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Studies of Metallocarboranes Incorporating the Early Transition Metals

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The synthesis and characterization of several new metallocarboranes incorporating the early transition metals is described. Complexes of the formula $[M^{II}(C_2B_{10}H_{10}R_2)_2]^{2-}$ (M = Ti, V, Cr, Mn, R = H; M = Ti, Zr, Hf, V, R = CH_3) are reported as well as the mixed-ligand titanacarboranes $[C_xH_xTiC_2B_nH_{n+2}]^{m-}$ ($x = 5$, $n = 10$, $m = 1$; $x = 8$, $n = 9$ or 10, $m = 0$ or 1). Magnetic studies were performed with the paramagnetic vanadium, chromium, and manganese complexes. The zirconium and hafnium metallocarboranes were found to undergo a facile polyhedral rearrangement in solution. The complexes are discussed in terms of the degree of formal polyhedral electron deficiency and the applicability of electron counting rules to this unique class of organometallic compounds.

Metallocarboranes have been termed electron deficient if the number of polyhedral framework plus metal valence electrons is less than the required $2n + 14$ for monometallocarboranes adopting closo n-vertex polyhedral geometries.[1] This can also be viewed in terms of the electronic requirements of the transition metals involved. If the metal atom fails to attain the 18-electron inert-gas configuration,[2] the metallocarborane is termed electron deficient. Previous to this work, the highest degree of electron deficiency in metallocarboranes had been achieved with chromium(III) complexes[3,4] of the formulas $[Cr(C_2B_9H_{11})_2]^-$ and $[Cr(CB_{10}H_{11})_2]^{3-}$ and Mn(IV) complexes[4] of the formula $[Mn(CB_{10}H_{11})_2]^{2-}$. These complexes are formally three-electron deficient, and a crystallographic study[5] of $[Cr(C_2(CH_3)_2B_9H_9)_2]^-$ showed no distortions from the 12-vertex icosahedral geometry, although the metal to bonding face distances were slightly longer than any found previously.

The cyclopentadienyl organometallic chemistry of the group 4 and 5 transition metals has been well established;[6] however, metallocarborane complexes of these metals have heretofore escaped synthesis. Reported here are the synthesis, characterization, and studies of the first metallocarboranes to incorporate the early transition metals titanium, zirconium, hafnium, and vanadium.[7] Also included are the first metallocarboranes containing formal chromium(II) and manganese(II) oxidation states.

Results and Discussion

Synthesis of Supraicosahedral Titanacarboranes. The polyhedral expansion of 1,2-$C_2B_{10}H_{12}$ to yield a series of 13-vertex metallocarboranes containing iron, cobalt, nickel, molybdenum, and tungsten was previously reported.[8] These complexes incorporated the η^6-$C_2B_{10}H_{12}^{2-}$ ligand which was shown to be fluxional in solution by ^1H and ^{11}B NMR spectroscopy.

The reaction of titanium tetrachloride 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 tetraethylammonium bromide caused precipitation of the diamagnetic red-orange crystalline compound $[(C_2H_5)_4N]_2[4,4'\text{-}Ti(1,6\text{-}C_2B_{10}H_{12})_2]$, I, in 75% yield. Recovery of 1,2-$C_2B_{10}H_{12}$ from the reaction mixture, without exposure to air, identified the carborane dianion as the reductant responsible for the formal Ti(II) product, according to

$$3Na_2C_2B_{10}H_{12} + TiCl_4 \rightarrow Na_2[Ti(C_2B_{10}H_{12})_2] + C_2B_{10}H_{12} + 4NaCl$$

In the solid state I was moderately stable to air and decomposed completely in about 48 h but was stable indefinitely when stored under nitrogen and could be handled for brief periods in the air without noticeable decomposition. Elemental analysis supported the proposed formulation. The NMR spectra (Tables I and II) indicated that I was fluxional in solution,[8] as evidenced by the equivalent carborane C–H groups in the ^1H NMR spectrum and the 2:2:2:1:1:1:1 symmetry in the ^{11}B NMR spectrum.

Cyclic voltammetry of I (Table IV) showed a reversible one-electron oxidation ($E_{p/2} = -0.24$ V) and a reversible reduction ($E_{p/2} = -2.03$ V). Attempted chemical and electrochemical oxidation of I did not produce an isolable metallocarborane complex. This is not surprising in view of the fact that I contains a formal 14-valence-electron titanium atom, and represents the first example of a four-electron-dificient metallocarborane.

Complex I could also be synthesized in 90% yield using titanium trichloride as described by the equation

$$5Na_2C_2B_{10}H_{12} + 2TiCl_3 \rightarrow 2Na_2[Ti(C_2B_{10}H_{12})_2] + C_2B_{10}H_{12} + 6NaCl$$

Titanium trichloride was superior to $TiCl_4$ as a metal reagent due to greater ease of handling and higher yields.

The dimethylcarboranyl homologue $[(C_2H_5)_4N]_2[4,4'\text{-}Ti(1,6\text{-}(CH_3)_2\text{-}1,6\text{-}C_2B_{10}H_{10})_2]$, II, was similarly isolated and found to contain one acetone molecule of crystallization per titanium atom. Bright red crystalline II was considerably more air stable both in solution and as a solid than complex I. Exposure of crystalline II to air for weeks to months caused only little or no decomposition. The ^1H NMR, ^{11}B NMR, and ir spectra of II appear in Tables I–III.

As with I, the fluxionality was established from the ^{11}B NMR spectrum by the symmetry and from the ^1H NMR by the equivalence of the carborane methyl groups. Cyclic voltammetry of II showed an irreversible oxidation (–0.34 V) and a reversible reduction (–2.10 V).

Complexes I and II represent metallocarborane analogues of titanocene, "$(C_5H_5)_2Ti$", which has only been isolated in the dimeric forms[9–12] $[(C_5H_5)_2Ti]_2$ and $[(C_5H_5)(C_5H_4)TiH]_2$, although permethyltitanocene, $[C_5(CH_3)_5]_2Ti$, has been isolated in a marginally stable monomeric form.[13] For these reasons, as well as the extreme electron-deficient nature of the titanacarboranes, the crystal structure of the tetramethylammonium salt of II was determined by an x-ray diffraction study.[14]

The structure consisted of two closed 13-vertex polyhedra fused through the titanium atom. The overall geometry, with respect to the polyhedral positions occupied by carbon and metal, was similar to that found for 4-(η^5-C_5H_5)4-Co-1,6-$C_2B_{10}H_{12}$.[15] However, the titanacarborane polyhedra showed less distortion from a symmetric structure than did the cobaltacarborane. A significant result was that the metal–boron and metal–carbon distances averaged 0.24 Å longer in $[(CH_3)_4N]_2$–II than in $C_5H_5CoC_2B_{10}H_{12}$ and 0.11 Å longer than in the three-electron-deficient Cr(III) metallocarborane[5] $[Cr(C_2(CH_3)_2B_9H_9)_2]^-$. The metal to cage distances in

Table I. 60-MHz ^{1}H NMR Data (in CD_3CN)

Complex[a]	Resonance, τ^b (rel area)	Assignment[a]
I, $[(C_2H_5)_4N]_2$-$[Ti(C_2B_{10}H_{12})_2]$	6.37 (1) br, s	C–H
	6.88 (4) q	Cation CH_2
	8.82 (6) t	Cation CH_3
II,[c] $[(C_2H_5)_4N]_2$-$[Ti(C_2Me_2B_{10}H_{10})_2]\cdot Me_2CO$	6.88 (8) q	Cation CH_2
	7.96 (3) s	Me_2CO
	8.82 (12) t	Cation CH_3
	9.00 (6) s	C–CH_3
VIII, $[(C_2H_5)_4N]_2$-$[Zr(C_2Me_2B_{10}H_{10})_2]$	6.81 (4) q	Cation CH_2
	8.63 (3) s	C–CH_3
	8.77 (6) t	Cation CH_3
X, $[(C_2H_5)_4N]_2$-$[Hf(C_2Me_2B_{10}H_{10})_2\cdot C_4H_8O$	6.33 (1) m	C_4H_8O
	6.81 (4) q	Cation CH_2
	8.28 (3) s	C–CH_3
	8.77 (6) t	Cation CH_3
XII, $[(C_2H_5)_4N]$-$[C_5H_5TiC_2B_{10}H_{12}]$	2.36 (2) br, s	C–H
	4.26 (5) s	C_5H_5
	6.82 (8) q	Cation CH_2
	8.78 (12) t	Cation CH_3
XIII, $[(C_2H_5)_4N]$-$[C_5H_5TiC_2Me_2B_{10}H_{10}]$	4.31 (5) s	C_5H_5
	6.85 (8) q	Cation CH_2
	7.21 (6) s	C–CH_3
	8.81 (12) t	Cation CH_3
XV,[d] $C_8H_8TiC_2B_{10}H_{12}$	2.33 (4) s	C_8H_8
	5.40 (1) br, s	C–H
XVII,[e] $C_8H_8TiC_2B_9H_{11}$	2.28 (4) s	C_8H_8
	6.72 (1) br, s	C–H
XIX,[e] $C_8H_8TiC_2B_9H_{11}$	2.32 (4) s	C_8H_8
	7.22 (1) br, s	C–H

[a] C–H = carborane C–H, C–CH_3 = carborane C–CH_3, Me = CH_3. [b] Chemical shifts are relative to TMS = τ 10.00; s = singlet, br = broad, q = quartet, t = triplet of 1:1:1 triplets, m = multiplet. [c] Obtained at 100 MHz. [d] Measured at 0 °C in $(CD_3)_2CO$. [e] Measured in $(CD_3)_2CO$.

Table II. 80.5-MHz ^{11}B NMR Data (in CH_3CN)

Complex	Rel areas	Chem shift[a] (J_{B-H}, 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)
VIII	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)
IX	1:1:1:1:2:1:2:1	−17.7, −5.8, −4.8, +0.6, +5.4, +8.8, +12.3, +20.6
X	1:2:1:2:2:1:1	−8.7, −7.3, −0.8, +7.1, +8.7, +18.0 (155), +22.6 (145)
XI	1:1:1:1:1:1:1:1:1:1	−16.9, −5.0, −3.6, −0.7, +0.7, +4.0, +6.0, +11.5, +13.1, +21.4
XII	1:3:3:2:1	−14.0 (130), −0.6, +0.1, +13.3 (155), +26.0 (135)
XIII	1:2:2:2:2:1	−15.4 (125), −3.6 (130), −2.6 (115), +3.1 (135), +10.0 (145), +24.8 (135)
XV[d]	1:2:3:1:1:2	−11.6 (150), −6.8 (140), −1.1 (140), +6.5 (180), +9.1 (150), +14.4 (150)
XVII[e]	1:2:2:2:2	−8.9 (145), +5.1, +5.9, +15.8 (145), +17.4 (140)
XIX[e]	2:2:2:2:1	+3.1 (145), +6.0 (160), +12.3 (160), +15.6 (160), +17.9 (150)

[a] Relative to $Et_2O\cdot BF_3$ = 0. [b] At 60 °C. [c] At 75 °C. [d] Measured in acetone at 50 °C. [e] Measured in acetone.

$[(CH_3)_4]_2$–II were, in fact, the longest observed in a metallocarborane. Thus the electron-deficient nature of the titanacarborane resulted in a relatively undistorted polyhedral structure with long metal-to-cage distances, as also found for the chromium(III) complexes. These results are in contrast to a recent crystallographic study[16] of the two-electron-deficient biferracarborane $(C_5H_5Fe)_2C_2B_6H_8$, which was found to distort to a novel ten-vertex polyhedral geometry.

