Organotransition-Metal Metallacarboranes. 4.[1] Stable η^8-C$_8$H$_8$ and η^7-C$_7$H$_7$ Complexes of Titanium, Vanadium, and Chromium: Synthesis and Crystal Structures of (η^8-C$_8$H$_8$)M[(C$_2$H$_5$)$_2$C$_2$B$_4$H$_4$] (M = Ti, V) and (η^7-C$_7$H$_7$)Cr[(C$_2$H$_5$)$_2$C$_2$B$_4$H$_4$]

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The reactions of C$_8$H$_8^{2-}$ and (C$_2$H$_5$)$_2$C$_2$B$_4$H$_5^-$ ions with TiCl$_3$ and VCl$_3$ in THF gave as the major isolable products (η^8-C$_8$H$_8$)Ti[(C$_2$H$_5$)$_2$C$_2$B$_4$H$_4$] (1) and (η^8-C$_8$H$_8$)V[(C$_2$H$_5$)$_2$C$_2$B$_4$H$_4$] (2), respectively. In the corresponding reaction of CrCl$_3$, no cyclooctatetraene complex was isolated; however, (η^7-C$_7$H$_7$)Cr[(C$_2$H$_5$)$_2$C$_2$B$_4$H$_4$] (3) was obtained in low yield. Complexes 1–3 were characterized spectroscopically and via X-ray crystal structure determinations. All three structures consist of a closo seven-vertex pentagonal-bipyramidal MC$_2$B$_4$ metallacarborane cage with the metal coordinated to a planar η^8-C$_8$H$_8$ ligand in 1 and 2 and to a planar η^7-C$_7$H$_7$ ligand in 3. Complexes 1–3 are indefinitely air-stable in the solid state; 2 and 3 exhibit no sensitivity to oxygen even in solution. The titanium complex 1 reacts with CH$_3$I/AlCl$_3$ to give the 5-iodo derivative and with I$_2$ in benzene to give the 4,5-diiodo derivative. Magnetic susceptibility and ESR studies of the vanadium complex 2 support the assignment of V(IV), but the low-temperature ESR spectrum does not exhibit hyperfine structure attributable to vanadium–boron interaction. Crystal data: complex 1, M_r = 282, space group $Pna2_1$, Z = 4, a = 14.309 (3) Å, b = 12.660 (2) Å, c = 8.476 (2) Å, V = 1535 Å^3, R = 0.049 for 1902 reflections having $F_o^2 > 3\sigma(F_o^2)$; complex 2, M_r = 286, space group $Pna2_1$, Z = 4, a = 14.264 (5) Å, b = 12.595 (4) Å, c = 8.449 (2) Å, V = 1518 Å^3, R = 0.047 for 1271 reflections having $F_o^2 > 3\sigma(F_o^2)$; complex 3, M_r = 273, space group $Pna2_1$, Z = 4, a = 14.334 (3) Å, b = 12.230 (4) Å, c = 8.356 (1) Å, V = 1465 Å^3, R = 0.065 for 1289 reflections having $F_o^2 > 3\sigma(F_o^2)$.
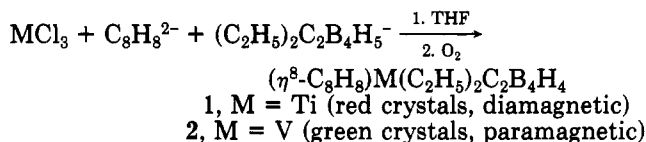
Introduction

Transition metals form exceptionally stable π-complexes with *nido*-carborane ligands, particularly those of the type R$_2$C$_2$B$_9$H$_9^{2-}$ and R$_2$C$_2$B$_4$H$_4^{2-}$ (R = H or alkyl), which present a planar-pentagonal face to which the metal is tightly bound.[2] Moreover, the dinegative charge on these carborane ligands induces relatively high formal oxidation states on the metal, ranging from +2 to +4 depending on the nature of the non-carborane ligands. These properties allow the synthesis and study of a wide variety of stable (carborane)metal(organoligand) complexes, including those in which the organic group is an arene[1b,c,3] or cyclic polyene.[1a,4] In particular, one might hope to stabilize otherwise reactive or nonexistent organic groups via coordination to metallacarborane moieties. The higher cyclic polyenes (C$_n$H$_n$ for n > 6) offer a special challenge, since few examples of structurally characterized complexes of first-row transition metals with planar C$_7$ or C$_8$ ligands exist, most of which contain Ti and are typically air- and moisture sensitive.[5]

In earlier papers in this series we reported[1b] the synthesis of a cyclooctatriene–iron complex, (η^6-C$_8$H$_{10}$)Fe[2,3-(CH$_3$)$_2$C$_2$B$_4$H$_4$] and its facile conversion, via ligand exchange, to several (arene)Fe[(CH$_3$)$_2$C$_2$B$_4$H$_4$] species whose structures were determined by X-ray crystallography.[1c] The present paper describes the synthesis and structural characterization of two *air-stable* early transition metal complexes containing the formal C$_8$H$_8^{2-}$ ligand (a planar 10π-electron aromatic system) and a third, fortuitously obtained species containing planar C$_7$H$_7^+$. A preliminary report on the vanadium complex (η^8-C$_8$H$_8$)V[(C$_2$H$_5$)$_2$C$_2$B$_4$H$_4$] appeared in an earlier paper.[1a]

Results

Reactions of TiCl$_3$, VCl$_3$, and CrCl$_3$·3THF with K$_2$C$_8$H$_8$ and Na$^+$[(C$_2$H$_5$)$_2$C$_2$B$_4$H$_5$]$^-$. In order to minimize the formation of bis(carborane)metal complexes and promote that of mixed-ligand (C$_8$H$_8$)M(carborane) species, conditions similar to those employed in the preparation of (η^6-C$_8$H$_{10}$)Fe[(C$_2$H$_5$)$_2$C$_2$B$_4$H$_4$][1b] were maintained. Accordingly, approximately equimolar quantities of the respective metal trihalide, K$_2$C$_8$H$_8$, and Na$^+$[(C$_2$H$_5$)$_2$C$_2$B$_4$H$_5$]$^-$ were mixed in cold tetrahydrofuran (THF) and slowly warmed to room temperature. Separation of the products on silica gel in air gave, in the titanium and vanadium reactions, the desired cyclooctatetraene metallacarborane as the major isolated complex.

$$\text{MCl}_3 + \text{C}_8\text{H}_8^{2-} + (\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_4\text{H}_5^- \xrightarrow[\text{2. O}_2]{\text{1. THF}}$$

$$(\eta^8\text{-C}_8\text{H}_8)\text{M}(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_4\text{H}_4$$

1, M = Ti (red crystals, diamagnetic)
2, M = V (green crystals, paramagnetic)

Compounds 1 and 2 are stable toward degradation by air and moisture in both the solid state and solution and were structurally characterized via spectroscopic techniques and X-ray diffraction studies as described below. The corresponding reaction of CrCl$_3$ did not yield an isolable cyclooctatetraenyl complex, giving instead thermally unstable solids that could not be characterized. However, a yellow-green paramagnetic product was isolated in very small quantity and characterized from its IR

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(5) (a) (η^8-C$_8$H$_8$)Ti(η^4-C$_8$H$_8$): Dietrich, H.; Soltwisch, M. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 765. (b) [(η^8-C$_8$H$_8$)Ti]$_2$(η^4,η^4-C$_8$H$_8$): Dietrich, H.; Dierks, H. *Ibid.* **1966**, *5*, 898. (c) (η^8-C$_8$H$_8$)Ti(η^5-C$_5$H$_5$): Kroon, P. A.; Helmholdt, R. B. *J. Organomet. Chem.* **1970**, *25*, 451. (d) [(η^8-C$_8$H$_8$)TiC$_2$(C$_6$H$_5$)(CH$_3$)]$_2$: Veldman, M. E. E.; van der Waal, H. R.; Veenstra, S. J.; de Liefde, H. J. *Ibid.* **1980**, *197*, 59.

