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Syntheses and Structural and Electrochemical Characterizations of Vanadatricarbadecaboranyl Analogues of Vanadocene and the Structural Characterization of the $[Li(CH_3CN)_2{}^+](6\text{-}CH_3\text{-}\textit{nido}\text{-}5,6,9\text{-}C_3B_7H_9{}^-)$ Tricarbadecaboranyl Anion

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Abstract: A single-crystal X-ray determination of the $[Li(CH_3CN)_2{}^+](6\text{-}CH_3\text{-}\textit{nido}\text{-}5,6,9\text{-}C_3B_7H_9{}^-)$ salt has shown that the $6\text{-}CH_3\text{-}\textit{nido}\text{-}5,6,9\text{-}C_3B_7H_9{}^-$ tricarbadecaboranyl anion has a *nido*-cage geometry based on an octadecahedron missing the unique six-coordinate vertex. The resulting six-membered open face is puckered, with two of the cage carbons (C6 and C9) occupying the low-coordinate cage positions above the plane of the four remaining atoms (C5, B7, B8, and B10). The Li^+ ion is centered over the open face and is solvated by two acetonitrile molecules. The reactions of the $6\text{-}CH_3\text{-}\textit{nido}\text{-}5,6,9\text{-}C_3B_7H_9{}^-$ anion with various vanadium halide salts, including VCl_4, VCl_3, and VBr_2, each resulted in the isolation of the same five paramagnetic products (**2**−**6**) of composition $V(CH_3\text{-}C_3B_7H_9)_2$. X-ray crystallographic determinations of **2**−**5** showed that the complexes consist of two octadecahedral VC_3B_7 fragments sharing a common vanadium vertex and established their structures as *commo-V*-(1-V-4′-CH$_3$-2′,3′,4′-C$_3$B$_7$H$_9$)(1-V-2-CH$_3$-2,3,4-C$_3$B$_7$H$_9$) (**2**), *commo-V*-(1-V-5′-CH$_3$-2′,3′,5′-C$_3$B$_7$H$_9$)(1-V-4-CH$_3$-2,3,4-C$_3$B$_7$H$_9$) (**3**), *commo-V*-(1-V-5′-CH$_3$-2′,3′,5′-C$_3$B$_7$H$_9$)(1-V-2-CH$_3$-2,3,4-C$_3$B$_7$H$_9$) (**4**), and *commo-V*-(1-V-2-CH$_3$-2,3,4-C$_3$B$_7$H$_9$)$_2$ (**5**). These complexes can be considered as tricarbadecaboranyl analogues of vanadocene, $(\eta^5\text{-}C_5H_5)_2V$. However, unlike vanadocene, these complexes are air- and moisture-stable and have only one unpaired electron. The five complexes differ with respect to one another in that they either (1) contain different enantiomeric forms of the $CH_3\text{-}C_3B_7H_9$ cages, (2) have a different twist orientation of the two cages, or (3) have the methyl group of the $CH_3\text{-}C_3B_7H_9$ cage located in either the 2 or 4 position of the cage. Subsequent attempts to oxidize the compounds with reagents such as Br_2 and Ag^+ were unsuccessful, illustrating the ability of the tricarbadecaboranyl anion to stabilize metals in low oxidation states. Consistent with this, both the electrochemical oxidation and the reduction of **2** were much more positive than those of the same oxidation state changes in vanadocene. The one-electron reduction of **2** is a remarkable 2.9 V positive of that of Cp_2V.