The structure of $[(CH_3)_4N]_2$–II was monomeric with the titanium atom sandwiched between approximately parallel six-membered rings. There was no significant distortion toward a structure in which the two ligands are "bent back" to present sufficient room for a donor molecule to approach. This is intriguing in view of the 14-electron configuration of the formal d^2 titanium(II) atom in I and II. Both "titanocene" and permethyltitanocene readily expand their coordination spheres and are converted to the formal 16-electron complexes $[(C_5H_5)(C_5H_4)TiH]_2$ and $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiH$, respectively.[11,13] Titanocene and permethyltitanocene also have been shown to react immediately with the neutral donor ligands dinitrogen, carbon monoxide, and triphenylphosphine to yield complexes[6b,11,13] such as $(L_2Ti)_2N_2$, $L_2Ti(CO)_2$ (L = C_5H_5 or $C_5(CH_3)_5$), and $[C_{10}H_{10}TiP(C_6H_5)_3]_2$. Reaction with H_2, HX, and X_2 (X = Cl, Br, I) produced titanium(IV) hydrides and halides[6b,11,13] of formula L_2TiH_2 and L_2TiX_2. The carbon monoxide complexes $L_2Ti(CO)_2$ as well as the halides L_2TiX_2 have tetrahedral geometries in which the cyclopentadienyl ligand occupies one coordination site. In contrast, complexes I and II showed no tendency to expand the coordination sphere of the titanium atom and were unreactive in solution toward 1 atm pressure of H_2, N_2, or CO; $P(C_6H_5)_3$ also did not react with the titanacarboranes. Reaction occured with HCl and Cl_2, but no stable metallocarboranes were isolated. These observations are congruent with the determined structure for II in addition to its surprising air stability. The reasons for the observed stabilities of the titanacarboranes seem largely to be electronic rather than steric. This is supported by the observation that II is much more air stable than I, both in solution and as a solid. Methyl substitution would tend to increase electron density at the titanium center (the electrochemical data (Table IV) also support this supposition, since II is harder to reduce and easier to oxidize than I) and thereby add to the stability of the formal 14-electron titanium atom. These arguments suggest that attachment of electron-withdrawing substituents to the carborane cage, such as CF_3, would tend to lower the metal reduction potential and be equivalent to decreasing electron density at the metal center. This could lead to more reactive titanacarboranes which may accept small electron-donor molecules such as nitrogen or carbon monoxide. Further investigation of these possibilities is under way.

Synthesis of Metallocarboranes Containing Vanadium. The interaction of vanadium trichloride with $Na_2C_2B_{10}H_{12}$, prepared by reduction of 1,2-$C_2B_{10}H_{12}$, required a short reflux in tetrahydrofuran solvent to produce the paramagnetic red-brown crystalline complex $[(C_2H_5)_4N]_2[4,4'$-V(1,6-$C_2B_{10}H_{12})_2]$, III, containing formal vanadium(II). The stoichiometry of the reaction was identical with that observed in the synthesis of I using $TiCl_3$. Elemental analysis confirmed the formulation of III as a V(II) complex. Complex III was essentially air stable in the solid state, although we observed a decrease in the magnetic moment upon several recrystal-

Table III. Infrared Spectra (Nujol Mull)

Complex	Frequency, cm^{-1}
I	2470 vs, 1400 m, 1310 w, 1185 s, 1155 w, 1120 m, 1080 m, 1040 m, 1025 m, 1005 s, 980 w, 907 w, 882 w, 865 w, 830 w, 816 w, 794 m, 757 m, 742 m
II	2480 vs, 1725 s, 1405 s, 1360 s, 1310 m, 1225 m, 1185 s, 1140 w, 1080 m, 1040 s, 1025 s, 1010 s, 988 m, 955 w, 920 m, 896 w, 858 w, 835 w, 821 w, 795 s, 772 w, 748 s, 712 w, 688 w
III	2500 vs, 2450 vs, 1475 s, 1385 m, 1305 w, 1185 m, 1175 m, 1120 w, 1080 m, 1020 m, 1010 s, 974 w, 963 w, 920 w, 896 w, 848 w, 796 m, 785 m, 757 m, 742 m
IV	2490 vs, 1710 m, 1400 m, 1355 m, 1300 w, 1220 m, 1180 s, 1135 w, 1075 w, 1035 m, 1025 s, 1010 m, 925 w, 903 w, 847 w, 825 w, 795 m, 752 w, 707 w
V	2500 vs, 1475 s, 1385 m, 1300 w, 1185 m, 1175 m, 1150 w, 1120 w, 1085 m, 1020 m, 1005 s, 977 w, 960 w, 904 w, 852 w, 828 w, 794 m, 785 m, 752 m, 740 m
VI	2510 vs, 1475 s, 1425 s, 1400 w, 1380 m, 1350 m, 1210 w, 1170 m, 1125 w, 1105 w, 1075 w, 1065 w, 1050 m, 1025 w, 1000 s, 977 m, 920 vw, 844 vw, 788 m, 740 w, 707 w
VII	2460 vs, 1475 s, 1385 s, 1300 w, 1185 m, 1170 m, 1125 w, 1095 w, 1030 s, 1010 s, 977 w, 965 w, 870 w, 855 w, 835 w, 793 w, 780 w, 765 m, 740 w, 722 w
VIII	2485 vs, 1400 m, 1305 w, 1185 s, 1135 w, 1070 m, 1035 s, 1020 s, 1010 s, 982 w, 940 w, 910 w, 886 w, 860 w, 813 w, 794 m, 740 s, 710 w
X	2490 vs, 1405 m, 1370 m, 1310 w, 1265 vw, 1185 s, 1140 w, 1075 m, 1035 s, 1020 s, 1010 s, 983 w, 940 w, 914 m, 888 w, 858 w, 813 w, 794 m, 760 w, 740 m, 708 w
XII	3040 w, 2450 vs, 1715 w, 1600 w, 1475 s, 1430 s, 1390 m, 1360 m, 1170 s, 1120 w, 1080 m, 1055 w, 1020 m, 1010 m, 1000 m, 980 w, 940 w, 927 w, 911 w, 848 w, 811 s, 802 s, 785 m, 750 w
XIII	3030 w, 2440 vs, 1715 w, 1600 w, 1480 s, 1440 s, 1420 w, 1385 m, 1360 m, 1210 w, 1175 m, 1070 w, 1055 w, 1025 s, 1015 m, 1000 m, 943 w, 924 w, 911 w, 893 w, 869 w, 852 w, 823 m, 804 vs, 786 m, 756 w
XIV	2470 vs, 1825 w, 1710 w, 1480 s, 1440 s, 1395 m, 1370 w, 1225 w, 1175 s, 1135 w, 1120 w, 1090 w, 1075 w, 1055 w, 1040 m, 1005 s, 990 m, 915 w, 825 m, 787 m, 763 s, 740 m
XV	2520 vs, 2490 vs, 1460 vs, 1430 s, 1330 w, 1320 w, 1220 w, 1130 w, 1085 w, 1045 w, 1025 w, 1005 w, 980 w, 970 w, 947 w, 920 w, 850 vw, 830 w, 818 m, 810 m, 774 w, 751 vs
XVI	2520 vs, 2490 vs, 1825 w, 1715 w, 1480 s, 1440 s, 1390 s, 1360 m, 1175 m, 1165 w, 1090 w, 1070 w, 1060 w, 1040 w, 1030 m, 1005 m, 977 m, 915 m, 888 w, 835 w, 822 w, 780 m, 765 s, 730 w, 708 w
XVII	3010 m, 2560 vs, 2510 vs, 2460 vs, 1840 w, 1690 w, 1470 s, 1440 s, 1335 w, 1240 w, 1160 m, 1090 s, 1060 w, 1030 m, 1020 w, 980 s, 920 w, 850 w, 810 m, 795 m, 772 m, 746 vs, 713 m
XVIII	2490 vs, 1800 w, 1685 w, 1475 vs, 1435 s, 1385 s, 1355 s, 1185 w, 1170 s, 1100 w, 1070 m, 1050 m, 1015 m, 1000 m, 990 m, 978 m, 916 m, 896 w, 820 w, 810 w, 782 m, 766 m, 755 vs
XIX	3000 m, 2530 vs, 1850 w, 1700 w, 1335 w, 1165 w, 1110 m, 1060 m, 1015 m, 988 m, 966 w, 937 w, 920 w, 854 w, 818 m, 805 w, 772 m, 749 vs, 706 m

Table IV. Electronic Spectra and Electrochemical Data

Complex	λ_{max}, nm (log ϵ)[a]	$E_{p/2}$, V, vs. SCE[b]
I	929 (3.00), 481 (4.21), 339 (3.75), 291 (3.97)	−2.03 red. −0.22 ox.
II	978 (2.645), 510 (3.975), 354 (3.565), 292 (3.81)	−2.10 red. −0.34 ox.[c]
III	831 (2.96), 465 sh (3.445), 412 (3.78), 375 sh (3.82), 334 (3.945), 288 (3.865)	−1.79 red. +0.04 ox.
IV	875 (2.825), 495 (3.49), 425 (3.74), 339 (3.87)	−1.80 red. −0.12 ox.
V	1018 (2.735), 454 (3.81), 363 (3.465), 288 (3.96)	−1.90 red. −0.11 ox.
VI	480 (2.83), 385 sh (3.175), 309 (4.065), 245 (4.21)	−0.56 red. +1.41 ox.[c]
VII	925 (1.48), 537 (2.20), 450 sh (2.83), 366 (3.67), 288 (4.03), 257 (4.14)	−1.52 red. −0.11 ox.[d]
XV	620 (1.74), 430 sh (2.74), 277 (4.494)	−0.55 red. +1.77 ox.[c]
XVII	556 (1.48), 368 (2.924), 261 (4.544)	−0.87 red. +1.70 ox.[c]
XIX	575 sh (1.78), 429 (2.74), 267 (4.595)	−0.87 red. +1.72 ox.[c]

[a] Measured in spectroquality CH_3CN. [b] Cyclic voltammetry in CH_3CN under nitrogen with 0.1 M $R_4N^+PF_6^-$ ($R = C_2H_5$ or C_4H_9) supporting electrolyte, platinum button electrode; reversible waves except where noted; red. = reduction, ox. = oxidation. [c] Irreversible wave. [d] Quasi-reversible wave.

lizations in the presence of air. Prolonged storage is recommended under a nitrogen atmosphere. Solutions slowly decomposed in air over a period of days to weeks.

The ^1H NMR spectrum of III exhibited broad resonances attributable to the tetraethylammonium cation. The 80.5-MHz ^{11}B NMR spectrum showed only extremely broadened and unresolved resonances around 0. In contrast, paramagnetic metallocarboranes containing chromium, iron, cobalt, and nickel have previously yielded interpretable ^{11}B spectra.[17]

The electron spin resonance spectrum (sealed tube, CH_2Cl_2 solution, 51 °C) exhibited an eight-line pattern centered at $g_0 = 2.001$ (due to coupling of the unpaired electron with ^{51}V, $I = {}^7/_2$). The magnetic moment at 298 K was $\mu_{eff} = 1.75$ (1) μ_B,[18] close to the spin-only value of 1.73 μ_B for one unpaired electron. Further magnetic studies of III are discussed below. As found for I, the titanium(II) analogue, cyclic voltammetry of III showed a reversible one-electron oxidation ($E_{p/2} = +0.04$ V) and a reversible reduction ($E_{p/2} = -1.79$ V). Electrochemical oxidation of an acetonitrile solution of III under nitrogen resulted in extensive decomposition. An attempted chemical oxidation with iodine was also unsuccessful.