Table I. 115.5-MHz ^{11}B FT NMR Data

compound	δ (J, Hz)^a	rel area
$(C_8H_8)Ti[(C_2H_5)_2C_2B_4H_4]$ (1)	22.12 (125), B(4,6) 16.16 (139), B(3) −21.97 (159) B(1)	1, 2, 1
$(C_8H_8)Ti[(C_2H_5)_2C_2B_4H_3-5-I]$ (1A)	17.66 (124), 9.36,^{b} −21.27 (167)	2, 1, 1
$(C_8H_8)Ti[(C_2H_5)_2C_2B_4H_2-4,5-I_2]$ (1B)	17.41 (145), 10.78,^{b} 8.62,^{b} −20.60 (171)	1, 1, 1, 1

^{a} CH_2Cl_2 solution; $BF_3 \cdot O(C_2H_5)_2$ shift is zero, positive shifts downfield. ^{b} Singlet (B–I resonance).

Table II. Infrared Absorptions $(cm^{-1})^a$

1	3120 s, 3025 s, 2990 s, 2930 m, 2580 vs, 2550 vs, 1970 w, 1930 w, 1865 w, 1670 m, br, 1480 s, 1470 s, 1410 s, 1360 s, 1130 w, 1095 w, 1060 w, 990 m, 940 m, 905 m, 835 s, 820 s, 800 s, 770 vs, 740 w, 700 w, 640 w, 540 w, 465 m
1A	3100 s, 3030 s, 2990 m, 2960 m, 2610 vs, 1665 m, br, 1485 s, 1465 s, 1410 w, 1370 w, 1350 w, 1095 w, 1075 s, 1060 s, 940 s, 880 s, 840 vs, 798 s, 767 vvs, 670 w, 650 m, 480 m
1B	3100 s, 3030 s, 2990 s, 2930 m, 2630 s, 2590 s, 1980 w, 1950 w, 1870 w, 1665 w, br, 1485 s, 1465 s, 1405 m, 1360 w, 1160 w, 1145 w, 1080 s, 1050 s, 890 s, 835 vs, 765 vvs, 670 w, br, 480 w
2	3070 m, 3020 w, 2975 s, 2935 s, 2880 m, 2530 vs, 2500 s, 1960 w, 1875 w, br, 1740 w, br, 1450 s, 1430 sh, 1380 s, 1340 s, 1300 w, 1265 w, 1155 w, 1130 w, 1070 w, 1030 w, 960 m, 920 w, 880 m, 835 s, 825 s, 795 w, 775 vs, 740 m
3	3120 m, 3020 vs, 2980 vs, 2925 m, 2580 vvs, 2550 vvs, 1940 w, 1870 w, 1750 w, br, 1660 m, br, 1470 s, 1455 m, 1405 m, 1370 w, 1325 w, 1275 m, 1150 w, 1130 w, 1090 m, 1055 w, 990 m, 950 w, 925 w, 900 m, 885 s, 860 s, 812 vs, 760 m, 735 w, 695 w, 635 w, 420 s

^{a} KBr pellets.

and mass spectra and X-ray crystallography as $(\eta^7\text{-}C_7H_7)Cr(C_2H_5)_2C_2B_4H_4$ (3). Attempts to prepare 3 by more "rational" routes, e.g., treatment of $(CO)_3Cr(C_7H_8)$ or $(CO)_3Cr(C_7H_7)^+BF_4^-$ with $(C_2H_5)_2C_2B_4H_6$ under UV light, were unsuccessful.

Properties and Structure of 1,2,3-$(\eta^8\text{-}C_8H_8)Ti$-$[(C_2H_5)_2C_2B_4H_4]$ (1). Complex 1 is an air-stable, diamagnetic red solid whose solutions decompose slowly (days) on exposure to air. Its high-resolution ^{11}B FT NMR spectrum (see data in Table I) is typical of seven-vertex closo MC_2B_4 metallacarborane cage systems with a first-row transition metal occupying one of the apical vertices,[2a] and the mass spectrum exhibits an intense parent grouping with a cutoff at m/e 285 corresponding to the $^{50}Ti^{13}C^{12}C_{13}{}^{11}B_4{}^1H_{22}{}^+$ ion and a base peak grouping in the m/e 150–155 region assigned to $Ti(C_8H_8)^+$. The parent envelope closely conforms to the pattern calculated from natural isotope abundances. The 360-MHz ^{1}H FT NMR spectrum (Experimental Section) contains well-defined resonances arising from the CH_3, CH_2, and C_8H_8 protons, and the IR spectrum (Table II) is unremarkable except for the split B–H stretching band near 2600 cm^{-1}, which is an unusual feature in the spectra of MC_2B_4-type metallacarborane systems.

Compound 1 is unreactive toward H_2, CO, CH_3CN, and $(C_6H_5)_3P$ under ambient conditions and is catalytically inactive toward the hydrogenation of 3-hexyne under 1 atm of H_2. In an investigation of the reactivity of the C_8H_8 ring toward methylation, 1 was heated with an $AlCl_3/CH_3I$ solution; however, no methylated products were found. Instead, the major product, obtained in 30% yield, was an iodo derivative characterized as 5-I-1,2,3-$(\eta^8\text{-}C_8H_8)Ti$-$(C_2H_5)_2C_2B_4H_3$ (1A). Direct iodination of 1 with I_2 in benzene gave a diiodo derivative, 4,5-I_2-1,2,3-$(\eta^8\text{-}C_8H_8)$-$Ti(C_2H_5)_2C_2B_4H_2$ (1B) in 76% yield. Both 1A and 1B were isolated as air-stable red-brown crystals and were characterized from their IR and mass spectra (cutoffs at m/e 411 and 537, respectively) and ^{11}B FT NMR spectra (Table I), in which the locations of iodine substitution were revealed by the singlet resonances (in the proton-coupled spectra). In 1A the mirror symmetry of the parent molecule is preserved and the high-field (apex) B–H resonance remains a doublet while the lower field area-1 resonance collapses; hence the halogenation occurs at B(5). In 1B, both iodine atoms are clearly on equatorial borons, and the absence of symmetry establishes 4,5 substitution.