Introduction

The tricarbadecaboranyl anion, $6\text{-}CH_3\text{-}\textit{nido}\text{-}5,6,9\text{-}C_3B_7H_9{}^-$,[4] has proven to be a highly versatile ligand that can function as a monoanionic η^6, six-electron or η^4, four-electron donor to transition metals.[5] Because of their equivalent charges and electron-donating abilities, the coordination properties of the tricarbadecaboranyl and cyclopentadienide monoanions are similar (Figure 1). As a result, metallatricarbadecaboranyl analogues of the metallocenes are possible in which both the complexes and the metals have the same overall charges and oxidation states, respectively, as the metallocenes. However, metallatricarbadecaboranyl complexes have proven[5] to have significantly greater oxidative, chemical, thermal, and hydrolytic stabilities than their metallocene counterparts. These properties of the metallatricarbadecaboranes may prove useful in the design of new metallocene-like complexes with enhanced and/or complementary chemical and bioactive properties. We have, in

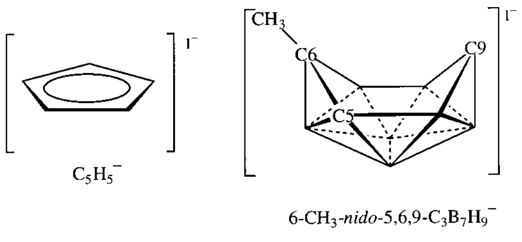

Figure 1. Comparison of the structures of the cyclopentadienyl and tricarbadecaboranyl anions.

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fact, already demonstrated[6] that cationic ferratricarbadecaboranyl complexes have potent cytotoxic activities which are different than those previously found for $[(\eta^5\text{-}C_5H_5)_2Fe]^+X^-$ complexes. As part of our interest in the design and properties of new types of bioactive complexes, we have been investigating the synthesis and structural characterization of the metallatricarbadecaboranyl analogues of early metal $(\eta^5\text{-}C_5H_5)_2MX_2$ complexes (M = Ti, V, Nb, Mo, and W) that are established metallocene antitumor agents.[7] In this paper, we report both the first structural determination of 6-CH_3-*nido*-5,6,9-$C_3B_7H_9^-$ and our studies of the reactions of this anion with various vanadium halides that have surprisingly led to the formation of a series of air- and water-stable vanadatricarbadecaboranyl analogues, i.e., $(CH_3\text{-}C_3B_7H_9)_2V$, of vanadocene $(\eta^5\text{-}C_5H_5)_2V$, rather than of the vanadocene dihalides, $(\eta^5\text{-}C_5H_5)_2VX_2$.

Experimental Section

General Synthetic Procedures, Materials, and Physical Methods. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen or argon atmosphere using the high-vacuum or inert atmosphere techniques described by Shriver and Drezdzon.[8] $[Li(CH_3CN)_2^+](6\text{-}CH_3\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-)$ in toluene was prepared via modifications to previously reported methods,[4,5a] as detailed below. The VBr_2 and VCl_3 (Strem), VCl_4, $Na^+(C_5H_5^-)$/THF, and LiH (Aldrich) were used as received. Acetonitrile (Fisher or Baker) was dried over P_2O_5, transferred onto activated 4-Å molecular sieves, and stored under vacuum. Toluene (Fisher or Baker) was dried over sodium benzophenone ketyl and freshly distilled before use. Other solvents (Fisher or Baker) were distilled from appropriate drying agents under nitrogen before use. Preparative thin-layer chromatography was conducted on 0.5-mm (20 × 20 cm) silica gel F-254 plates (Merck 5744). Silica gel (230−400 mesh, Merck) was used for column chromatography.

The ^{11}B NMR spectra at 64.3 MHz and ^1H NMR spectra at 200 MHz were obtained on a Bruker AC 200 Fourier transform spectrometer equipped with the appropriate decoupling accessories. The effective magnetic moments of the complexes were measured by using the Evans method.[9] High- and low-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer using negative ionization techniques. IR spectra were obtained on a Perkin-Elmer System 2000 FTIR spectrometer. Elemental analyses were performed at the University of Pennsylvania microanalysis facility or Robertson Microlit Laboratories, Inc., Madison, NJ. Melting points were obtained on a standard melting point apparatus and are uncorrected.