The infrared spectrum of III (Table III) was nearly identical with that of I, suggesting similar structures for the two analogues. The vanadium complex presumably contains slightly shorter metal–cage bonding distances than I, due to the presence of one additional bonding electron.

The dimethylcarboranyl homologue, $[(C_2H_5)_4N]_2[4,4'-V(1,6-(CH_3)_2-1,6-C_2B_{10}H_{10})_2]$, IV, was similarly synthesized from $1,2-(CH_3)_2-1,2-C_2B_{10}H_{10}$ and VCl_3 as dark red-brown crystals. The infrared spectrum was nearly identical with that of II and indicated the presence of acetone of crystallization. Elemental analysis of both II and IV indicated one acetone molecule was present per metal atom. Unlike III, the 80.5-MHz ^{11}B NMR spectrum of IV showed one well-defined broad resonance at +1.18 ppm, relative to $Et_2O{\cdot}BF_3$ (width at half-height 600 Hz). The cyclic voltammogram of IV showed a reversible oxidation and a reversible reduction (Table IV).

The vanadacarboranes III and IV incorporate formal 15-valence-electron vanadium(II) atoms and are thus three-electron-deficient species. They are similar to the chromium(III) metallocarboranes $[Cr(C_2B_9H_{11})_2]^-$ in this respect; however, the d^3 vanadium(II) metal atoms possess one unpaired electron, while the d^3 chromium(III) metallocarboranes have magnetic moments consistent with three unpaired electrons.[3]

Synthesis of Chromium(II) and -(III) Metallocarboranes. The reaction of chromium trichloride with $Na_2C_2B_{10}H_{12}$ in tetrahydrofuran at reflux also resulted in reduction of the metal to the formal 2+ state, and $[(C_2H_5)_4N]_2[4,4'\text{-}Cr\text{-}(1,6\text{-}C_2B_{10}H_{12})_2]$, V, could be isolated in the same manner as for the titanacarboranes. Elemental analysis was in agreement with the proposed formula. Orange-brown crystalline V was found to be air stable as a pure solid, while solutions decomposed only slowly when exposed to air.

The paramagnetism of V indicated by its broadened ^1H and ^{11}B NMR spectra. The latter showed a single broad resonance (width at half-height 600 Hz) at +5.46 ppm, relative to $Et_2O{\cdot}BF_3$. The magnetic moment at 299 K was $\mu_{eff} = 2.77$ (1) μ_B, slightly lower than the spin-only value of 2.83 μ_B for two unpaired electrons.

The cyclic voltammogram of V was similar to the Ti(II) and V(II) analogues and showed a reversible one-electron oxidation at $E_{p/2} = -0.11$ V and a reversible reduction at $E_{p/2} = -1.90$ V. Yellow-orange solutions of V could be oxidized electrochemically or chemically with H_2O_2 or Ag^+, to give a deep red, air-stable solution containing the Cr(III) anion $[4,4'\text{-}Cr\text{-}(1,6\text{-}C_2B_{10}H_{12})_2]^-$. The $(C_2H_5)_4N^+$ salt of this anion has been isolated as red-purple crystals, complex VI, and characterized by its infrared and electronic spectra and cyclic voltammogram (Tables III and IV). The electronic spectrum of VI showed no band in the near-infrared region, as found for V. The cyclic voltammogram showed a reversible reduction at $E_{p/2} = -0.56$ V, presumably corresponding to the Cr(III)–Cr(II) couple.

The isolation of a chromium(II) complex from the reaction of $CrCl_3$ with $Na_2C_2B_{10}H_{12}$ is interesting because the analogous reaction of $CrCl_3$ with $Na_2C_2B_9H_{11}$ produced the chromium(III) metallocarborane[3] $[Cr(C_2B_9H_{11})_2]^-$. This Cr(III) species showed no reversible waves in its cyclic voltammogram and could not be reduced to a stable Cr(II) complex. This is one example of the marked difference between the $\eta^5\text{-}C_2B_9H_{11}^{2-}$ and $\eta^6\text{-}C_2B_{10}H_{12}^{2-}$ carborane ligands, with respect to the electronic environment produced by them at the metal center. A further discussion of the differences between these carborane ligands appears below.

Synthesis of a Metallocarborane Containing Manganese(II). The isolation of stable titanium(II), vanadium(II), chromium(II), and iron(II)[8] metallocarboranes of the $C_2B_{10}H_{12}^{2-}$ ligand led us to attempt to complete the first-row transition series with the synthesis of a manganese(II) complex. We found that manganese bromide, $MnBr_2$, reacted immediately with $Na_2C_2B_{10}H_{12}$ in tetrahydrofuran to produce a red-brown solution from which $[(C_2H_5)_4N]_2[4,4'\text{-}Mn(1,6\text{-}C_2B_{10}H_{12})_2]$, VII, could be isolated as green-brown crystals. The formulation of the metallocarborane as a Mn(II) complex was confirmed by elemental analysis and magnetic susceptibility data (below). The infrared spectrum was nearly identical with those of the titanium, vanadium, and chromium analogues, suggesting similar structures for this series of $(C_2B_{10}H_{12})_2$ complexes. It is likely that the metal–bonding face distances increase in the order Fe < Mn < Cr < V < Ti, as the complexes become more electron deficient with fewer electrons available for metal–cage bonding. The manganese(II) metallocarborane is deficient in only one electron. The synthesis of VII completes a series of $(C_2B_{10}H_{12})_2$ first-row transition metal complexes from titanium through nickel,[8] with all isolated compounds containing the formal 2+ metal oxidation states except for the Co(III) analogue.

Table V. Summary of Magnetic Properties for the $[4,4'\text{-}M(1,6\text{-}C_2B_{10}H_{12})_2]^{2-}$ Metallocarboranes[a]

Metal (M)[b]	Unpaired electrons	μ_{eff},[c] μ_B	Curie constant (C)	Weiss constant (Θ), K
Ti d^2	0		Diamagnetic	
V d^3	1	1.75 (1)	0.236 (3)	21 (2)
Cr d^4	2	2.77 (1)	0.791 (6)	9 (1)
Mn d^5	1	1.70 (1)	0.233 (4)	28 (3)
Fe[d] d^6	0		Diamagnetic	

[a] The numbers in parentheses are the estimated standard deviations in the last digits. [b] Following the metal is the formal d-electron configuration. [c] The effective magnetic moments were calculated at 298 K for V, 299 K for Cr, and 294 K for Mn. [d] From ref 8.

Complex VII is slightly air sensitive in solution and in the solid state, although it can be handled in the air for periods of hours without noticeable decomposition. The ^1H NMR spectrum showed broad peaks attributable to the tetraethylammonium cation. The 80.5-MHz ^{11}B NMR spectrum exhibited one extremely broad resonance centered at about 0, relative to $Et_2O{\cdot}BF_3$, and being about 15 000 Hz wide. The cyclic voltammogram was similar to those of the M(II) analogs (M = Ti, V, Cr) and showed a quasi-reversible oxidation of $E_{p/2} = -0.11$ V and a reversible reduction at −1.52 V.

The magnetic moment of VII at 294 K was $\mu_{eff} = 1.70$ (1) μ_B, just slightly below the spin-only value of 1.73 μ_B for one unpaired electron. The metallocene analogue manganocene, $Mn(C_5H_5)_2$, is a d^5 system with five unpaired electrons. Various studies have shown, however, that manganocene and 1,1′-dimethylmanganocene, $Mn(C_5H_4CH_3)_2$, may undergo high-spin, low-spin equilibria depending upon temperature, physical state, and chemical environment.[19] A further discussion of the magnetic properties of the paramagnetic vanadium, chromium, and manganese metallocarboranes appears next.

Magnetic Studies of Paramagnetic Metallocarboranes. The molar susceptibilities of the homologous complexes $[(C_2H_5)_4N]_2[4,4'\text{-}M(1,6\text{-}C_2B_{10}H_{12})_2]$ (M = V, Cr, Mn) were measured from ~40 K to room temperature. The plots of $1/\chi$ vs. temperature were linear in all cases, indicating normal paramagnetic behavior. The complexes were found to obey the Curie–Weiss law

$$\chi_M^{cor} = C/(T - \Theta)$$

where χ_M^{cor} is the corrected molar susceptibility, C is the Curie constant, T is the temperature in kelvin, and Θ is the Weiss constant. The results are summarized in Table V.

The room-temperature magnetic moments were consistent with one, two, and one unpaired electrons for the vanadium, chromium, and manganese complexes, respectively. These data are consistent with a molecular orbital scheme containing one low-energy orbital with two closely spaced or degenerate orbitals at higher energy. These would be primarily metal d orbitals in character. The highest occupied molecular orbital (HOMO) would correspond to the single filled low-energy "d" orbital, and the lowest unoccupied molecular orbital (LUMO) would correspond to the two unfilled or partially filled, closely spaced "d" orbitals. There would also be an additional two d orbitals at even higher energy.

The monomeric early transition metal metallocenes $Ti[C_5(CH_3)_5]_2$, $V(C_5H_5)_2$, $Cr(C_5H_5)_2$, and $Mn(C_5H_5)_2$ have two, three, two, and five unpaired electrons, respectively. The electronic structure of manganocene does not conform to the series because it is essentially ionic in character. For the covalent titanium, vanadium, and chromium metallocenes, these observations are consistent with three closely spaced primarily d-type molecular orbitals of a_{1g} and e_{2g} symmetry.[20] The metallocarborane complexes contain a single low-energy orbital, in comparison, seemingly a result of incorporation of the less symmetric carborane ligand which causes larger ligand field splittings than the cyclopentadienide ligand, $C_5H_5^-$.

The formal manganese(II) complex, VII, is a d^5 system with one unpaired electron. Comparable metallocenes with a d^5-electron configuration are "ionic" manganocene ($Mn(C_5H_5)_2$, five unpaired electrons) and "covalent" ferricinium ion ($[Fe(C_5H_5)_2]^+$, one unpaired electron). Hence it may be concluded that a considerable amount of covalent bonding occurs in complex VII, as compared to the ionic metallocene analogue.

Comparisons of Electrochemical Data and Electronic Spectra. The homologous metallocarboranes $[4,4'\text{-}M(1,6\text{-}C_2B_{10}H_{12})_2]^{2-}$ (M = Ti, V, Cr, Mn) all possessed some noteworthy similarities. In addition to similar infrared spectra as previously mentioned, the cyclic voltammograms of these complexes were all similar in showing a reversible oxidation close to 0 and a reversible reduction at about −1.6 to −1.9 V (Table IV). This general pattern was characteristic of the 2+ metal oxidation state for these metallocarboranes. Also characteristic of these metallocarboranes was the presence of a near-infrared band in the electronic spectra (Table IV). Metallocarboranes I–V and VII all exhibited a near-infrared band which most likely corresponds to a low-energy d–d transition. It is interesting that the Cr(III) complexes VI and $[Cr(C_2B_9H_{11})_2]^-$ do not exhibit a near-infrared band. The presence of this band in the titanium(II) d^2 complexes, I and II, indicates that it may correspond to a transition from the lowest energy d orbital to the next highest energy d orbitals, those partially occupied in the d^3 vanadium, d^4 chromium, and d^5 manganese complexes. The symmetric Gaussian shape of the near-infrared bands observed in these metallocarboranes suggests that this set of two orbitals may be degenerate (i.e., of e symmetry). An average value for this transition is about 930 nm and corresponds to an energy of 10 750 cm^{-1}, or 1.33 eV.