Table III. Experimental Parameters and Crystal Data

	1	2	3
M_r	282	286	273
space group	$Pna2_1$	$Pna2_1$	$Pna2_1$
a, Å	14.309 (3)	14.264 (5)	14.334 (3)
b, Å	12.660 (2)	12.595 (4)	12.230 (4)
c, Å	8.476 (2)	8.449 (2)	8.356 (1)
V, Å^3	1535	1518	1465
μ, cm^{-1}	5.6	6.7	7.9
D(calcd), g/cm^3	1.218	1.250	1.236
A^a	0.60	0.60	0.60
B^a	0.35	0.35	0.35
max trans coeff^b	0.88	0.90	0.76
min trans coeff	0.66	0.88	0.59
2θ range, deg	3.8–60	1–52	1.5–54
reflectns obsd	2396	1506	1727
reflectns refined	1902	1271	1289
R	0.049	0.047	0.065
R_w	0.058	0.053	0.074
esd unit wt	1.0	2.1	1.2
Z	4	4	4

^{a} For explanation, see ref 25. ^{b} Crystal dimensions (mm from centroid): for 1, 1̄10 (0.035), 1̄10 (0.035), 011 (0.030), 01̄1̄ (0.030), 011̄ (0.020), 01̄1 (0.020); for 2, 11̄0 (0.019), 1̄10 (0.019), 110 (0.019), 1̄1̄0 (0.019), 010 (0.015), 01̄0 (0.015), 001 (0.050), 001̄(0.050), 201 (0.040), 2̄01̄ (0.040), 3̄01̄ (0.018); for 3, 110 (0.040), 1̄1̄0 (0.040), 11̄0 (0.060), 1̄10 (0.060), 011 (0.050), 01̄1̄ (0.050), 011̄ (0.040) 01̄1 (0.040).
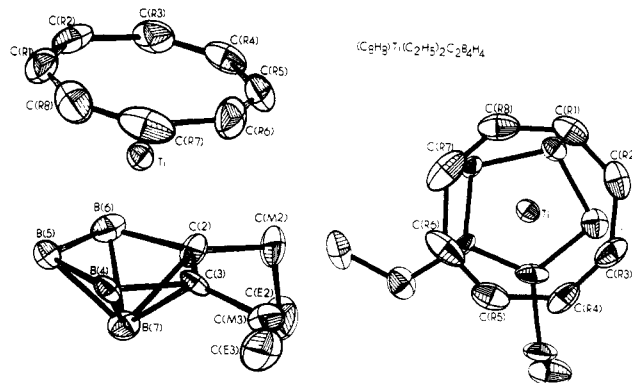

Figure 1. Molecular structure of 1 viewed obliquely (left) and along the metal–B(7) axis (right). In the right view the C_8 and C_2B_3 rings are projected onto the same plane, so that the ring sizes are directly comparable.

Table IV. Positional Parameters

atom	x	y	z	atom	x	y	z
			$(C_8H_8)Ti[(C_2H_5)_2C_2B_4H_4]$				
Ti	0.13463 (5)	0.12155 (6)	0.2500 (0)	H(4)	0.188 (5)	−0.017 (6)	0.492 (10)
C(R1)	−0.0239 (3)	0.1156 (4)	0.2618 (19)	H(5)	0.106 (3)	−0.135 (4)	0.284 (7)
C(R2)	0.0005 (4)	0.1410 (5)	0.1005 (9)	H(6)	0.203 (3)	−0.028 (4)	−0.044 (6)
C(R3)	0.0767 (6)	0.2059 (6)	0.0362 (8)	H(7)	0.333 (3)	−0.114 (4)	0.279 (8)
C(R4)	0.1472 (5)	0.2723 (5)	0.0994 (12)	H(R1)	−0.071 (4)	0.062 (4)	0.231 (10)
C(R5)	0.1709 (4)	0.2975 (4)	0.2574 (21)	H(R2)	−0.022 (4)	0.113 (5)	−0.014 (9)
C(R6)	0.1417 (5)	0.2709 (5)	0.4035 (8)	H(R3)	0.074 (4)	0.202 (4)	−0.053 (7)
C(R7)	0.0736 (5)	0.2067 (5)	0.4703 (10)	H(R4)	0.181 (4)	0.293 (5)	−0.000 (8)
C(R8)	0.0092 (5)	0.1416 (6)	0.4111 (10)	H(R5)	0.226 (4)	0.338 (5)	0.221 (9)
C(2)	0.2800 (4)	0.0617 (5)	0.1605 (7)	H(R6)	0.178 (5)	0.302 (6)	0.474 (10)
C(M2)	0.3518 (4)	0.1226 (5)	0.0633 (12)	H(R7)	0.080 (5)	0.202 (6)	0.590 (9)
C(E2)	0.4363 (5)	0.0511 (7)	0.0212 (13)	H(R8)	−0.029 (4)	0.094 (5)	0.461 (7)
C(3)	0.2772 (3)	0.0684 (4)	0.3349 (7)	H(M21)	0.379 (4)	0.166 (9)	0.141 (15)
C(M3)	0.3554 (4)	0.1212 (6)	0.4306 (7)	H(M22)	0.326 (4)	0.158 (11)	−0.027 (19)
C(E3)	0.3489 (6)	0.1190 (7)	0.6073 (10)	H(M31)	0.362 (3)	0.201 (6)	0.394 (11)
B(4)	0.2049 (4)	−0.0123 (5)	0.4065 (7)	H(M32)	0.414 (4)	0.097 (10)	0.393 (18)
B(5)	0.1518 (3)	−0.0657 (4)	0.2492 (21)	H(E31)	0.362 (6)	0.046 (13)	0.627 (23)
B(6)	0.2028 (5)	−0.0114 (5)	0.0935 (10)	H(E32)	0.293 (5)	0.105 (11)	0.618 (21)
B(7)	0.2753 (4)	−0.0597 (4)	0.2538 (21)	H(E33)	0.385 (6)	0.185 (15)	0.648 (27)
			$(C_8H_8)V[(C_2H_5)_2C_2B_4H_4]$				
V	0.13777 (7)	0.12200 (7)	0.2500 (0)	H(4)	0.192 (5)	−0.024 (5)	0.550 (8)
C(R1)	−0.0208 (4)	0.1141 (5)	0.2546 (28)	H(5)	0.100 (4)	−0.128 (5)	0.256 (19)
C(R2)	0.0074 (6)	0.1416 (6)	0.0936 (10)	H(6)	0.204 (5)	−0.023 (6)	−0.032 (10)
C(R3)	0.0776 (8)	0.2094 (7)	0.0354 (9)	H(7)	0.334 (4)	−0.108 (4)	0.256 (17)
C(R4)	0.1490 (8)	0.2729 (6)	0.0847 (12)	H(R1)	−0.070 (4)	0.061 (5)	0.259 (21)
C(R5)	0.1743 (5)	0.2983 (5)	0.2322 (15)	H(R2)	−0.025 (5)	0.111 (6)	0.000 (10)
C(R6)	0.1435 (6)	0.2694 (6)	0.3959 (9)	H(R3)	0.079 (6)	0.207 (6)	−0.083 (11)
C(R7)	0.0762 (6)	0.2038 (7)	0.4633 (12)	H(R4)	0.191 (5)	0.309 (6)	0.025 (10)
C(R8)	0.0061 (6)	0.1422 (7)	0.3990 (13)	H(R5)	0.230 (4)	0.343 (5)	0.232 (14)
C(2)	0.2809 (5)	0.0674 (5)	0.1656 (10)	H(R6)	0.176 (5)	0.296 (6)	0.497 (11)
C(M2)	0.3515 (5)	0.1219 (6)	0.0655 (11)	H(R7)	0.078 (5)	0.201 (6)	0.565 (10)
C(E2)	0.4378 (6)	0.0508 (8)	0.0314 (15)	H(R8)	−0.029 (5)	0.107 (6)	0.472 (10)
C(3)	0.2731 (5)	0.0671 (6)	0.3413 (8)	H(M21)	0.368 (5)	0.182 (6)	0.119 (10)
C(M3)	0.3566 (7)	0.1238 (8)	0.4261 (9)	H(M22)	0.324 (5)	0.141 (6)	−0.028 (10)
C(E3)	0.3482 (8)	0.1196 (9)	0.6017 (11)	H(M31)	0.421 (5)	0.089 (6)	0.394 (10)
B(4)	0.1997 (6)	−0.0031 (6)	0.408 (1)	H(M32)	0.361 (6)	0.199 (6)	0.387 (10)
B(5)	0.1494 (5)	−0.0618 (5)	0.257 (2)	H(E31)	0.376 (5)	0.044 (5)	0.615 (9)
B(6)	0.2026 (6)	−0.0120 (6)	0.094 (1)	H(E32)	0.287 (6)	0.123 (7)	0.631 (11)
B(7)	0.2721 (5)	−0.0577 (5)	0.254 (3)	H(E33)	0.387 (6)	0.171 (6)	0.650 (10)
			$(C_7H_7)Cr[(C_2H_5)_2C_2B_4H_4]$				
Cr	0.13831 (9)	0.1148 (1)	0.2500 (0)	B(7)	0.2675 (7)	−0.0671 (8)	0.247 (3)
C(2)	0.2779 (6)	0.0649 (8)	0.342 (1)	H(4)	0.196 (5)	−0.032 (6)	−0.041 (9)
C(M2)	0.3463 (8)	0.1225 (10)	0.434 (1)	H(5)	0.103 (6)	−0.134 (8)	0.277 (18)
C(E2)	0.4301 (9)	0.0531 (13)	0.482 (2)	H(6)	0.177 (7)	−0.017 (10)	0.552 (14)
C(3)	0.2704 (6)	0.0611 (9)	0.164 (1)	H(7)	0.327 (5)	−0.133 (7)	0.255 (24)
C(M3)	0.3510 (8)	0.1193 (11)	0.068 (2)	H(R1)	0.077 (8)	0.200 (10)	−0.071 (14)
C(E3)	0.3395 (12)	0.1153 (14)	−0.109 (2)	H(R2)	0.180 (8)	0.304 (10)	0.048 (15)
C(R1)	0.0751 (8)	0.2058 (10)	0.050 (1)	H(R3)	0.209 (7)	0.332 (9)	0.333 (13)
C(R2)	0.1420 (8)	0.2711 (9)	0.124 (1)	H(R4)	0.125 (8)	0.257 (10)	0.550 (14)
C(R3)	0.1565 (7)	0.2800 (9)	0.297 (1)	H(R5)	0.003 (9)	0.133 (10)	0.525 (17)
C(R4)	0.1033 (9)	0.2385 (12)	0.430 (2)	H(R6)	−0.066 (7)	0.063 (8)	0.304 (13)
C(R5)	0.0278 (9)	0.1611 (11)	0.420 (2)	H(R7)	−0.026 (7)	0.099 (10)	0.047 (14)
C(R6)	−0.0135 (7)	0.1185 (9)	0.280 (2)	H(M21)	0.356 (6)	0.200 (7)	0.381 (10)
C(R7)	0.0072 (8)	0.1378 (9)	0.123 (1)	H(M22)	0.321 (7)	0.144 (9)	0.561 (13)
B(4)	0.2006 (9)	−0.0122 (10)	0.101 (2)	H(M31)	0.422 (7)	0.062 (9)	0.069 (13)
B(5)	0.1455 (7)	−0.0701 (7)	0.261 (3)	H(M32)	0.359 (8)	0.166 (10)	0.090 (15)
B(6)	0.1965 (8)	−0.0179 (10)	0.420 (2)				

