.813 (5)
B3–B8	1.783 (9)	1.801 (9)	1.792 (5)
B5–B8	1.918 (9)	1.909 (9)	1.881 (6)
B5–B9	1.866 (9)	1.897 (9)	1.865 (6)
B5–B11	1.810 (10)	1.826 (9)	1.787 (5)
C6–CM6	1.546 (7)	1.532 (7)	
C6–B9	1.693 (8)	1.706 (7)	1.686 (5)
C6–B10	1.708 (8)	1.720 (8)	1.708 (5)
C6–B12	1.710 (8)	1.713 (8)	1.665 (4)
B7–B8	1.751 (8)	1.756 (8)	1.786 (6)
B7–B10	1.757 (9)	1.762 (9)	1.881 (6)
B7–B13	1.762 (9)	1.770 (9)	1.785 (5)
B8–B11	1.738 (8)	1.744 (9)	1.741 (5)
B8–B13	1.740 (9)	1.750 (9)	1.770 (5)
B9–B11	1.732 (9)	1.746 (9)	1.733 (6)
B9–B12	1.749 (9)	1.738 (8)	1.720 (6)
B10–B12	1.798 (8)	1.798 (9)	1.802 (5)
B10–B13	1.795 (9)	1.787 (9)	1.783 (6)
B11–B12	1.781 (9)	1.766 (9)	1.773 (5)
B11–B13	1.786 (9)	1.769 (9)	1.789 (5)
B12–B13	1.733 (9)	1.727 (9)	1.788 (5)

[a] D and D' are bond distances in the two independent polyhedra of the titanium complex and D_c are distances obtained by Churchill and DeBoer[5] for the cobalt complex.

A total of 3214 reflections (Mo Kα radiation) with intensities greater than three times their standard deviations were used in the solution and refinement of the structure. Conventional Fourier and least-squares techniques have resulted in R = 0.056, R_w = 0.059.[4] Full details of the refinement procedure will be discussed in a subsequent manuscript.

The compound is comprised of two 13-vertex closed polyhedra fused through the titanium atom, with cations and solvent molecules positioned in sites between the large anions. The geometry of the anion is depicted in Figure 1, which also indicates the numbering system employed.

The observed structure of the 13-vertex polyhedra is similar to that determined by Churchill and DeBoer[5] in the neutral cobaltacarborane $C_5H_5CoC_2B_{10}H_{12}$ in that the metal atom occupies high-coordinate vertex positions. The Ti–C and Ti–B bonds are much longer than their analogs in the cobalt complex; Ti–C averages 2.181 (5) Å (to the low-coordinate carbon atoms) and 2.468 (5) Å (to the high-coordinate carbon atoms), while Ti–B averages 2.399 (6) Å. The overall geometries of the two independent polyhedra are identical within experimental error but differ significantly from the cobalt-containing polyhedron (Table I).

Specifically, extremely long boron-boron bonds between the high-coordinate boron atom 5 and boron atoms 2 and 3 (B5–B2 = 2.081 (10) and B5–B3 = 1.947 (6) Å *vs.* a nor-

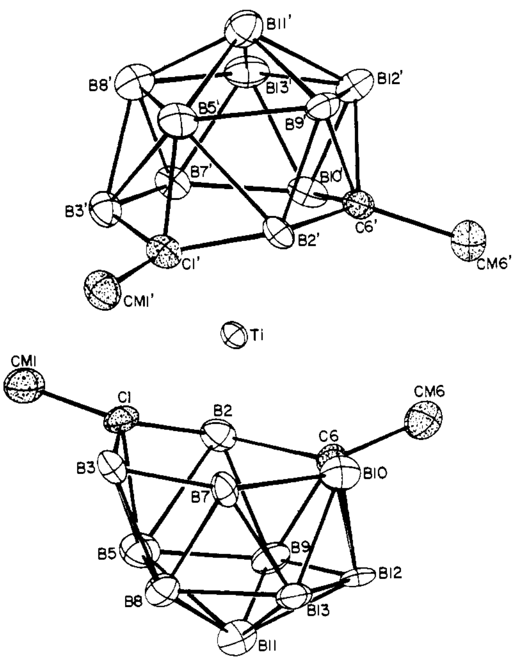

Figure 1. Molecular geometry of the titanacarborane dianion.

