The homodinuclear complexes, **5a**, can be prepared as in the method above by adjusting the mole ratio to 1:1. Complexes, **5b**, are obtained through *in situ* displacement of COD from **5a** by carbon monoxide.[12] Dimers, **5b**, may be prepared by the stoichiometric reaction of $M(CO)_2acac$ with H_2BiIm. However, unlike reactions with $[M(COD)(OMe)]_2$ only dimeric species are obtained regardless of molar ratios. The ir spectrum (CH_2Cl_2 solution, cm^{-1}) of **5b** (M = Rh) contains four CO stretching bands at 2095 (m), 2081 (s), 2026 (m), and 2014 (m); this is indicative of a solution species with symmetry lowered from that for a totally symmetric molecule (D_{2h} with two ir active stretching modes). The spectrum of **5b** (M = Rh) labeled with 90% ^{13}CO likewise contains four bands shifted as expected to 2046 (m), 2032 (s), 1980 (m), and 1968 (m). Complexes **5a**, bright yellow (M = Rh) and red-orange (M = Ir), and **5b**, dark red (M = Rh), are air and solution stable, whereas the deep purple **5b** (M = Ir) is not air stable. H_2BiIm may be recovered quantitatively and unaltered from **5** by reaction with HCl.[13] No N-H infrared absorption modes, as identified in the ir spectra of complexes containing H_2BiIm, are observed in the spectra of **5a** and **5b** indicating that the ligand is the dianion BiIm.

Since each of the mononuclear derivatives **4** contains one reactive pyrrole hydrogen, it may be considered an intermediate in dimer formation. Thus, **5a** may be prepared from **4a** by the reaction of **4a** and $[M(COD(OMe)]_2$ (Scheme I). The mixed ligand homodinuclear complex **6** may be obtained through the reaction of RhL_2acac and the appropriate mononuclear derivative **4**.[14] The complete series of heterodinuclear derivatives $L_2M(BiIm)M'L'_2$, where L_2 and L'_2 may be identical, is readily prepared through suitable combinations of **4a** or **4b** and $M'L'_2acac$. The use of the mononuclear derivatives as intermediates for the incorporation of other metals is under investigation.

The nmr spectra of complexes **5a** and **5b** (M = Rh) revealed unexpected solvent-dependent behavior. The ^1H nmr spectrum of **5a** contained a single resonance (for example, δ ($CDCl_3$) 6.38; δ (CCl_4) 6.21) assigned to chemically equivalent biimidazole ring hydrogens[15] of a symmetrical dinuclear structure **5a.** For the tetracarbonyl derivative **5b** again one resonance was observed (δ 6.58) when the solvent was either C_6D_6 or $C_6D_5CD_3$; however, two peaks of equal area appeared when other solvents were used (for example, δ ($CDCl_3$) 6.88, 6.77; δ (CCl_4) 6.83, 6.67; δ (CD_3COCD_3) 7.00, 6.94). These resonances are due to chemically shifted protons as confirmed by spectra at both 60 and 100 MHz. Stepwise addition of $CDCl_3$ to a C_6D_6 solution of **5b** resulted in initial broadening of the single resonance followed by separation into two resonances of equal area. Temperature-dependent studies in $CDCl_3$ from -55 to $+60°$ and in $C_6D_5NO_2$ (δ 7.00, 6.86) from 25 to 110° indicate stereochemical rigidity over that temperature range. For iridium complexes **5a** and **5b,** two resonances, chemically shifted, are observed for the ring hydrogens independent of solvent. The ^{13}C nmr spectrum of **5b** (M = Rh) in toluene and chloroform contained two overlapping doublets of approximately the same chemical shift (δ ($C_6D_5CD_3$) = 187.56, 186.55; δ ($CDCl_3$) 186.32, 185.02; both relative to TMS) and intensity with J_{Rh-C} = 65-70 Hz. These chemical shifts and coupling constants are in the range expected for terminal Rh-CO species.[16] Although the specific origin of the different chemical shifts has not been determined, the data indicate the presence of an unsymmetrical solution species which may be due to solvent association.

The methods described herein provide routes for the selective preparation of a wide variety of complexes containing anionic biimidazolates. Oxidation studies of all complexes and X-ray crystal structure determinations on $[Rh(CO)_2(BiIm)_{1/2}]_2$ and $[Rh(COD)(BiIm)_{1/2}]_2$ are in progress.

Acknowledgment. We wish to thank Drs. T. J. Truex and W. O. Siegl of the Scientific Research Staff for many helpful comments.