In order to examine the structural details of the C_8H_8 ring and its coordination to the metal, an X-ray diffraction study was conducted on **1**. Tables III–VI contain the relevant data, and an ORTEP view of the structure is presented in Figure 1. The cyclooctatetraenyl ring is planar within experimental error (largest deviation from the calculated plane is <0.03°) and is nearly parallel to the C_2B_3 ring of the carborane ligand, with a dihedral angle of 2.8°. The titanium atom is essentially equidistant from the eight ring carbons, and the mean Ti–C distance of 2.290 (4) Å is slightly shorter than the corresponding values in other $(\eta^8\text{-}C_8H_8)$Ti complexes,[5] in which the average Ti–C

distances exceed 2.30 Å. The C_8H_8 hydrogen atoms are bent out of the C_8 plane toward the metal, by an average of 4.7°; this is qualitatively in agreement with the argument of Elian et al.,[6] which holds that the deflection of C–H hydrogens in large-ring C_nH_n π-complexes of first-row transition metals should be in the direction of the metal.

(6) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.

(7) (a) Brauer, D. J.; Krüger, C. *J. Organomet. Chem.* **1972**, *42*, 129; **1975**, *14*, 3053. (b) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1975**, *14*, 3053. (c) Brauer, D. J.; Krüger, C. *Organometallics* **1982**, *1*, 204, 207 and references therein.

Table V. Bond Distances (Å) in $(\eta^n\text{-}C_nH_n)M[(C_2H_5)_2C_2B_4H_4]$

	1 (M = Ti, n = 8)	2 (M = V, n = 8)	3 (M = Cr, n = 7)
M-C(R1)	2.272 (5)	2.264 (4)	2.204 (4)
M-C(R2)	2.313 (12)	2.295 (11)	2.183 (4)
M-C(R3)	2.261 (12)	2.288 (8)	2.171 (4)
M-C(R4)	2.302 (14)	2.365 (18)	2.193 (5)
M-C(R5)	2.287 (5)	2.286 (4)	2.200 (5)
M-C(R6)	2.297 (12)	2.230 (9)	2.191 (5)
M-C(R7)	2.326 (12)	2.254 (9)	2.175 (5)
M-C(R8)	2.269 (13)	2.276 (11)	
C(R1)-C(R2)	1.447 (23)	1.460 (17)	1.395 (6)
C(R2)-C(R3)	1.470 (20)	1.405 (16)	1.477 (6)
C(R3)-C(R4)	1.418 (21)	1.360 (17)	1.476 (6)
C(R4)-C(R5)	1.417 (24)	1.336 (15)	1.440 (6)
C(R5)-C(R6)	1.350 (22)	1.497 (13)	1.408 (7)
C(R6)-C(R7)	1.389 (18)	1.389 (15)	1.364 (7)
C(R7)-C(R8)	1.335 (22)	1.377 (17)	
C(R7)-C(R1)			1.420 (6)
C(R8)-C(R1)	1.392 (25)	1.327 (19)	
M-C(2)	2.341 (11)	2.269 (10)	2.228 (6)
M-C(3)	2.266 (10)	2.190 (9)	2.130 (6)
M-B(4)	2.375 (11)	2.248 (10)	2.183 (7)
M-B(5)	2.384 (5)	2.321 (4)	2.265 (3)
M-B(6)	2.355 (12)	2.335 (11)	2.310 (7)
C(2)-C(3)	1.481 (7)	1.488 (6)	1.492 (4)
C(2)-C(M2)	1.526 (16)	1.484 (12)	1.430 (8)
C(2)-B(6)	1.549 (17)	1.618 (14)	1.677 (8)
C(2)-B(7)	1.729 (15)	1.749 (11)	1.805 (7)
C(M2)-C(E2)	1.552 (14)	1.549 (9)	1.525 (8)
C(3)-C(M3)	1.535 (14)	1.563 (12)	1.573 (8)
C(3)-B(4)	1.576 (16)	1.482 (14)	1.443 (9)
C(3)-B(7)	1.761 (13)	1.735 (11)	1.715 (8)
C(M3)-C(E3)	1.501 (13)	1.489 (11)	1.495 (9)
B(4)-B(5)	1.677 (18)	1.642 (16)	1.707 (11)
B(4)-B(7)	1.746 (18)	1.797 (14)	1.692 (10)
B(5)-B(6)	1.658 (20)	1.695 (16)	1.643 (11)
B(5)-B(7)	1.769 (7)	1.751 (6)	1.754 (5)
B(6)-B(7)	1.816 (19)	1.777 (14)	1.866 (10)
⟨C-H⟩	0.95	0.96	1.00
⟨B-H⟩	1.00	1.12	1.13