Synthesis and Rearrangements of Metallocarboranes Containing Zirconium and Hafnium. The reaction of zirconium tetrachloride with $Na_2C_2(CH_3)_2B_{10}H_{10}$ in tetrahydrofuran was instantaneous at room temperature producing a very air-sensitive purple solution. Purple, diamagnetic crystals of $[(C_2H_5)_4N]_2[4,4'\text{-}Zr(1,6\text{-}(CH_3)_2\text{-}1,6\text{-}C_2B_{10}H_{10})_2]$, VIII, were isolated in the same manner as for the titanium analogue; elemental analysis agreed well with this formulation. Recovery of $1,2\text{-}(CH_3)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ from the reaction mixture confirmed the carborane dianion as the reductant responsible for the production of this formal zirconium(II) complex. As a solid, VIII decomposed completely in about 10–20 min upon exposure to air but was stable under nitrogen. The symmetry found in the ^{11}B NMR spectrum (Table II) and the equivalent carborane $C\text{–}CH_3$ groups observed in the ^1H NMR spectrum (Table I) suggest the existence of a fluxional system as found for the titanium analogues I and II. The infrared spectrum of VIII was similar to the titanium analogue, complex II, suggesting similar structures for the two complexes. Cyclic voltammetry of VIII showed no reversible oxidation or reduction waves.

When heated at 90–95 °C, under nitrogen or in vacuo, VIII underwent a striking color change to orange, indicative of a facile thermal rearrangement[21] of the 13-vertex metallocarborane. This transformation from purple to orange also occurred rapidly in acetonitrile solution and was essentially complete in about 10 h at 75 °C, as followed by ^{11}B NMR spectroscopy. Only one new isomer could be isolated from rearrangement experiments; this isomer remained unchanged in a sealed NMR tube at 75 °C for 65 h. The carbon atom rearrangement was found to proceed rapidly through the 1,8 isomer to the thermally most stable 1,12 isomer, as followed by ^{11}B NMR spectroscopy. Thus, a characteristic high-field doublet at +26.2 ppm appeared upon initial heating of VIII to 75 °C in CH_3CN solution, continued to grow for about 20 min, then gradually diminished in size, and disappeared with continued heating at 75 °C. This resonance was probably due to the intermediate 1,8 isomer. The proposed structure of the orange product is then $[(C_2H_5)_4N]_2[4,4'\text{-}Zr(1,12\text{-}(CH_3)_2\text{-}1,12\text{-}C_2B_{10}H_{10})_2]$, IX. This polyhedral rearrangement of VIII occurred slowly (1–2 weeks) in the solid state even at room temperature and necessitated storage at −20 °C.

As expected, IX exhibited nonequivalent carborane $C\text{–}CH_3$ groups in the ^1H NMR spectrum at τ 6.92 and 7.86 while the ^{11}B NMR spectrum showed six area 1 peaks suggesting an asymmetric polyhedral structure (Table II).

The zirconacarboranes were stable in solution under nitrogen; hence no evidence for the formation of dinitrogen complexes was found. Bercaw[22] has recently isolated a dinitrogen complex of permethylzirconocene, $[(C_5(CH_3)_5Zr]_2(N_2)_3$, by reduction of $(C_5(CH_3)_5)_2ZrCl_2$ under nitrogen. Further investigations into the chemistry of these zirconium(II)–carborane complexes are currently under way.

The close chemical similarity of zirconium and hafnium led us to investigate the reaction of hafnium tetrachloride with $Na_2C_2(CH_3)_2B_{10}H_{10}$. A very air-sensitive green solution was produced, and dark green crystals of $[(C_2H_5)_4N]_2\text{-}[4,4'\text{-}Hf(1,6\text{-}(CH_3)_2\text{-}1,6\text{-}C_2B_{10}H_{10})_2]$, X, could subsequently be isolated. Recrystallization from CH_2Cl_2/THF produced a complex having approximately one molecule of THF of crystallization per hafnium atom, as deduced from the ^1H NMR spectrum. Complex X contained formal hafnium(II) and possessed an air sensitivity and chemical reactivity approximately the same as the zirconium analogue. The infrared spectra of VIII and X were also similar. The cyclic voltammogram of X in CH_3CN under nitrogen showed an irreversible oxidation wave at $E_{p/2} = -0.52$ V (vs. SCE).

The 60-MHz ^1H NMR spectrum of diamagnetic X showed equivalent carborane $C\text{–}CH_3$ groups at τ 8.28 (Table I). An acceptable 80.5-MHz ^{11}B NMR spectrum of pure X was difficult to obtain. Because of the fluxional nature of the complex, some of the resonances were slightly broadened and lost B–H coupling resolution at temperatures of 25 °C and below (this was also observed for the titanium complexes I and II). Upon warming of the solution to about 40–50 °C, the peaks sharpened considerably but rearrangement to a new isomer (vide infra) had already occurred to a significant extent within the first minute at the warmer temperature. Nevertheless, the ^{11}B NMR spectrum of X was carefully assigned and appears in Table II. The observed symmetry is consistent with a fluxional complex as found for the titana- and zirconacarboranes.

The hafnacarborane also underwent a slow polyhedral rearrangement in the solid state at room temperature, necessitating storage at −20 °C. Heating of crystals at 85–90 °C resulted in a color change to orange; this change could also be effected in acetonitrile solution at 75 °C within a few minutes. As followed by ^{11}B NMR spectroscopy, the rearrangement proceeded rapidly to the 1,12 isomer and was essentially complete after 4–6 h at 75 °C. No further change was observed in the ^1H and ^{11}B NMR spectra after 65 h at 75 °C. The orange product is formulated as $[(C_2H_5)_4N]_2\text{-}[4,4'\text{-}Hf(1,12\text{-}(CH_3)_2\text{-}1,12\text{-}C_2B_{10}H_{10})_2]$, XI. The 60-MHz ^1H NMR spectrum of XI showed nonequivalent carborane $C\text{–}CH_3$ groups (τ 6.85 and 7.82), while the ^{11}B NMR spectrum contained resonances attributable to ten boron atoms. The ten unique boron resonances (Table II) were indicative

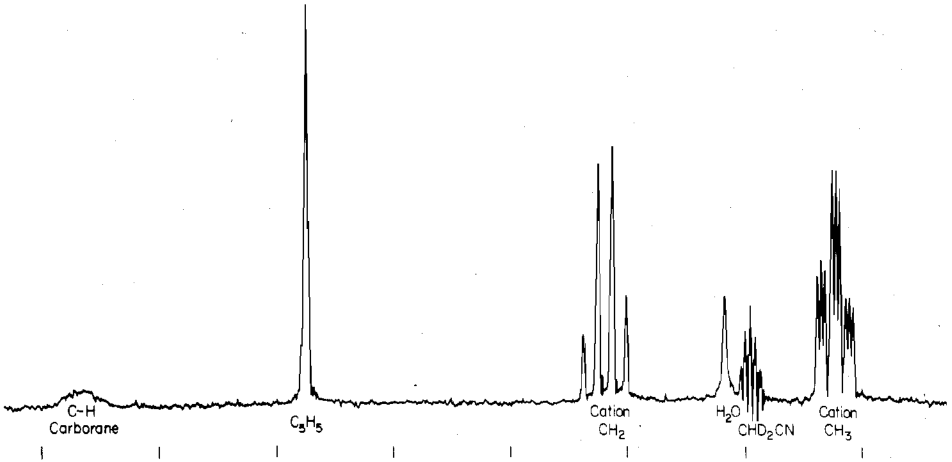

Figure 1. The 60-MHz ^1H NMR spectrum of $[(C_2H_5)_4N][4\text{-}(\eta^5\text{-}C_5H_5)\text{-}4\text{-}Ti\text{-}1,6\text{-}C_2B_{10}H_{12}]$, XII, in CD_3CN solution.

of a completely asymmetric polyhedral structure, as previously observed[8] for $4\text{-}(\eta^5\text{-}C_5H_5)\text{-}4\text{-}Co\text{-}1,12\text{-}C_2B_{10}H_{12}$.

It is noteworthy that the hafnacarborane rearrangement was considerably more facile than the rearrangement of the zirconium analogue, despite predictably similar ionic radii for Zr^{2+} and Hf^{2+}. It is likely that the metal–cage distances are similar for the zirconium and hafnium metallocarboranes, and yet the hafnacarborane rearrangement was found to be noticeably faster in solution. Thus, polyhedral rearrangement may be influenced by the metal orbitals used in bonding to the carborane cage; the zirconacarboranes use 4d orbitals while the hafnacarboranes use the more diffuse 5d orbitals. As expected, the titanacarboranes underwent polyhedral rearrangement much slower than the zirconacarborane—so that no changes were detected in the ^{11}B NMR spectra after 2 h at 70 °C. After 60 h in CH_2Cl_2/CH_3CN solution at 50 °C, I showed a complex ^{11}B NMR spectrum containing starting material in addition to several new resonances, two of which were clearly discernible at +33.0 and +37.7 ppm, relative to $Et_2O\cdot BF_3$. A polyhedral rearrangement is implied from these data; however, the isomers could not be separated due to their similar solubilities and decomposition on chromatographic supports.

The zirconium(II) and hafnium(II) metallocarboranes described here contain formal 14-valence electron metal atoms and thus represent metallocarborane polyhedra which are deficient in four electrons. The polyhedral rearrangement found for these species is the first such process observed for an electron-deficient metallocarborane. These results suggest that the polyhedral electron-counting rules[1] which predict the relative stabilities of metallocarborane polyhedra may now be amended to include the early transition metal complexes (vide infra).

Synthesis of Supraicosahedral Titanacarboranes Incorporating the Cyclopentadienyl Ligand. The remarkable stability of the $Ti^{II}\text{–}(C_2B_{10}H_{12})_2$ metallocarboranes led to attempts to prepare mixed-ligand titanacarboranes incorporating a cyclopentadienyl ligand. It seemed probable that such complexes would more closely resemble titanocene in terms of chemical reactivity.

Addition of $C_5H_5TiCl_x$ (x = 2 or 3) to a tetrahydrofuran (THF) solution of $Na_2C_2B_{10}H_{12}$ under argon gave a green solution presumably containing the neutral species $C_5H_5TiC_2B_{10}H_{12}$ or a solvated analogue. The green complex was soluble in benzene but could not be isolated in pure form due to extreme air sensitivity and even decomposition under vacuum. The green THF solution was unchanged upon exposure to N_2, CO, or $P(C_6H_5)_3$ and slowly decomposed at room temperature under argon. However, upon treatment with zinc dust for 2–3 h the solution became red, and bright red crystalline $[(C_2H_5)_4N][4\text{-}(\eta^5\text{-}C_5H_5)\text{-}4\text{-}Ti\text{-}1,6\text{-}C_2B_{10}H_{12}]$, XII, could be isolated in the same manner as the previously mentioned titanacarboranes. Elemental analysis was in agreement with the above formulation. When pure, complex XII survived exposure to air for 24 h or more without noticeable decomposition, although solutions were more air sensitive and decolorized quickly upon exposure to air if dilute. Concentrated acetone solutions of XII appeared air stable for short periods and showed no immediate reaction with water.