mal icosahedral B-B distance[6] of 1.78 Å) were observed in the structure of the cobaltacarborane. This pattern is also observed in the titanacarborane studied here, the average of these two distances being 1.989 (9) Å, but the sizable 0.134 Å difference between the two bonds detected by Churchill and DeBoer is not present here; the maximum difference between the four bonds is 0.017 Å in the titanacarborane. Similarly, the difference in the short B-C distances in the cobaltacarborane (C1-B3 = 1.527 (6), C1-B2 = 1.429 (10) Å) is in the case of the titanacarborane much less (C1-B3 = 1.589 (8), 1.561 (8); C1-B2 = 1.564 (8), 1.549 (8) Å). The long B7-B10 bond length of 1.881 (6) Å observed in the cobaltacarborane corresponds to boron-boron distances of 1.757 (9) and 1.762 (9) Å in the titanium complex. In general, the titanacarborane polyhedra show less distortion from "normal" bond distances and less deviation from a symmetric structure, than does the cobaltacarborane.

While the metal-carbon and metal-boron bonds in the titanacarborane are considerably longer than those observed in the cobaltacarborane, the coordination geometries in the two complexes are similar. In each case the low-coordinate carbon atom, C1, exhibits a short metal-carbon distance, and the boron atom opposite C1 on the six-membered B_4C_2 ring, B10, is the next nearest neighbor of the metal. The other four atoms of the B_4C_2 rings have longer and roughly equal distances to the metal atom. The five-member boron rings in the titanium polyhedra are planar within experimental error even though long bonds to the high-coordinate B5 atom result in a large deviation from fivefold symmetry.

The coordination geometry of the formally d^2 titanium(II) atom in this compound is of particular interest since monomeric titanocene, the isoelectronic cyclopentadienyl analog of this titanacarborane, has not been isolated. At least two compounds with the stoichiometry $(C_{10}H_{10}Ti)_2$ have, however, been identified. Marvich and Brintzinger[7] have characterized a metastable compound to which they assign the $((\eta^5\text{-}C_5H_5)_2Ti)_2$ structure. This compound thermally rearranges to form a green isomer which has been identified by Davison and Wreford[8] on the basis of ^{13}C nmr as μ-(η^5:η^5-fulvalene)-di-μ-hydrido-bis(cyclopentadienyltitanium). In these two dimeric isomers the titanium atoms achieve 15- and 16-valence electron configurations, respectively, while the titanacarborane and monomeric titanocene are both 14-electron systems.

Steric constraints have been postulated to explain the lack of dimerization of permethyltitanocene,[9,10] $[\eta^5\text{-}C_5(CH_3)_5]_2Ti$. This species is only marginally stable and exists in solution in tautomeric equilibrium with the isomeric complex $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiH$; this process involves ring methyl hydrogen abstraction and consequent internal oxidative addition to produce a 16-electron configuration about the metal. A similar electronic configuration is present in the distorted tetrahedral $(C_5H_5)_2TiCl_2$.[11]

The titanium atom in the metallocarborane is sandwiched between roughly parallel (dihedral angle between best least-squares planes 6.1°) six-membered rings and exhibits no significant distortion toward a structure in which the two ligands are "bent back" to present sufficient room for a donor molecule to approach. The long distances between the titanium and the cage atoms would facilitate such a bending without producing unfavorable interactions between hydrogen atoms on the two independent polyhedra, but the molecule shows no inclination to adopt such a configuration. The acetone molecules of solvation present in the crystal are distant from the metal center.

This compound represents another example of an electron-deficient metallocarborane and shows the largest amount of electron deficiency yet observed. Other crystallographically studied molecules of this type are the $(C_2B_9H_{11})_2Cr(III)$ monoanion,[12] formally a 15-valence electron compound, which exhibits a symmetrical sandwich structure,[13] and $(C_5H_5)_2Fe_2C_2B_6H_8$, which exhibits a large distortion from the idealized polyhedral geometry expected for this ten-vertex system.[l] Electron-rich metallocarboranes appear to show a preference for "slipped sandwich" structures,[14] but at this stage little can be said about any systematic geometric effects of electron deficiency in metallocarboranes.

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