Table VI. Selected Bond Angles (deg)

			1	2	3
C(R2)	C(R1)	C(R8)	136.4 (5)	135.6 (4)	
C(R2)	C(R1)	C(R7)			127.9 (4)
C(R1)	C(R2)	C(R3)	130.8 (11)	131.8 (9)	127.8 (4)
C(R2)	C(R3)	C(R4)	136.0 (12)	141.7 (9)	127.3 (4)
C(R3)	C(R4)	C(R5)	131.3 (13)	128.90 (10)	127.8 (5)
C(R4)	C(R5)	C(R6)	137.5 (6)	136.4 (5)	127.5 (4)
C(R5)	C(R6)	C(R7)	137.4 (11)	136.6 (9)	129.8 (4)
C(R6)	C(R7)	C(R8)	133.8 (13)	132.50 (10)	
C(R7)	C(R8)	C(R1)	136.4 (14)	136.30 (11)	
C(R6)	C(R7)	C(R1)			131.8 (4)
M	C(2)	C(M2)	127.6 (8)	130.5 (6)	131.7 (5)
C(M2)	C(2)	C(3)	121.9 (12)	128.4 (10)	126.9 (3)
C(M2)	C(2)	B(6)	125.7 (10)	122.7 (8)	124.5 (5)
C(M2)	C(2)	B(7)	136.3 (9)	135.2 (8)	137.1 (5)
C(3)	C(2)	B(6)	112.4 (12)	108.8 (9)	108.5 (6)
C(2)	C(M2)	C(E2)	110.7 (9)	112.2 (7)	114.1 (6)
M	C(3)	C(M3)	134.0 (8)	133.5 (7)	133.2 (5)
C(M3)	C(3)	C(2)	122.2 (11)	113.5 (10)	115.9 (6)
C(M3)	C(3)	B(4)	123.9 (9)	129.4 (8)	127.3 (5)
C(M3)	C(3)	B(7)	128.2 (9)	127.9 (8)	129.5 (5)
C(2)	C(3)	B(4)	111.4 (11)	115.8 (9)	115.7 (6)
C(3)	C(M3)	C(E3)	118.3 (10)	112.3 (8)	114.0 (5)
C(3)	B(4)	B(5)	104.6 (8)	106.2 (8)	107.0 (5)
B(4)	B(5)	B(6)	105.4 (4)	105.8 (3)	105.4 (3)
C(2)	B(6)	B(5)	105.6 (10)	103.4 (8)	103.4 (5)

There is no indication of a "long–short–long" pattern in the ring C–C distances. The C(R1)–C(R2), C(R3)–C(R4), C(R5)–C(R6), and C(R7)–C(R8) bond lengths average 1.388 (11) Å, while the mean of the other four distances is 1.417 (11) Å, the difference corresponding to only three standard deviations. Previously reported titanium[5] and
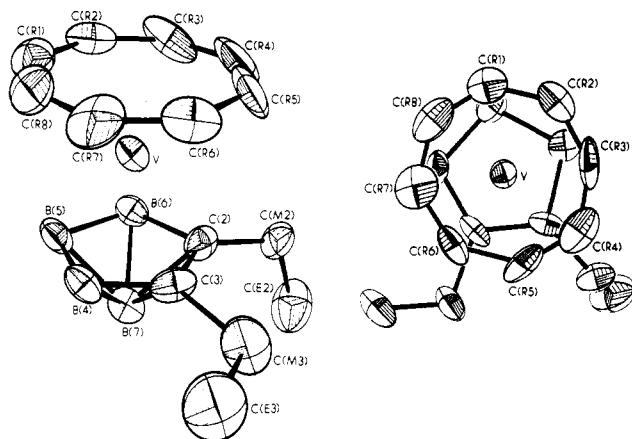

Figure 2. Molecular structure of **2** shown as in Figure 1.

zirconium[7] complexes similarly exhibit no such pattern.

The titanium–carborane ligand distance (vector normal to the C_2B_3 ring plane) is quite long at 1.916 Å, which is 0.25–0.35 Å larger than the corresponding distances in typical iron and cobalt complexes containing $R_2C_2B_4H_4{}^{2-}$ ligands.[1b,c,3c,8] The larger covalent radius of Ti(1.32 vs. 1.17 and 1.16 Å for Fe and Co)[9] does not fully account for this long metal–carborane distance and suggests a greater degree of ionic character in the metal–carborane bond in **1** as compared to the related ferra- and cobaltacarboranes. A similar observation can be made with respect to the vanadium complex **2**, discussed below.

The $(C_2H_5)_2C_2B_4H_4{}^{2-}$ carborane ligand exhibits normal bond distances and angles, with a typically short [1.481 (7) Å] C(2)–C(3) distance on the bonding face, suggestive of localized C–C bonding as has been proposed for other metallacarboranes containing $R_2C_2B_4H_4{}^{2-}$ ligands.[1b,c,8]

Properties and Structure of 1,2,3-$(\eta^8$-$C_8H_8)$V-[$(C_2H_5)_2C_2B_4H_4$] (2). The vanadium species is a dark green paramagnetic air-stable solid, whose solutions also exhibit no sign of decomposition on exposure to air for prolonged periods. Its mass spectrum contains a strong parent envelope with a cutoff at m/e 286 corresponding to the $^{51}V^{13}C^{12}C_{13}{}^{11}B_4{}^1H_{22}{}^+$ ion and a base peak at m/e 155 arising from $V(C_8H_8)^+$. Except for slight loss of hydrogen, the observed intensities in the parent region closely match the pattern calculated from natural isotope distributions.

The magnetic susceptibility and ESR data on **2** are consistent with its formulation as a complex of formal V^{4+} with 17 electrons (one unpaired) in its valence shell.[10] The magnetic moment is slightly temperature dependent with a maximum near 6 K, indicating a substantially smaller orbital effect than would be expected for a d^1 metal in a regular octahedral $(^2T_2)$ environment. Extrapolation of

(8) (a) Borodinsky, L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 1928. (b) Weiss, R.; Bryan, R. F. *Acta Crystallogr., Sect. B* **1977**, *B33*, 589. (c) Pipal, J. R.; Maxwell, W. M.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 1447. (d) Pipal, J. R.; Grimes, R. N. *Ibid.*, **1979**, *18*, 263. (e) Grimes, R. N.; Maynard, R. B.; Sinn, E.; Brewer, G. A.; Long, G. J. *J. Am. Chem. Soc.* **1982**, *104*, 5987. (f) Maxwell, W. M.; Sinn, E.; Grimes, R. N. *Ibid.* **1976**, *98*, 3490.

(9) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 256.