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(9) For all complexes routine proton nmr, infrared, and mass spectroscopic studies and elemental analyses are consistent with the given formulation. Proton nmr spectra were obtained on Bruker HX-60 and Jeolco JNM-PS-100 spectrometers.
(10) No acid dissociation of H_2BiIm is observed to a pH of 11.5; ref. 7.
(11) Reactions with chloro-bridged metal complexes resulted in low yields possibly due to reprotonation and subsequent generation of uncharacterized side products.
(12) The quantitative determination of molar uptake of carbon monoxide is 4.16 to 1 for this reaction as compared with the theoretical ratio of 4 to 1.
(13) Rather than *adding* oxidatively, HCl cleaves the dimer to form protonated H_2BiIm and chloro-bridged complexes $[ML_2Cl]_2$. The neutral ligand H_2BiIm is recovered through the addition of Na_2CO_3 to an aqueous solution of the ligand salt.
(14) Reactions of equimolar rhodium and iridium reagents with H_2BiIm have produced mixtures of homo- and heterodinuclear complexes.
(15) Integration of peak ratios revealed the expected 4:1 COD to BiIm proton ratio.
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Metallocarborane Complexes of Titanium, Zirconium, and Vanadium

Sir:

The cyclopentadienyl organometallic chemistry of the group IV and V transition metals has now been well established,[1] and, although the stabilizing influence exerted by a carboranyl ligand as compared to a cyclopentadienyl ligand is also well known,[2] metallocarborane complexes of these metals have heretofore escaped synthesis. We now report the first metallocarboranes of the early transition metals titanium, zirconium, and vanadium with the observation that their stabilities considerably exceed those of the corresponding cyclopentadienyl analogs.

The reduction of closo carboranes ($C_2B_nH_{n+2}$) with 2 equiv of sodium followed by complexation with various transition metals to yield (n + 3) vertex metallocarboranes has been accomplished.[3] We have found that the dianion generated from $1,2\text{-}C_2R_2B_{10}H_{10}$(R = H, Me) reacts with the metal halides $TiCl_4$, $ZrCl_4$, and VCl_3 to generate a series of anionic metallocarboranes formulated as $[M(C_2R_2B_{10}H_{10})_2]^{2-}$ with M in the formal +2 oxidation state (M = Ti, R = H, Me; M = Zr, R = Me; M = V, R = H) and isolable in good yield (60–75%) as tetraalkylammonium salts.[4]

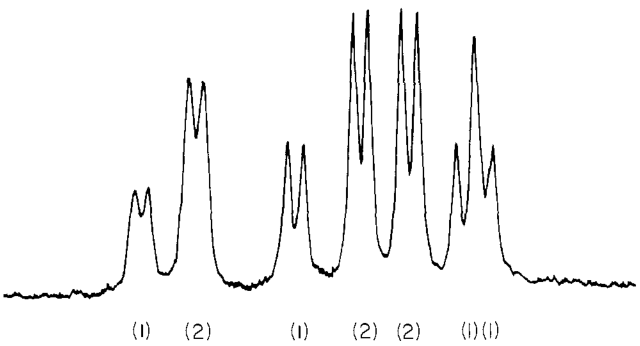

Figure 1. The 80.5-MHz ^{11}B nmr spectrum of $[Et_4N]_2[Ti(C_2B_{10}H_{12})_2]$ in CH_3CN at 60°.

Table I. 60-MHz ^1H Nmr Data (CD_3CN Solution)

Compound	Resonance, τ^a (rel area)	Assignment
I	8.82 (6)	Cation CH_3
	6.88 (4)	Cation CH_2
	6.37 (1)	Carborane C-H
II	6.94 (2)	Cation CH_3
	8.98 (1)	Carborane $C-CH_3$
III	8.77 (6)	Cation CH_3
	6.81 (4)	Cation CH_2
	8.63 (3)	Carborane $C-CH_3$

[a] Chemical shifts are relative to tetramethylsilane. All resonances were singlets except cation resonances for I and III: cation CH_2, quartet; cation CH_3, triplet of triplets.

Table II. 80.5-MHz ^{11}B Nmr Data (CH_3CN Solution)

Compound	Relative intensities	Chem shifts, δ^a (J_{BH}, Hz)
I[b]	1:2:1:2:2:1:1	−20.6 (120), −14.1 (135), −2.7 (145), +5.0 (135), +10.5 (150), +17.0 (170), +19.5 (160)
II[c]	3:1:2:2:1:1	−19.9, −12.4 (150), +3.8 (150), +4.9 (150), +13.2 (160), +18.4 (140)
III	1:2:1:2:2:1:1	−14.1 (130), −12.0 (120), −4.3 (155), +4.6, +5.0, +15.6 (160), +19.2 (150)

[a] Relative to $Et_2O \cdot BF_3$. [b] At 60°. [c] At 75°.