The diamagnetic character of this formal titanium(II) metallocarborane was indicated by the NMR spectra. The 60-MHz ^1H NMR spectrum, shown in Figure 1, exhibited a sharp cyclopentadienyl resonance at τ 4.26 and a broad carborane C–H resonance at τ 2.36, of relative areas 5:2 (Table I). The 80.5-MHz ^{11}B NMR spectrum contained resonances of area 1:3:3:2:1 at −14.0, −0.6, +0.1, +13.3, and +26.0 ppm. These data are consistent with a fluxional $C_2B_{10}H_{12}$ ligand.

The cyclic voltammogram of XII showed only irreversible oxidations (at $E_{p/2}$ = +0.51 and +0.85 V) and a reversible reduction of $E_{p/2}$ = −1.78 V. The irreversible oxidation waves correlate with the instability observed for the green solution presumably containing the Ti(III) species "$C_5H_5TiC_2B_{10}H_{12}$".

In dichloromethane solution XII was unreactive toward $P(C_6H_5)_3$ and 1 atm of N_2, CO, and H_2; it was also unreactive toward 100 atm of CO. In these respects the stability of XII was similar to the $(C_2B_{10}H_{12})_2$ complex $[Ti(C_2B_{10}H_{12})_2]^{2-}$, I.

The dimethylcarboranyl homologue, $[(C_2H_5)_4N][(1,6\text{-}(CH_3)_2\text{-}4\text{-}(\eta^5\text{-}C_5H_5)\text{-}4\text{-}Ti\text{-}1,6\text{-}C_2B_{10}H_{10}]$, XIII, was similarly isolated as dark red diamagnetic crystals. The characterization data appear in Tables I–III. The NMR spectra exhibited the symmetry expected for a fluxional complex. The cyclic voltammogram showed an irreversible oxidation at $E_{p/2}$ = +0.51 V and a reversible reduction at $E_{p/2}$ = −1.87 V.

Metallocarborane XIII showed chemical reactivity similar to that of XII and appeared to exhibit a slightly greater air stability in the solid state. Both complexes reacted with HCl and Cl_2 in solution although no stable metallocarboranes could be isolated from these reactions. The observed inertness of complexes XII and XIII toward both small neutral electron donor molecules and air suggests that the molecular structures contain approximately parallel bonding faces, as opposed to a structure containing the bonding planes "tipped" to a significant extent, such as the two C_5H_5 planes in $(C_5H_5)_2TiCl_2$.

The chemical stability of these formal 14-valence-electron titanium(II) analogues of titanocene is indeed remarkable and provides perhaps the best example yet of the extremely powerful stabilizing influence exhibited by a carboranyl ligand as compared to the case of a cyclopentadienyl ligand. As previously discussed, attachment of electron-withdrawing substituents to the carborane cage in $[C_5H_5TiC_2B_{10}H_{12}]^-$ might significantly alter the chemical reactivity. Also, incorporation of a positively charged substituent L, such as $-P(C_6H_5)_3^+$ or $-N(CH_3)_3^+$, would yield a neutral complex $C_5H_5Ti^{II}C_2B_{10}H_{11}L$. The reactivity might also be significantly altered in progressing from an anionic complex to a neutral complex since metallocenes such as titanocene are neutral. These considerations are currently being explored.

Synthesis of Titanacarboranes Incorporating the η^8-Cyclooctatetraenyl Ligand. It seemed possible that isolation of titanacarboranes incorporating higher formal metal oxidation states would provide further insight into this new and interesting area of organometallic chemistry. Accordingly, the reaction of $(C_8H_8TiCl)_2$ with $Na_2C_2B_{10}H_{12}$ in THF yielded a green solution from which air-sensitive paramagnetic orange-brown crystals of $[(C_2H_5)_4N][4-(\eta^8-C_8H_8)-4-Ti-1,6-C_2B_{10}H_{12}]$, XIV, were isolated. Formulation of XIV as a titanium(III) complex was confirmed by the elemental analysis and observed paramagnetism.

The 60-MHz ^1H NMR spectrum showed broad peaks due to the tetraethylammonium cation, while the 80.5-MHz ^{11}B NMR spectrum exhibited one broad resonance (width at half-height 220 Hz) at −12.0 ppm, relative to $Et_2O{\cdot}BF_3$.

The infrared spectrum of XIV (Table III) was consistent with an $\eta^8-C_8H_8$ ligand,[23] showing peaks at 915 (w), 825 (m), 787 (m) and 763 (s) cm^{-1}. Also supportive of this formulation is a crystallographic study[24] of $C_8H_8TiC_5H_5$, the analogous titanium(III) complex incorporating a cyclopentadienyl ligand in place of a carboranyl ligand. It was shown that both rings in $C_8H_8TiC_5H_5$ were completely π bonded to the metal (i.e., $(\eta^8-C_8H_8)Ti(\eta^5-C_5H_5)$) and approximately parallel. Complex XIV contains a formal titanium(III) d^1 metal atom with a 17-valence-electron configuration.

The cyclic voltammogram of XIV exhibited a reversible one-electron oxidation at $E_{p/2} = -0.61$ V. Treatment of acetone solutions of XIV with air or hydrogen peroxide, followed by slow addition of excess water, resulted in the formation of a green crystalline precipitate. Recrystallization from dichloromethane/hexane gave a high yield of the green, neutral, and air-stable titanium(IV) complex $4-(\eta^8-C_8H_8)-4-Ti-1,6-C_2B_{10}H_{12}$, XV. The mass spectrum exhibited a cutoff at *m/e* 298 corresponding to the $^{12}C_{10}{}^1H_{20}{}^{11}B_{10}{}^{48}Ti^+$ ion. The infrared spectrum of XV showed peaks at 920 (w), 818 (m), 810 (m), 774 (w), and 751 (vs) cm^{-1} consistent with an $\eta^8-C_8H_8$ ligand.

The 60-MHz ^1H NMR spectrum showed no C_8H_8 peak at 30 °C, but a single peak at τ 2.33 appeared upon cooling to 0 °C and continued to sharpen down to −40 °C. The broad carborane C–H resonance (τ 5.40) was of area 1 as compared to a relative area of 4 for the C_8H_8 resonance, indicating equivalent carborane C–H groups and a fluxional $C_2B_{10}H_{12}$ ligand. The fluxionality of the carborane ligand apparently affected the C_8H_8 resonance in the ^1H NMR spectrum, as slowing down the fluxional process resulted in the expected sharp single peak for the $\eta^8-C_8H_8$ ligand.

The fluxionality of this complex was confirmed from the temperature-dependent 80.5-MHz ^{11}B NMR spectra, as shown in Figure 2. The ^{11}B NMR spectrum was unchanged below −50 °C, indicating the fluxional process had been essentially halted at −50 °C. The high-field area 1 peak at +24.2 ppm was assigned to the unique seven-coordinate boron atom[25] in the "frozen" structure. At 50 °C, the process whereby enantiomers are interconverted was rapid on the NMR time scale, and a time-averaged structure was observed. The 1:2:3:1:1:2 symmetry observed at 50 °C was as expected if the

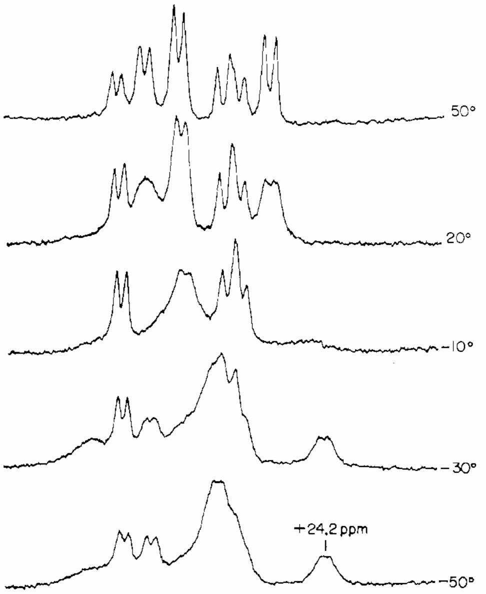

Figure 2. Temperature-dependent 80.5-MHz ^{11}B NMR spectrum of $4-(\eta^8-C_8H_8)-4-Ti-1,6-C_2B_{10}H_{12}$, XV, in acetone/tetrahydrofuran solution.

area 3 resonance was formed by coincidental overlap of an area 2 and an area 1 resonance. An estimate of the coalescence temperature (~260 K) resulted in an estimate of the free energy of activation $\Delta G^{\ddagger} \approx 11$ kcal/mol for the fluxional process. It is interesting that the ^{11}B NMR spectra of both complex I and $4-(\eta^5-C_5H_5)-4-Co-1,6-C_2B_{10}H_{12}$ were essentially unchanged above −50 °C; the fluxionality of the cobaltacarborane was shown[8] by ^{11}B NMR to stop only below −90 °C.

The cyclic voltammogram of XV showed a reversible reduction at $E_{p/2} = -0.55$ V corresponding to the process $Ti(IV) + e^- \rightarrow Ti(III)$.

Polyhedral rearrangements in 13-vertex metallocarborane complexes have been shown to be among the most facile yet discovered.[21] It was shown that $4-(\eta^5-C_5H_5)-4-Co-1,6-C_2B_{10}H_{12}$ rearranged to the thermally most stable isomer, with carbon atoms at the 1,12 positions, in 24 h at 80 °C in solution.[8] The rearrangements of the 13-vertex zirconium and hafnium complexes were shown to be even more facile, requiring only a few hours in solution at 75 °C. Attempted rearrangements of XV in acetone/benzene solution at 62 °C for 80 h and in toluene solution at 110 °C for 24 h resulted only in a high-yield recovery of unchanged starting material. Sublimation of XV under vacuum at 220 °C through a hot zone heated to 500 °C gave only pure meta carborane, $1,7-C_2B_{10}H_{12}$, condensed on the cold finger. Subsequently, it was found that when heated above the melting point to 250 °C under vacuum, complex XV decomposed to produce a high yield (>95%) of $1,7-C_2B_{10}H_{12}$. This conversion is shown in Figure 3 and represents a much lower energy pathway from ortho to meta carborane. The direct expulsion of meta carborane from the metallic complex was confirmed by the experiment at 250 °C, as this temperature was far too low to cause rearrangement of $1,2-C_2B_{10}H_{12}$ to $1,7-C_2B_{10}H_{12}$.

Metallocarborane XV is a formal d^0 16-valence-electron titanium(IV) complex—thus, it can be viewed as a two-electron-deficient metallocarborane. The lack of polyhedral rearrangement for this complex is surprising in view of the polyhedral rearrangements observed in the four-electron-deficient zircona- and hafnacarboranes. As these results define an extension of the electron-counting rules[1] which predict relative polyhedral stability and capacity for rearrangement, it may be tentatively postulated that within the group 4

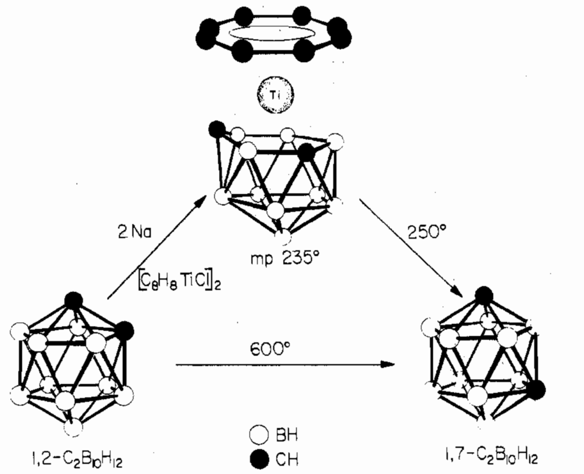

Figure 3. Comparison of two modes of conversion of $1,2-C_2B_{10}H_{12}$ to $1,7-C_2B_{10}H_{12}$.

metallocarboranes, the four-electron-deficient complexes may undergo polyhedral rearrangement while the two-electron-deficient complexes may not.