(10) Formal V^{4+} (d^1) is considered to accept 6 and 10 electrons, respectively, from the $(C_2H_5)_2C_2B_4H_4{}^{2-}$ and $C_8H_8{}^{2-}$ ligands. We assume that the electron deficiency is localized on the metal "nonbonding" orbitals rather than in the metallacarborane framework bonding MO's (see Maynard, R. B.; Wang, Z-T.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1983**, *22*, 873 and papers cited therein). This permits the seven-vertex VC_2B_4 cage to have a full complement of 16 skeletal electrons, consistent with its observed *closo* geometry as predicted by Wade's rules.[2a,11]

(11) O'Neill, M. E.; Wade, K. In "Metal Interactions with Boron Clusters"; Grimes, R. N., Ed.; Plenum Press: New York, 1983; Chapter 1, and references therein.
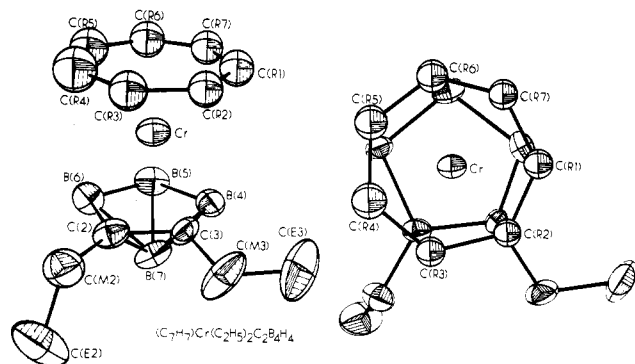
Figure 3. Molecular structure of **3** shown as in Figure 1.

the magnetic moment data gives a room-temperature value of $g = 1.91$, which compares with the value of 1.94 obtained from the room-temperature ESR spectrum in toluene/ CH_2Cl_2 solution. This spectrum reveals vanadium hyperfine coupling ($\langle A \rangle = 155$ G), but unfortunately there is no clear evidence of ligand hyperfine arising from vanadium–boron interaction. Low-temperature ESR spectra of **2** exhibit extreme signal broadening, indicating formation of a glass at about -80 °C. The -160 °C spectrum contains a clear eight-line spectrum as expected for vanadium, but still no boron hyperfine can be detected.

The X-ray-determined structure of **2** (Figure 2 and Tables III–VI) is essentially isostructural (but not isomorphous) with **1**. As in **1**, the C_8H_8 ring is planar and symmetrically bonded to the metal; however, while the average ring C–C distance of 1.394 (6) Å is close to that in **1** [1.402 (8) Å], the C–C bond lengths in **2** do not vary in an obvious "long–short–long" pattern. As was the case in the titanium complex **1** mentioned above, the hydrogen atoms on the C_8H_8 ring are bent toward the metal atom, in this case by an average of 2.5°.

It is of interest to note that, although the vanadium atom in **2** is substantially closer to the carborane ligand than is the titanium in **1** (1.830 vs. 1.916 Å), the metal–C_8H_8 distance is nearly the same in the two complexes. As **2** is the only structurally characterized example of an (η^8-C_8H_8)V complex of any type,[12] further evaluation of this finding in relation to experimental data on other vanadium species is not possible at present.

The $R_2C_2B_4H_4^{2-}$ carborane ligand in **2** has no unusual features and is nearly identical with that in **1** save for a slightly longer C(2)–C(3) distance [1.488 (6) Å]. As in **1**, the two ethyl groups in **2** are aligned such that the C–C axis of one is roughly parallel to the C_2B_3 ring plane, while that of the other is nearly perpendicular; this rather odd finding is attributed to packing forces within the crystals, as the C_2H_5 groups in both **1** and **2** are equivalent in solution on the NMR time scale.

Properties and Structure of 1,2,3-(η^7-C_7H_7)Cr-[(C_2H_5)$_2C_2B_4H_4$] (3). As noted earlier, complex **3** was isolated as a trace product during an attempt to prepare the corresponding C_8H_8 chromacarborane analogous to **1** and **2**. Although we have not yet found a high-yield route to **3**, its structure and spectroscopic properties are of interest in that it is (i) the first example of a (tropylium)-metal(carborane) sandwich complex and (ii) evidently the first (η^7-C_7H_7)Cr complex for which an X-ray crystal structure determination has been published. Compound **3** is a paramagnetic yellow-green solid that is stable to

air-oxidation both in the dry state and in solution. Its solid-state molecular geometry (Figure 3 and Tables III–VI) consists of a chromium atom sandwiched between a nearly planar C_7 ring (largest deviation 0.013 Å) and a pyramidal $(C_2H_5)_2C_2B_4H_4$ unit, the C_7H_7 and C_2B_3 rings being almost parallel (dihedral angle 2.76°). The C_7H_7 ring closely approximates a regular heptagon, the mean value of the C–C–C angles being 128.6°, corresponding to the "ideal" value of 128.57°. The C–C distances in the ring average 1.426 (3) Å with some deviations from the mean, particularly the somewhat longer C(R2)–C(R3) and C-(R3)–C(R4) distances of $\sim$1.48 Å. In the only previously reported structural characterizations of η^7-C_7H_7 complexes of first-row transition metals, the average ring C–C bond lengths are 1.397 Å in (η^7-C_7H_7)Ti(η^5-C_5H_5),[13] 1.412 Å in a ring-substituted derivative of that compound,[14] and 1.403 Å in (η^7-C_7H_7)V(η^5-C_5H_5);[15] in addition, Zeinstra and Nieuwpoort[16] quote a value of 1.409 Å for an unpublished structure of (η^7-C_7H_7)Cr(η^5-C_5H_5).

The chromium atom is symmetrically bonded to the C_7H_7 ligand is **3**, there being no large deviation from the mean Cr–C value of 2.188 (2) Å. This distance is very close to that of 2.16 Å given in the literature[16] for (η^7-C_7H_7)-Cr(η^5-C_5H_5). The carboranyl C–C distance [C(2)–C(3)] of 1.492 (4) Å is slightly larger than the average value for MC_2B_4 metallacarborane systems but still within the range of observed distances in such molecules.[1b,c,3c,8]

Consistent with our findings in the C_8H_8 complexes **1** and **2**, the C_7H_7 ring hydrogens lie an average 2.9° out of the C_7 ring plane on the metal side. While none of the hydrogens in these structures were located with high precision, this trend seems clearly significant and in accord with theoretical predictions.[6]

Discussion

The planar $C_8H_8^{2-}$ carbocyclic system forms stable η^8-bonded sandwich complexes with large metal atoms such as the actinides[17] (in which the f orbitals are believed to play a significant role in bonding), lanthanides[18] (in which the bonding is largely ionic), and zirconium.[7] In contrast, η^8-coordination of this ligand to first-row transition metals is rare[19] and (prior to the present work) gives less robust complexes that are notoriously air-sensitive. In light of this, the greatly enhanced oxidative stability of the complexes reported herein is particularly significant and must be attributed to the $R_2C_2B_4H_4^{2-}$ carborane ligand, which differs in at least two respects from conventional hydrocarbon π-type ligands such as $C_5H_5^-$ and arenes. First, the carborane unit carries a formal dinegative charge, which in combination with $C_8H_8^{2-}$ stabilizes a high (+4) formal oxidation state on the metal. Second, the presence of boron (specifically, three boron atoms on the C_2B_3 binding face) presumably leads to more covalent metal–ligand bonding that is generally the case in metal–hydrocarbon π-complexes, reflecting the lower electronegativity of boron

(12) The recently reported dimetallic species [(C_5H_5)V]$_2C_8H_8$ has two vanadium atoms each of which is η^5-bound to a bent (124°) $C_8H_8^{2-}$ ligand: Elschenbroich, C.; Heck, J.; Massa, W.; Nun, E.; Schmidt, R. *J. Am. Chem. Soc.* **1983**, *105*, 2905.

(13) Zeinstra, J. D.; de Boer, J. L. *J. Organometal. Chem.* **1973**, *54*, 207.