The reaction of $TiCl_4$ with $Na_2C_2B_{10}H_{12}$ was instantaneous in tetrahydrofuran (THF) to yield an air sensitive red-orange solution. Removal of solvent followed by addition of an ethanol solution of Et_4NBr caused precipitation of the diamagnetic red-orange crystalline compound $[Et_4N]_2[Ti(C_2B_{10}H_{12})_2]$ (I), which was recrystallized from acetone–ethanol. In the solid state I was moderately stable to air and decomposed completely in about 48 hr but was stable indefinitely when stored under nitrogen and could be handled for brief periods in the air without noticeable decomposition. The dimethylcarboranyl homolog $[Me_4N]_2[Ti(C_2Me_2B_{10}H_{10})_2]$ (II) was similarly isolated and found to contain two acetone molecules of crystallization. Bright red crystalline II was air stable in the solid state and suffered only slight decomposition after many weeks exposure to air. Both the ^{11}B and ^1H nmr data (Tables I and II) support these formulations and also indicate the fluxionality[3a] of the metallocarboranes in solution. Figure 1 shows the high temperature limiting ^{11}B nmr spectrum of I, containing the symmetry properties of the time-averaged species involved in the fluxional process.[5] Cyclic voltammetry[6] of I showed a reversible one-electron oxidation at $E_{p/2} = -0.24$ V and a reversible reduction at $E_{p/2} = -2.03$ V. Attempted electrochemical and chemical oxidation of I has thus far been unsuccessful. A nonreversible oxidation (−0.34 V) and a reversible reduction (−2.10 V) was observed for II.

The reaction of $ZrCl_4$ with $Na_2C_2Me_2B_{10}H_{10}$ in THF was also instantaneous at room temperature producing a very air sensitive solution which yielded $[Et_4N]_2[Zr(C_2Me_2B_{10}H_{10})_2]$ (III) as purple diamagnetic crystals.[7] As a solid, III decomposed completely in about 20 min upon exposure to air but was stable under nitrogen. The nmr data for III (Tables I and II) suggest the existence of a fluxional system as for I and II. Cyclic voltammetry[6] showed no reversible oxidation or reduction waves. When heated at 90–95° (*in vacuo* or under nitrogen) III underwent a striking color change to orange; preliminary data are indicative of a facile thermal rearrangement[8] of the 13-vertex metallocarborane to a nonfluxional isomer.[3a] This polyhedral rearrangement occurred slowly in the solid state even at room temperature and necessitated the storage of III at −20°.

The interaction of VCl_3 with $Na_2C_2B_{10}H_{12}$ required a short reflux in THF solvent to produce the paramagnetic (μ_{eff} = 1.65 BM) red-brown crystalline complex $[Et_4N]_2[V(C_2B_{10}H_{12})_2]$ (IV). The esr spectrum (CH_2Cl_2 solution, sealed tube 51°) exhibited an eight-line pattern[9] centered at $g_0 = 2.001$. Concurrent with this was our inability to observe a 80.5-MHz ^{11}B nmr spectrum of the paramagnetic species, although other paramagnetic metallocarboranes have previously yielded interpretable ^{11}B nmr spectra.[10] While IV was apparently air stable, we observed a decrease in the magnetic moment upon several recrystallizations in the presence of air. As found for I, cyclic voltammetry[6] showed a reversible one-electron oxidation ($E_{p/2}$ = +0.04 V) and a reversible reduction ($E_{p/2}$ = −1.79 V). In the case of all the compounds reported here, the recovery of $1,2\text{-}C_2R_2B_{10}H_{10}$ from the reaction mixture confirmed the carborane dianion as the species responsible for the reductions resulting in *formal* +2 metal oxidation states.

As these complexes constitute a new class of electron deficient metallocarboranes, their structural parameters are of great interest. We have previously observed significant polyhedral distortions in both electron-rich and electron-deficient metallocarboranes.[11] Compound II has been subjected to a single-crystal X-ray diffraction study and its structure was shown[12] to be a monomeric entity containing the metal atom symmetrically bound to two carborane cages, with essentially parallel B_4C_2 bonding faces. The metal-to-cage distances were significantly longer than any previously observed. We propose a similar structure for complexes I, III, and IV. The low symmetry of the ligand is apparently sufficient to effect d orbital splittings favoring a diamagnetic d^2 ground state. It is also interesting that while carboranyl ligands tend to stabilize formally high oxidation states with the later transition metals, low oxidation states seem to be favored with the early transition metals.[13] This may be due to the extremely electron deficient nature of these compounds; I–III are formally 14-electron complexes.[14]

We are presently engaged in the extension of this work to other group IV and V transition metals as well as to other $C_2B_nH_{n+2}$ carboranes. Also of interest is the chemistry of these new metallocarboranes and its relationship to that of the early transition metal metallocenes.

Acknowledgment. We thank Dr. K. P. Callahan for useful discussions and Ms. Donna Hoel for the esr spectrum. This work was supported in part by the Office of Naval Research.

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(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).

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(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.

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(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 $\{4,4'\text{-Ti-}[1,6\text{-}C_2B_{10}H_{10}(CH_3)_2]_2\}^{2-}$.

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–Cl	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 K*α* 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-