These data imply that complexes of the formula $C_8H_8TiC_2B_nH_{n+2}$ will not undergo polyhedral rearrangement, as also found for the $C_5H_5FeC_2B_nH_{n+2}$ complexes, and could prove interesting candidates for isolation of metallocarboranes with unusual heteroatom positions.[26] Coupling this possibility with the carborane expulsion reaction, these titanacarboranes could serve as templates for the isolation of new isomers of the carboranes.

The reaction of $(C_8H_8TiCl)_2$ with $Na_2C_2B_9H_{11}$, prepared by reaction of sodium hydride with $1,2-C_2B_9H_{12}^-$, produced an air-sensitive green solution from which yellow-green paramagnetic crystals of $[(C_2H_5)_4N][3-(\eta^8-C_8H_8)-3-Ti-1,2-C_2B_9H_{11}]$, XVI, could be isolated. This formal titanium(III) complex was very air sensitive in solution and as a solid and decomposed within a few seconds upon exposure to air.

The infrared spectrum of XVI showed the characteristic absorptions of $(C_2H_5)_4N^+$, $\eta^8-C_8H_8^{2-}$, and $\eta^5-1,2-C_2B_9H_{11}^{2-}$ (Table III). The 80.5-MHz ^{11}B NMR spectrum (in CD_3CN) showed one resonance at +30.3 ppm, relative to $Et_2O\cdot BF_3$, as found for the other early transition metal paramagnetic metallocarboranes.

Cyclic voltammetry of XVI showed a reversible one-electron oxidation at $E_{p/2} = -0.91$ V. Complex XVI could be oxidized in a similar manner as for $[C_8H_8TiC_2B_{10}H_{12}]^-$, to yield the neutral, air-stable titanium(IV) complex $3-(\eta^8-C_8H_8)-3-Ti-1,2-C_2B_9H_{11}$, XVII. Green-brown, crystalline XVII exhibited a mass spectrum with a cutoff at m/e 286 corresponding to the $^{12}C_{10}{}^1H_{19}{}^{11}B_9{}^{48}Ti^+$ ion. The infrared spectrum showed characteristic bands attributable to the $\eta^8-C_8H_8$ and $\eta^5-1,2-C_2B_9H_{11}$ ligands. The cyclic voltammogram exhibited a reversible reduction at $E_{p/2} = -0.87$ V corresponding to the process $Ti(IV) + e^- \rightarrow Ti(III)$.

The 60-MHz ^1H NMR spectrum of diamagnetic XVII (Table I) showed a sharp single resonance at τ 2.28 (C_8H_8) and a broad resonance at τ 6.72 (carborane C–H) of relative areas 4:1, respectively. The 80.5-MHz ^{11}B NMR spectrum (Table II) contained resonances of area 1:2:2:2:2 at −8.9, +5.1, +5.9, +15.8, and +17.4 ppm. These data are consistent with a proposed structure for XVII as shown in Figure 4. This basic structure is also proposed for the titanium(III) anion in complex XVI and is qualitatively similar to the crystallographically determined structure[24] of $C_8H_8TiC_5H_5$.

The isomeric complexes $[(C_2H_5)_4N][2-(\eta^8-C_8H_8)-2-Ti-1,7-C_2B_9H_{11}]$, XVIII, and $2-(\eta^8-C_8H_8)-2-Ti-1,7-C_2B_9H_{11}$, XIX, were prepared in a similar manner from $1,7-C_2B_9H_{12}^-$ and $(C_8H_8TiCl)_2$. The characterization data for these icosahedral titanacarboranes are given in Tables I–IV. Yellow-green paramagnetic crystals of XVIII were very air sensitive and exhibited a reversible oxidation in the cyclic voltammogram at $E_{p/2} = -0.91$ V. The 80.5-MHz ^{11}B NMR showed one peak (width at half-height 600 Hz) at +54.7 ppm, relative to $Et_2O\cdot BF_3$. Complex XVIII was easily oxidized to yield air-stable, dark red crystals of XIX. The mass and NMR spectra of XIX were similar to those of the isomeric complex, XVII. The infrared spectrum of XIX was simple and contained four peaks (those at 1165, 1060, 1015, and 988 cm^{-1}) similar in position and relative intensities to four peaks found in the infrared spectrum of $1,7-C_2B_{10}H_{12}$.

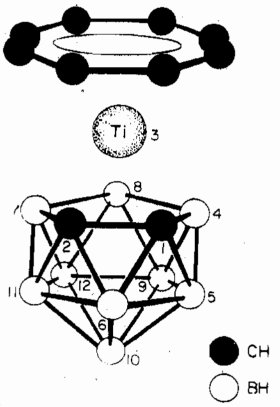

Figure 4. Proposed structure of $3-(\eta^8-C_8H_8)-3-Ti-1,2-C_2B_9H_{11}$, XVII.

The neutral isomeric titanacarboranes of formula $C_8H_8TiC_2B_9H_{11}$, XVII and XIX, were completely air-stable and did not melt or decompose upon heating to 300 °C in the presence of air. In these respects they are similar in stability to the related diamagnetic, green titanium complex containing cyclooctatraene and cyclobutadiene ligands, $(\eta^8-C_8H_8)Ti(\eta^4-C_4(C_6H_5)_4)$.[27] These complexes are among the few air-stable early transition metal species containing the cyclooctatetraene ligand. Complexes XIV–XIX represent the first metallocarboranes containing the C_8H_8 ligand; therefore it is pertinent to note the high stability of the neutral titanium(IV) complexes and the observation that they may be purified without decomposition by liquid chromatography on silica.

The mass spectra of the neutral titanacarboranes $C_8H_8TiC_2B_nH_{n+2}$ (n = 9 and 10) were also in agreement with the formulation of η^8-bonded C_8H_8 ligands.[27] The peak of highest intensity occurred at m/e 152 corresponding to $C_8H_8Ti^+$. The mass spectra also showed large peaks at m/e 126 ($C_6H_6Ti^+$) and m/e 113 ($C_5H_5Ti^+$)—these are characteristic of the previously observed[27] degradation pattern of the $C_8H_8Ti^+$ ion in the mass spectrometer.

The demonstrated ability of formal titanium(II), -(III), and -(IV) to stabilize metallocarboranes containing a variety of organic ligands is certainly encouraging in terms of the further development of this unique area of organometallic chemistry. For example, the preparation of complexes of formula $[(\eta^x-C_xH_x)TiC_2B_nH_{n+2}]^{m-}$, where $x = 6$ ($m = 0$) and $x = 7$ ($m = 1$), now seems possible. The stability of these titanacarboranes may be accounted for by viewing the titanium atom as an electron-deficient heteroatom similar to boron. For example, in complex XVII the titanium atom may be considered to contribute two electrons to the cyclooctatetrane ligand, thus accounting for the latter's planar aromatic character. Formally, two titanium valence electrons would remain to be contributed to the carborane framework, just as the {BH} vertex contributes two electrons to polyhedral bonding. Thus $\{\eta^8-C_8H_8Ti\}$ is electronically analogous to {BH}

Table VI. Comparison of Electrochemical Data for Homologous Metallocarboranes

Complex	$E_{p/2}$, V, vs. SCE[a]
$3,1,2\text{-}C_8H_8TiC_2B_9H_{11}$	−0.87
$2,1,7\text{-}C_8H_8TiC_2B_9H_{11}$	−0.87
$4,1,6\text{-}C_8H_8TiC_2B_{10}H_{12}$	−0.55
$3,1,2\text{-}C_5H_5CoC_2B_9H_{11}$	−1.22
$2,1,7\text{-}C_5H_5CoC_2B_9H_{11}$	−1.03
$4,1,6\text{-}C_5H_5CoC_2B_{10}H_{12}$	−0.72
$3,1,2\text{-}C_5H_5FeC_2B_9H_{11}$	−0.08
$4,1,6\text{-}C_5H_5FeC_2B_{10}H_{12}$	+0.16
$[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$	−1.46
$[2,2'\text{-}Co(1,7\text{-}C_2B_9H_{11})_2]^-$	−1.17
$[4,4'\text{-}Co(1,6\text{-}C_2B_{10}H_{12})_2]^-$	−0.33

[a] Potentials given correspond to reversible one-electron reductions; the potentials of the iron and cobalt complexes are from ref 8, 34, and 35.

and would be expected to replace {BH} in a polyhedral environment with retention of chemical stability. In this regard, it has previously been shown[28,29] that $\{C_5H_5Co\}$ and $\{C_5H_5Ni\}$ are analogous to {BH} and {CH}, respectively. Though this field is still relatively unexplored, the work reported here establishes a firm foundation for further work, with an indication of which formal oxidation states and electronic conditions may be required for the isolation of stable early transition metal–carborane complexes.

Comparisons between Carborane Ligands. These results lead to some interesting conclusions regarding the differences between the $\eta^5\text{-}C_2B_9H_{11}^{2-}$ and $\eta^6\text{-}C_2B_{10}H_{12}^{2-}$ carborane ligands. Table VI lists typical electrochemical data for various B_9–B_{10} homologous metallocarboranes. As can be seen, the isolated air-stable $C_2B_{10}H_{12}$ complexes show consistently lower reduction potentials (which are primarily metal in character[17]) than the $C_2B_9H_{11}$ complexes. Thus the B_{10} complexes are easier to reduce and this implies that the $\eta^6\text{-}C_2B_{10}H_{12}$ carborane ligand may donate less overall electron density to the metal center than does the $\eta^5\text{-}C_2B_9H_{11}$ ligand. This seems reasonable in view of the larger bonding face of the $\eta^6\text{-}C_2B_{10}H_{12}$ ligand, which contains six electrons delocalized in the open face among six hybridized ~sp^3 orbitals. This constitutes a more diffuse electronic environment than exists in the $\eta^5\text{-}C_2B_9H_{11}$ ligand, which contains six electrons delocalized over the smaller five-membered bonding face containing five hybridized ~sp^3 orbitals.

The marked difference between the two carborane ligands is exemplified even more convincingly by the chemical evidence concerning the homologous chromium complexes of these carborane ligands. It was found that the $C_2B_{10}H_{12}$ ligand could stabilize both chromium(II) and chromium(III) complexes of formula $[Cr(C_2B_{10}H_{12})_2]^{m-}$ while the $C_2B_9H_{11}$ ligand could only stabilize chromium(III). In addition, geometric variation among carborane ligands may be an important factor in determining relative electronic environments. The knowledge of differences such as these between carborane ligands considerably improves the ability to systematically synthesize metallocarboranes with varying electronic properties, stabilities, and chemical reactivities.

Experimental Section

Physical Measurements. The 80.5-MHz ^{11}B NMR spectra were obtained with an instrument designed by Professor F. A. L. Anet of this department. The ^1H NMR spectra were measured with Varian A-60D or HA-100 spectrometers. The electrochemical apparatus for cyclic voltammetry has been described previously.[30] Ultraviolet–visible–near-infrared spectra were measured with a Cary 14 spectrophotometer. Infrared spectra were determined using a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Mass spectra were measured using an Associated Electrical Industries MS-9 spectrometer.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Melting points were determined in sealed capillaries under nitrogen, and NMR samples of air-sensitive compounds were prepared on the vacuum line, whereby dry, degassed solvents were condensed into an NMR tube containing the solid sample followed by sealing off under high vacuum.