(14) Demerseman, B.; Dixneuf, P. H.; Douglade, J.; Marcher, M. *Inorg. Chem.* **1982**, *21*, 3942.

(15) Engbretson, G. R.; Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 481.

(16) Zeinstra, J. D.; Nieuwpoort, W. C. *Inorg. Chim. Acta* **1978**, *30*, 103, ref 3.

(17) (a) Streitweiser, A., Jr.; Müller-Westerhoff, U.; Sonnichsen, G.; Mares, F.; Morrell, D. G.; Hodgson, K. O.; Harmon, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 8644 and references therein. (b) Avdeef, A.; Raymond, K. N.; Hodgson, K. O.; Zalkin, A. *Inorg. Chem.* **1972**, *11*, 1083.

(18) Hodgson, K. O.; Mares, F.; Starks, D. F.; Streitweiser, A., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 8650 and references therein.

(19) Fray, G. I.; Saxton, R. G. "The Chemistry of Cyclo-octatetraene and Its Derivatives"; Cambridge University Press: London, 1978.

compared to carbon. The general observation of strong metal–carborane π-bonding is well-known and traces back to the earliest metallacarboranes,[2a,20] which incorporated the icosahedral-fragment $C_2B_9H_{11}^{2-}$ ligand. There is reason to believe that the pentagonal-pyramidal $R_2C_2B_4H_4^{2-}$ ligands bind even more tightly to transition metals than does $C_2B_9H_{11}^{2-}$, since the bonding orbitals in $R_2C_2B_4H_4^{2-}$ are more favorably oriented toward the metal.[21]

If the properties of complexes 1–3 are typical of $(\eta^n$-$C_nH_n)$metal$(R_2C_2B_4H_4)$ species (and the fact that three different metals are involved strongly suggests that they are), then it appears that the stabilization of metal–hydrocarbon bonding interactions via simultaneous coordination of the metal to $R_2C_2B_4H_4^{2-}$ ligands furnishes a useful new tool in transition-metal organometallic synthesis.

Experimental Section

Materials. C,C'-Diethyldicarbahexaborane(8), $(C_2H_5)_2C_2B_4H_6$, and $Na^+[(C_2H_5)_2C_2B_4H_5]^-$ were prepared by previously described methods.[22] Dipotassium cyclooctatetraenide, $K^+_2C_8H_8^{2-}$, was obtained as a solution in THF (tetrahydrofuran) by the procedure of Streitweiser et al.[23] Anhydrous metal halides were stored under nitrogen prior to use. Tetrahydrofuran (THF) and benzene were dried by reflux over sodium benzophenone ketyl. Cyclooctatetraene (Aldrich, 98%) was stored cold and distilled in vacuo prior to use. Column chromatography was conducted with silica gel 60 (Merck), and preparative-layer and thin-layer chromatography (TLC) were conducted on precoated plates of silica gel (Merck).

Instrumentation. ^{11}B (115.8 MHz) and ^1H (360 MHz) pulse Fourier transform NMR spectra were obtained on a Nicolet Magnetics Corp. NT-360/Oxford spectrometer, and data manipulation utilized standard Nicolet software with a 1280/293B data system. Broad-band heteronuclear decoupling was employed. Unit resolution mass spectra (EI) were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Chemical-ionization mass spectra (CI) were provided by Harvey Laboratories, Inc., Charlottesville, VA. Infrared spectra were recorded on a Perkin-Elmer Model 1430 spectrometer. Magnetic susceptibilities were measured on a Squid magnetometer; the calibration of the instrument and procedures followed in measurement have been described previously.[24] Electron spin resonance (ESR) spectra were recorded on a Varian E-109 spectrometer at 9.1 GHz, whose cavity temperature was maintained with a Varian variable-temperature controller with nitrogen as carrier gas.

Preparation of $(\eta^8$-$C_8H_8)Ti[(C_2H_5)_2C_2B_4H_4]$ (1). A THF solution of $K_2C_8H_8$ was prepared[23] from 0.475 g (12.2 mmol) of potassium metal and 0.624 g (6.00 mmol) of cyclooctatetraene in 25 mL of dry THF. This solution was filtered in vacuo onto 0.780 g (5.06 mmol) of $TiCl_3$ (Alfa) in a 100-mL round-bottom flask immersed in liquid nitrogen. A THF solution of $Na^+(C_2H_5)_2C_2B_4H_5^-$ was prepared from 0.625 g (4.74 mmol) of 2,3-$(C_2H_5)_2C_2B_4H_6$ and 0.128 g (5.33 mmol) of NaH in 25 mL of THF. The $Na^+(C_2H_5)_2C_2B_4H_5^-$ was filtered onto the frozen reaction mixture, and the reactor was placed in an ice bath and stirred for 30 min. During this time the mixture, which was originally greenish-yellow, evolved H_2 and became dark orange. The liquid nitrogen bath was removed and stirring was continued at room temperature for 3 h with no further color change. After exposure to air the solvent was removed by rotary evaporation and the residue was washed twice with n-hexane. The crude product was extracted with 25 mL of n-hexane/THF (1:1) and

filtered through a sintered glass frit. A small amount of the red-orange filtrate was placed on a silica gel plate and developed in n-hexane/methylene chloride (1:1), yielding only a single red-orange band. The solvent was removed from the remaining n-hexane/THF filtrate by rotary evaporation, and the dark red product was washed with n-hexane and air-dried. Recrystallization from a minimum amount of methylene chloride gave 0.653 g (2.31 mmol, 48.8% yield based on carborane employed) of $(\eta^8$-$C_8H_8)$-$Ti[(C_2H_5)_2C_2B_4H_4]$ (1) as air-stable red crystals, mp 250–252 °C. The 360-MHz ^1H FT NMR spectrum of 1 in C_6D_6 contains a sharp singlet at δ 6.27 (C_8H_8), a CH_3 triplet at δ 1.21 (J = 8.1 Hz), and CH_2 multiplets centered at δ 2.13 (J = 9.4 Hz) and 2.42 (J = 7.3 Hz).

Preparation of 5-I-1,2,3-$(\eta^8$-$C_8H_8)Ti[(C_2H_5)_2C_2B_4H_3]$ (1A). In a 50-mL round-bottom flask 0.103 g (0.365 mmol) of 1 was dissolved in 20 mL of methyl iodide. To this solution was added 0.120 g (0.899 mmol) of $AlCl_3$ with stirring. The initially red reaction mixture immediately turned green. After the mixture was refluxed for 12 h, the methyl iodide was removed by rotary evaporation and the residue was extracted with methylene chloride. The red-brown extract was reduced in volume and placed on a silica gel TLC plate. Development with methylene chloride/n-hexane (1:1) produced 16 mg (0.040 mmol, 30% yield based on 0.138 mmol of 1 consumed) of 1A as a red-brown solid: mp 208–210 °C, R_f 0.67.

Preparation of 4,5-I_2-1,2,3-$(\eta^8$-$C_8H_8)Ti[(C_2H_5)_2C_2B_4H_2]$ (1B). In a 100-mL round-bottom flask 0.085 g (0.301 mmol) of 1 was dissolved in 25 mL of benzene. With stirring, a solution of 0.075 g (0.295 mol) of iodine was added dropwise. The color of the reaction mixture became brown-red as the iodine solution was added. After the mixture was stirred for 20 min at room temperature, the solvent was removed by rotary evaporation. The residue was dissolved in a small amount of methylene chloride and placed on a silica gel TLC plate. Development with methylene chloride/n-hexane (1:1) gave 1B and a small amount of unreacted 1. The product 1B was isolated as a red-brown air-stable solid: mp ~250 °C dec; R_f 0.64; yield 0.122 g (0.228 mmol, 76%).