Materials. The literature method[31] was used to prepare the blue complex $C_5H_5TiCl_2\cdot THF$, which upon heating under vacuum[31] gave purple $(C_5H_5TiCl_2)_n$. The titanium(III) complex $[C_8H_8TiCl(THF)]_2$ was prepared by reaction of $TiCl_3$ with $Na_2C_8H_8$ in tetrahydrofuran.[32] This reaction yielded green crystals precipitating from THF solution after 1–2 h at 50 °C; the solid was not isolated but used in solution for subsequent reactions. Cyclooctatetraene was obtained from Aldrich Chemical Co. Zinc dust, obtained from Mallinckrodt, was washed with dilute HCl and water, vacuum-dried, and stored under nitrogen. The metal halides MCl_4 (M = Ti, Zr, Hf), MCl_3 (M = Ti, V, Cr), $MnBr_2$, and $C_5H_5TiCl_3$ were obtained from Alfa-Ventron Corp. and stored under nitrogen. Literature methods[33] were used to prepare the trimethylammonium salts of 1,2- and $1,7\text{-}C_2B_9H_{12}^-$. The tetraalkylammonium halides and spectral quality acetonitrile were obtained from Matheson Coleman and Bell. Sodium metal was purchased from Allied Chemical Co. Sodium hydride, as a 50% dispersion in mineral oil, was obtained from ROC/RIC Chemical Corp. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride and stored under nitrogen prior to use. Acetone was pretreated with Drierite; ethanol solutions of tetraalkylammonium halides were dried by treatment with Linde 3A Molecular Sieves.

All reactions and manipulations were performed under an atmosphere of purified argon, unless otherwise specified.

Synthesis of $[(C_2H_5)_4N]_2[Ti(C_2B_{10}H_{12})_2]$, I, from $TiCl_4$. Into a 250-ml, three-necked, round-bottom flask equipped with an argon inlet and mechanical stirrer were placed 3.024 g of $1,2\text{-}C_2B_{10}H_{12}$ (21 mmol), 100 ml of THF, and 0.97 g of Na metal (42 mmol). The solution was stirred until the sodium was consumed (about 3–5 h). The clear solution of $Na_2C_2B_{10}H_{12}$ was cooled to 0 °C and 0.77 ml of $TiCl_4$ (7 mmol) was added dropwise with a syringe. The solution was stirred 1 h at 0 °C and then filtered through Celite, and the solvent was removed under vacuum. Addition of a degassed ethanol solution of $(C_2H_5)_4NBr$ caused precipitation of a red-orange crystalline compound. This was filtered and washed with ethanol and ether. The infrared spectrum was identical with that of the recrystallized product, obtained by dissolution of the solid in dry, degassed acetone, addition of ethanol, and slow rotary evaporation of the solvent under reduced pressure, 10^{-3} mm. The yield of recrystallized product was 3.15 g (75% based on Ti) of red-orange needles of I, mp 238–239 °C dec. Anal. Calcd for $C_{20}H_{64}B_{20}N_2Ti$: C, 40.25; H, 10.81; B, 36.22; N, 4.69; Ti, 8.03. Found: C, 40.38; H, 10.94; B, 36.07; N, 4.77; Ti, 8.21. From the combined filtrates was obtained 0.86 g (5.96 mmol) of recovered $1,2\text{-}C_2B_{10}H_{12}$, by removal of solvent and sublimation at 100 °C under vacuum. Complex I is moderately soluble in CH_2Cl_2 and very soluble in acetone and CH_3CN.

Synthesis of I from $TiCl_3$. The reaction was performed as above, with 1.44 g (10 mmol) of $1,2\text{-}C_2B_{10}H_{12}$ and 0.77 g (5 mmol) of $TiCl_3$ used. The $TiCl_3$ was added to the reaction solution as a THF slurry and the mixture was stirred 3 h. Workup as above gave 2.15 g of recrystallized I (90% based on $C_2B_{10}H_{12}$).

$[(C_2H_5)_4N]_2[Ti(C_2(CH_3)_2B_{10}H_{10})_2]\cdot(CH_3)_2CO$, II. This complex was synthesized as above from $1,2\text{-}C_2(CH_3)_2B_{10}H_{10}$ (1.72 g, 10 mmol) and $TiCl_4$ (0.55 ml, 5 mmol). The yield was 1.25 g (53% based on carborane) of red crystals of II, mp 272 °C. Anal. Calcd for $C_{27}H_{78}B_{20}N_2OTi$: C, 45.61; H, 11.06; B, 30.41; N, 3.94; Ti, 6.74. Found: C, 45.65; H, 11.20; B, 30.45; N, 3.78; Ti, 6.94. The tetramethylammonium salt could be isolated by addition of $(CH_3)_4NCl$ in place of $(C_2H_5)_4NBr$.

$[(C_2H_5)_4N]_2[V(C_2B_{10}H_{12})_2]$, III. This metallocarborane was synthesized from $Na_2C_2B_{10}H_{12}$ and VCl_3 in THF solution at reflux for 3 h. The complex was isolated as described above. Use of 18 mmol of $1,2\text{-}C_2B_{10}H_{12}$ and 6 mmol of VCl_3 gave 2.37 g (66% based on V) of red-brown crystals of III, mp 260 °C. Anal. Calcd for $C_{20}H_{64}B_{20}N_2V$: C, 40.04; H, 10.75; B, 36.04; V, 8.49. Found: C, 39.48; H, 11.07; B, 35.52; V, 8.09.

$[(C_2H_5)_4N]_2[V(C_2(CH_3)_2B_{10}H_{10})_2]\cdot(CH_3)_2CO$, IV. Synthesized as above from 12 mmol of $1,2\text{-}C_2(CH_3)_2B_{10}H_{10}$ and 4 mmol of VCl_3 was 1.22 g (43% based on V) of dark red-brown crystals of IV, mp 261–262 °C. Anal. Calcd for $C_{27}H_{78}B_{20}N_2OV$: C, 45.42; H, 11.01;

B, 30.28; N, 3.92; V, 7.13. Found: C, 45.35; H, 11.30; B, 30.16; N, 4.16; V, 7.48.

$[(C_2H_5)_4N]_2[Cr(C_2B_{10}H_{12})_2]$, V. Complex V was prepared in the same manner as the vanadacarboranes except that the reaction mixture was refluxed 16 h; 15 mmol of 1,2-$C_2B_{10}H_{12}$ and 6 mmol of $CrCl_3$ yielded 2.65 g (73%) of orange-brown crystals of V, mp 246–247 °C. Anal. Calcd for $C_{20}H_{64}B_{20}N_2Cr$: C, 39.97; H, 10.73; B, 35.98; N, 4.66; Cr, 8.65. Found: C, 39.89; H, 10.65; B, 36.03; N, 4.50; Cr, 8.57.

$[(C_2H_5)_4N][Cr(C_2B_{10}H_{12})_2]$, VI. Complex V (160 mg) was dispersed in 20 ml of ethanol and 5 ml of 10% aqueous $AgNO_3$ solution was added, with stirring. The solution immediately deposited silver metal while turning a red color. It was stirred 20 min and filtered. Addition of a small amount of water to the solution, followed by slow rotary evaporation, produced 100 mg of red crystals of slightly impure VI. Recrystallization from hot acetone/ethanol/water with slow cooling to −20 °C yielded 25 mg of pure red-purple crystals of VI, soluble in acetone, ethanol, and CH_3CN. Anal. Calcd for $C_{12}H_{44}B_{20}NCr$: C, 30.62; H, 9.42; B, 45.94. Found: C, 30.56; H, 8.88; B, 45.76.

$[(C_2H_5)_4N]_2[Mn(C_2B_{10}H_{12})_2]$, VII. This metallocarborane was synthesized from $Na_2C_2B_{10}H_{12}$ (20 mmol) and $MnBr_2$ (2.15 g, 10 mmol) in THF solution; the mixture was stirred 5 h at room temperature and worked up as above. The yield was 3.25 g (54%) of green-brown crystals of VII, mp 235–236 °C. Anal. Calcd for $C_{20}H_{64}B_{20}N_2Mn$: C, 39.78; H, 10.68; B, 35.80; Mn, 9.10. Found: C, 39.79; H, 10.90; B, 35.23; Mn, 9.34.

$[(C_2H_5)_4N]_2[Zr(C_2(CH_3)_2B_{10}H_{10})_2]$, VIII. This zirconacarborane was prepared from 1,2-$C_2(CH_3)_2B_{10}H_{10}$ (2.064 g, 12 mmol) and $ZrCl_4$ (0.93 g, 4 mmol) in THF in a similar manner as for the titanium analogues. The reaction mixture was stirred 1 h at 25 °C and worked up as above, yielding 2.0 g (72%) of purple crystalline solid from the initial precipitation from ethanol solution. This solid was >99% pure by NMR spectroscopy. It could be recrystallized from degassed, dry CH_2Cl_2/THF in small quantities—typically 200 mg required 150–200 ml of CH_2Cl_2 for dissolution and gave 85 mg of pure product, mp 257–258 °C. The complex initially dissolved and then rapidly turned colorless in acetone; thus it could not be recrystallized using this solvent. Anal. Calcd for $C_{24}H_{72}B_{20}N_2Zr$: C, 41.40; H, 10.42; B, 31.05; N, 4.02; Zr, 13.10. Found: C, 41.70; H, 10.60; B, 30.73; N, 4.05; Zr, 12.92. Storage at −20 °C was required due to facile polyhedral rearrangement.

$[(C_2H_5)_4N]_2[Hf(C_2(CH_3)_2B_{10}H_{10})_2]\cdot C_4H_8O$, X. This complex was synthesized and purified in a manner identical with that for the zirconium complex. Thus, 10 mmol of 1,2-$C_2(CH_3)_2B_{10}H_{10}$ and 3 mmol of $HfCl_4$ (95% Hf, ≤4% Zr) yielded 1.9 g (81%) of green crystalline solid upon initial precipitation from ethanol. Dark green crystals of pure X, mp 198–200 °C, required storage at −20 °C due to facile polyhedral rearrangement. Anal. Calcd for $C_{28}H_{80}B_{20}N_2OHf$: C, 38.84; H, 9.39; B, 25.70; N, 3.33; Hf, 21.2. Found: C, 39.09; H, 9.60; B, 25.84; N, 3.56; Hf, 22.2.

$[(C_2H_5)_4N][C_5H_5TiC_2B_{10}H_{12}]$, XII. Complex XII was prepared from $Na_2C_2B_{10}H_{12}$ and $C_5H_5TiCl_x$ (x = 2 or 3) in THF solution at room temperature. In a typical preparation, 1,2-$C_2B_{10}H_{12}$ (0.576 g, 4 mmol) was reduced with sodium in THF; then was added a THF slurry of ~4 mmol of $C_5H_5TiCl_2\cdot$THF or $(C_5H_5TiCl_2)_n$, followed by ~1.0 g of zinc dust. The mixture was stirred 5 h and worked up similarly to the other titanacarboranes. The product could be recrystallized from CH_2Cl_2/benzene or acetone/ethanol to give 750 mg (48%) of red crystals of XII, mp >300 °C. Anal. Calcd for $C_{15}H_{37}B_{10}NTi$: C, 46.50; H, 9.63; B, 27.90; N, 3.61; Ti, 12.36. Found: C, 46.26; H, 9.65; B, 27.94; N, 3.88; Ti, 12.26.

$[(C_2H_5)_4N][C_5H_5TiC_2(CH_3)_2B_{10}H_{10}]$, XIII. Synthesized as above from 1,2-$C_2(CH_3)_2B_{10}H_{10}$ (1.38 g, 8 mmol) and $C_5H_5TiCl_2\cdot$THF (2.1 g, 8 mmol) was 1.50 g (45%) of dark red crystals of XIII, mp 287–288°. Anal. Calcd for $C_{17}H_{41}B_{10}NTi$: C, 49.14; H, 9.95; B, 26.02; N, 3.37; Ti, 11.53. Found: C, 49.34; H, 10.12; B, 25.87; N, 3.51; Ti, 11.30.

$[(C_2H_5)_4N][C_8H_8TiC_2B_{10}H_{12}]$, XIV. Into a three-necked, 250-ml, round-bottom flask was placed 75 ml of THF, 0.9 ml of C_8H_8 (8 mmol), and ~0.38 g of Na (16 mmol). The solution was stirred 24 h at 25 °C yielding a colorless to yellow solution containing a white crystalline precipitate, presumably $Na_2C_8H_8$. Then was added $TiCl_3$ (1.24 g, 8 mmol) as a THF slurry, and the solution was heated to 50 °C for 2 h. At the end of this time, bright green crystals of $[C_8H_8TiCl(THF)]_2$ were visible in the flask. To this solution was added a THF solution of 8 mmol of previously prepared $Na_2C_2B_{10}H_{12}$. The combined solutions were stirred 2 h at 25 °C and worked up as were the other titanacarboranes; 2.3 g (67%) of pure, recrystallized product was obtained as orange-brown crystals, mp 249–251 °C dec. Anal. Calcd for $C_{18}H_{42}B_{10}NTi$: C, 50.45; H, 9.88; B, 25.23; Ti, 11.18. Found: C, 50.62; H, 9.48; B, 25.19; Ti, 11.13.

$C_8H_8TiC_2B_{10}H_{12}$, XV. Into a 100-ml, three-necked flask was placed 200 mg of complex XIV and ~8 ml of acetone. With stirring, 12 ml of 6% aqueous H_2O_2 was added slowly. A green crystalline precipitate formed, which was exposed to the air, filtered, and washed with water, cold ethanol, and hexane. Recrystallization from CH_2Cl_2/hexane gave 135 mg (96%) of dark green crystals of XV, mp 235 °C. Anal. Calcd for ${}^{12}C_{10}{}^{1}H_{20}{}^{11}B_{10}{}^{48}Ti^+$: 298.1975. Found: 298.1973. Complex XV was soluble in acetone, THF, and $(CH_3)_2SO$ and moderately soluble in CH_2Cl_2, CH_3CN, and benzene.

Titanacarboranes of Formula $[(C_2H_5)_4N][C_8H_8TiC_2B_9H_{11}]$, XVI and XVIII. These complexes were synthesized analogously to complex XIV. The THF solution of $Na_2C_2B_9H_{11}$ was prepared by reaction of excess NaH with the appropriate $[(CH_3)_3NH][C_2B_9H_{12}]$ isomer, followed by filtration. Thus, a 4-mmol scale reaction yielded 1.1 g (66%) of pale yellow-green crystals of XVI, mp 158–159 °C, and 1.0 g (60%) of pale yellow-green needles of XVIII, mp 212–215 °C. Anal. Calcd for $C_{18}H_{39}B_9NTi$: C, 52.13; H, 9.48; B, 23.46; Ti, 11.55. Found for XVI: C, 50.51; H, 9.48; B, 23.49; Ti, 11.48. Found for XVIII: C, 52.34; H, 9.61; B, 23.16; Ti, 11.44.

Titanacarboranes of Formula $C_8H_8TiC_2B_9H_{11}$, XVII and XIX. These were synthesized from XVI and XVIII by treatment with H_2O_2 and excess water as described for the analogous $C_8H_8TiC_2B_{10}H_{12}$ complex. Typically, 250 mg of XVI produced 120 mg (70%) of green-brown crystals of XVII, mp >300 °C. Anal. Calcd for ${}^{12}C_{10}{}^{1}H_{19}{}^{11}B_9{}^{50}Ti^+$: 288.1772. Found: 288.1777. Complex XVIII (190 mg) was oxidized giving 130 mg (68%) of dark red crystals of XIX, mp >300 °C. Anal. Calcd for ${}^{12}C_{10}{}^{1}H_{19}{}^{11}B_9{}^{50}Ti^+$: 288.1772. Found: 288.1777.

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Registry No. I, 55266-90-5; II, 60270-23-7; III, 55266-94-9; IV, 60294-82-8; V, 60270-25-9; VI, 60270-16-8; VII, 60270-18-0; VIII, 56089-61-3; IX, 60270-20-4; X, 60270-22-6; XI, 60270-30-6; XII, 59061-46-0; XIII, 60270-13-5; XIV, 60270-14-6; XV, 59049-21-7; XVI, 59049-24-0; XVII, 59041-10-0; XVIII, 60270-27-1; XIX, 60270-28-2; 1,2-$C_2B_{10}H_{12}$, 16872-09-6; $TiCl_4$, 7550-45-0; $TiCl_3$, 7705-07-9; 1,2-$C_2(CH_3)_2B_{10}H_{10}$, 17032-21-2; VCl_3, 7718-98-1; $CrCl_3$, 10025-73-7; $MnBr_2$, 13446-03-2; $ZrCl_4$, 10026-11-6; $HfCl_4$, 13499-05-3; $(C_5H_5TiCl_2)_n$, 35398-20-0; $C_5H_5TiCl_2\cdot$THF, 35398-24-4; $[(CH_3)_3NH][1,2\text{-}C_2B_9H_{12}]$, 54531-56-5; $[(CH_3)_3NH][1,7\text{-}C_2B_9H_{12}]$, 54531-56-5; ${}^{11}B$, 14798-13-1.

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Temperature-Jump Studies on the Equilibration of Thiocyanate and Pyridine with the Di-μ-oxo-bis[aquooxalatooxomolybdenum(V)] Complex. Substitution Cis to a Terminal Oxo Ligand

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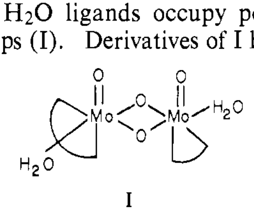
The rapid 1:1 equilibrations of thiocyanate and pyridine with the title complex, $Mo_2O_4(C_2O_4)_2^{2-}$ (I), have been studied by the temperature-jump technique over a range of temperatures 10–32 °C, I = 1.00 M ($NaClO_4$). Replacement of an H_2O ligand cis to a terminal oxo group occurs in both cases. Rate constants k_f for complex formation ($M^{-1}\ s^{-1}$) and activation parameters $\Delta H^{\ddagger}$ (kcal mol^{-1}) and $\Delta S^{\ddagger}$ (cal $K^{-1}\ mol^{-1}$) at 25 °C are respectively 0.50×10^4, 11.2, −4.2 (NCS^-) and 0.30×10^4, 10.8, −6.5 (py). These values are consistent with a dissociative S_N1 nonlimiting (or I_d) mechanism for substitution. Comparisons are made with other studies of complexes having terminal oxo ligands, and features of reactions involving substitution at positions cis and trans to oxo ligands are discussed.

The kinetics of equilibration of NCS^- with the molybdenum(V)–aquo dimer $Mo_2O_4^{2+}$, have been studied previously.[1] On the basis of comparisons with data for reactions of VO^{2+} it was suggested that replacement of an H_2O cis (rather than trans) to one of the terminal oxo ligands is involved. Cotton and Morehouse[2] have carried out an x-ray crystallographic study of the barium salt of the di-μ-oxo-bis[aquooxalatomolybdenum(V)] complex, $Mo_2O_4(C_2O_4)_2^{2-}$,[3] and demonstrated that the H_2O ligands occupy positions cis to the terminal oxo groups (I). Derivatives of I have been prepared by Mitchell.[4] With a view to further clarifying mechanistic assignments for substitution at Mo(V) it seemed desirable to extend the earlier work to a consideration of substitution processes at the cis H_2O sites of I.



I

Experimental Section

Reactants. The Mo(V) oxidation state was generated by reduction of sodium molybdate (8.2 g) in 10 M HCl (180 ml) with hydrazine hydrochloride (6.6 g) at 80 °C for 2–3 h. The solution was concentrated ca. fourfold using a rotary evaporator. Aliquots of this green-brown solution (as required) were diluted ca. 100-fold by addition of oxygen-free water to give a final [H^+] of ca. 0.1 M. Under these conditions the Cl^- is aquated and the aquo dimer $Mo_2O_4^{2+}$ is formed. The solution was passed down a column of Dowex 50W-X8 ion-exchange resin using air-free conditions, and after being washed free of Cl^-, the $Mo_2O_4^{2+}$ eluted with 1 M $HClO_4$. Stock solutions obtained were standardized spectrophotometrically, $Mo_2O_4^{2+}$ peak at 384 nm (ϵ 103 $M^{-1}\ cm^{-1}$), and stored under N_2.

Sodium thiocyanate (Hopkin and Williams, GPR) was recrystallized from water and standardized by titration with Hg(II). All other reagents used were of Analar grade purity. Ionic strengths were adjusted to I = 1.00 M using $NaClO_4$.

The oxalato complex, $Mo_2O_4(C_2O_4)_2^{2-}$, was prepared freshly each day in situ by addition of a 5% excess of oxalic acid (BDH, Analar) to $Mo_2O_4^{2+}$ (ca. 10^{-3} M) and adjusting the pH to the range 3–4.5. From spectrophotometric measurements at λ 384 nm, [H^+] = 0.5–2.0 M, it was estimated that for the conditions of our experiments $Mo_2O_4(C_2O_4)_2^{2-}$ was in excess of $Mo_2O_4^{2+}$ by ca. 10^5:1. Identical kinetic behavior was observed when the oxalate added was in 10% excess. There is no evidence for coordination of a third oxalate.[4] The oxalato complex has a broad peak at ca. 384 nm, ϵ 297 $M^{-1}\ cm^{-1}$. Above pH 5.5 the spectrum of $Mo_2O_4(C_2O_4)_2^{2-}$ is pH dependent with drastic changes occurring in the 350–450-nm region. Such changes are consistent with acid dissociation processes involving the aquo ligands of I. Precipitation occurs at pH >6.0 with [$Mo_2O_4(C_2O_4)_2^{2-}$] = 6×10^{-4} M. Care was taken not to exceed pH 5 in the preparation of all $Mo_2O_4(C_2O_4)_2^{2-}$ solutions. The reactants NCS^- and pyridine were added to $Mo_2O_4(C_2O_4)_2^{2-}$ as required, followed by the buffer in the case of the pyridine study. The pH was adjusted by addition of NaOH.

Although it was necessary to store all Mo(V) solutions in air-free conditions, rigorous air-free techniques were not necessary for ~20-min periods as required for each temperature-jump experiment.

Solutions for studies on the complexing of pyridine to $Mo_2O_4(C_2O_4)_2^{2-}$ required a higher range of pH and were buffered with 0.05–0.10 M acetate. At these concentrations of acetate there is no