Preparation of $(\eta^8$-$C_8H_8)V[(C_2H_5)_2C_2B_4H_4]$ (2). A THF solution of $K_2C_8H_8$, prepared from 5.32 mmol of C_8H_8 and 10.4 mmol of potassium metal in 25 mL of dry THF at –30 °C, was filtered in vacuo onto 0.752 g (4.78 mmol) of anhydrous VCl_3 (Alfa) in a 100-mL round-bottom flask, which was immersed in liquid nitrogen. A solution of $Na[(C_2H_5)_2C_2B_4H_5]$, prepared from 0.597 g (4.52 mmol) of $(C_2H_5)_2C_2B_4H_6$ and 0.260 g (5.42 mmol) of NaH in 25 mL of THF, was filtered in vacuo into the reaction flask maintained at –196 °C. The reaction mixture was allowed to thaw, and stirring was continued at 0 °C for 2 h, during which time the solution acquired a brown-green color. The mixture was warmed to room temperature and stirred for 3.5 h, following which the color of the solution was brown-red. On exposure of the reaction mixture to the air a brown precipitate began to form; when the precipitation was complete, a green-yellow supernatant remained. The supernatant was filtered, evaporated to dryness, and dissolved in a minimum amount of methylene chloride. This solution was placed on a silica gel TLC plate and developed with 25% CH_2Cl_2 in n-hexane to give 2 as an air-stable dark green solid: mp 240–250 °C dec; R_f 0.47; yield 41 mg (0.144 mmol, 3.2%).

Reaction of $Na^+(C_2H_5)_2C_2B_4H_5^-$, $CrCl_3$·3THF, and $K_2C_8H_8$. A THF solution of $K_2C_8H_8$, prepared from 13.62 mmol of potassium metal and 6.39 mmol of cyclooctatetraene in 25 mL of dry THF at –30 °C, was filtered in vacuo onto a frozen solution of 2.50 g (6.68 mmol) of $CrCl_3$·3THF (Strem) in 25 mL of THF. A THF solution of $Na^+(C_2H_5)_2C_2B_4H_5^-$, prepared from 0.647 g (4.94 mmol) of 2,3-$(C_2H_5)_2C_2B_4H_6$ and 0.138 g (5.75 mmol) of NaH in 25 mL of THF, was filtered in vacuo into the reaction flask containing $CrCl_3$·3THF and $K_2C_8H_8$ at liquid nitrogen temperature. The reactor was placed in an ice bath and stirred for 2 h. During this time the purple $CrCl_3$·3THF solution slowly became golden-brown. The bath was removed and stirring was continued for 4 h at room temperature. After exposure to air, the solvent was removed by rotary evaporation. The resulting residue was extracted into 10 mL of methylene chloride and filtered through 1 cm of silica gel on a sintered glass frit. The silica gel was washed with methylene chloride until the effluent became colorless. As unstable material in the filtrate began to decompose, an insoluble green precipitate formed. After this decomposition was complete,

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filtration produced a pale yellow solution. This solution was concentrated by rotary evaporation and placed on a silica gel TLC plate. Development with methylene chloride in *n*-hexane (1:3) gave an orange band (R_f 0.47), which produced 3 mg of (η^7-C_7H_7)Cr[(C_2H_5)$_2C_2B_4H_4$] (3) as an air-stable yellow-green solid.

X-ray Structure Determinations on (η^8-C_8H_8)Ti-[(C_2H_5)$_2C_2B_4H_4$] (1), (η^8-C_8H_8)V[(C_2H_5)$_2C_2B_4H_4$] (2), and (η^7-C_7H_7)Cr[(C_2H_5)$_2C_2B_4H_4$] (3). Single crystals of 1, 2, 3 were grown by slow evaporation in air of dichloromethane, benzene, and acetone solutions, respectively. In each case, selected crystals were mounted on glass fibers, examined by precession photography, and found acceptable.

Relevant parameters for the data collection and structure determination are given in Table III. The procedures followed in data collection and processing have been described elsewhere.[25] Space groups were chosen on the basis of chemical and spectroscopic information taken together with systematic absences.

The intensities of three standard reflections, monitored at regular intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and then for absorption. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics ($p = 0.03$),[26] were used in the final refinement of the structural parameters, after averaging for equivalent reflections.

Solution and Refinement of the Structures. Full-matrix least-squares refinement was based on F, and the function minimized was $w(|F_o| - |F_o|)^2$. The weights w were taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber[27] and those for hydrogen from Stewart et al.[28] The effects of anomalous dispersion for all non-hydrogen atoms were included in F, using the values of Cromer and Ibers[29] for $\Delta f'$ and $\Delta f''$.

In each structure, the metal atom was located from a three-dimensional Patterson difference map calculated from all intensity data. Subsequent Fourier difference maps revealed the positions of all other non-hydrogen atoms. After introducing anisotropic thermal parameters for all cage non-hydrogen atoms, additional Fourier syntheses located most of the hydrogen atoms. Several of the ethyl hydrogens were inserted into calculated positions and included in subsequent refinement. All hydrogen positions were held fixed in the final least-squares cycles. In the structure of 3, the ring carbon atoms exhibited slight librational disorder and were refined isotropically; otherwise the refinement of the data was handled as for the structures of 1 and 2.

In each case, the model converged to the final R and R_w values given in Table III, where $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. Tables of observed and calculated structure factors and thermal parameters are available (see paragraph at end of paper on supplementary material). The computing system and programs are described elsewhere.[30]

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η^4-Bonding in (Arene)ruthenium Complexes of Octamethylnaphthalene

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The reaction of [RuCl$_2$(arene)]$_2$ (arene = *p*-cymene, benzene, mesitylene, prehnitene, hexamethylbenzene, 1,3,5-triethylbenzene, and 1,3,5-triisopropylbenzene) with octamethylnaphthalene (OMN) under three sets of conditions leads to the bis(arene) complexes [Ru(OMN)(arene)]$^{2+}$. These 18-electron cations containing two η^6-rings can be easily reduced with sodium amalgam to complexes with the formula Ru(OMN)(arene). The neutral complexes contain a η^6-arene and a η^4-OMN ring as shown by a single-crystal X-ray crystallographic analysis of Ru(OMN)(C$_6$Me$_6$) [$P2_1/n$ space group, $Z = 8$, $a = 19.768$ (6) Å, $b = 14.524$ (3) Å, $c = 19.676$ (6) Å, $\beta = 117.13$ (2)°]. Protonation of the complexed OMN ring in Ru(OMN)(C$_6$H$_6$) yields an isolable cyclohexadienyl species, [Ru(C$_{10}$Me$_8$H)(C$_6$H$_6$)]$^+$, while reaction of Ru(OMN)(C$_6$H$_6$) with Cr-(CO)$_3$(CH$_3$CN)$_3$ produces the binuclear compound (C$_6$H$_6$)Ru(μ-OMN)Cr(CO)$_3$. The reactivity of the neutral complexes with hydrogen is discussed.

Introduction

Structurally characterized examples of the η^4-bonding of aromatic rings to transition metals remain rare.[2] The reduction of hapticity is often invoked as a route to arene substitution and other reactions, the most interesting of which is the homogeneous hydrogenation of arenes.[2-4] One of the premier examples of η^4-bonding occurs in Ru-(C$_6$Me$_6$)$_2$, I, that was reported[5] by Fischer and Elschen-

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