Electrochemical Procedures. Electrochemical experiments were carried out in a Vacuum Atmospheres drybox under nitrogen at ambient temperatures. A Ag/AgCl electrode served as the experimental reference electrode. The potentials in this paper are referred, however, to that of the ferrocene/ferrocenium couple (Fc), which was obtained by adding ferrocene to the solution at an appropriate point in the experiment. The supporting electrolyte was 0.1 M $[NBu_4][PF_6]$. Tetrahydrofuran (THF) was distilled from potassium under bulb-to-bulb static vacuum immediately prior to use and then taken into the drybox. Electrochemical glassware was removed from a 110 °C oven and put immediately into the antechamber of the drybox. A standard three-electrode electrochemical cell was employed, utilizing a luggin capillary to minimize solution resistance. Pt working electrodes were pretreated by polishing with diamond pastes. A large Pt basket was used as the working electrode in bulk electrolyses. The potentiostat was a Princeton Applied Research model 273 system interfaced to a personal computer.

Preparation of $[Li(CH_3CN)_2^+](6\text{-}CH_3\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-)$ (1) in Toluene. In a glovebag under nitrogen, 0.090 g (11.3 mmol, 0.95 equiv) of LiH and 1.34 g (11.9 mmol, 1.0 equiv) of *arachno*-4,6-$C_2B_7H_{13}$ were added to a two-neck round-bottom flask fitted with a stirbar, septum, and vacuum connector/nitrogen inlet. The flask was then connected to a vacuum line, and dry CH_3CN was condensed into the flask at −196 °C. After being stirred at room temperature for 45 min, the reaction mixture was filtered in a glovebag under nitrogen to remove any unreacted LiH. The filtrate was then heated at reflux for 1−2 days under N_2. When ^{11}B NMR analysis indicated that the reaction was complete, the solution was filtered under nitrogen, and the CH_3CN was then removed from the filtrate by vacuum evaporation to give an oily residue in 85% yield (1.44 g, 10.1 mmol). Toluene was added to the oily residue to make an ~0.50 M solution, which was stored in the refrigerator. The exact concentration of the stock solution was then determined by integrating the resonances in the ^{11}B NMR spectrum of a $B_{10}H_{14}$ sample of known concentration and comparing that value with the integrated value of the resonances of the stock $[Li(CH_3CN)_2^+](6\text{-}CH_3\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-)$ solution. Spectroscopic data for **1** are consistent with those reported previously.[4]

Reaction of 1 with VCl_4. A toluene solution of **1** (4.05 mL of 0.7 M, 3.0 mmol) was added dropwise to a stirring solution of VCl_4 (0.16 mL, 1.50 mmol) in toluene (35 mL), resulting in a dark green solution. After being stirred for 36 h at reflux, the reaction mixture was opened to the air and filtered through a small amount of silica gel. The silica gel was washed with CH_2Cl_2 to extract any remaining product from the silica gel. The solvent was vacuum evaporated and the resulting dark green solid chromatographed on TLC plates (silica gel/hexane) to give five bands (overall 15% yield, 0.073 g, 0.23 mmol).

For **2**: *commo*-*V*-(1-V-4′-CH_3-2′,3′,4′-$C_3B_7H_9$)(1-V-2-CH_3-2,3,4-$C_3B_7H_9$), dark green, $R_f = 0.49$, 0.023 g, (0.07 mmol, 5%); mp 161 °C; $\mu = 1.43\ \mu B$; HRMS calcd for $^{12}C_8{}^1H_{24}{}^{11}B_{14}{}^{51}V_1$ 325.2620, found 325.2618; IR (KBr, cm^{-1}) 3050 (m), 3021 (w), 2930 (w), 2862 (w), 2603 (m), 2555 (s), 1542 (w), 1456 (w), 1382 (w), 1159 (w), 1040 (w), 928 (m), 854 (w), 720 (m), 669 (s), 651 (w), 592 (w). Anal. Calcd for $C_8H_{24}B_{14}V$: C, 29.79; H, 7.50. Found: C, 29.68; H, 7.57.

For **3**: *commo*-*V*-(1-V-5′-CH_3-2′,3′,5′-$C_3B_7H_9$)(1-V-4-CH_3-2,3,4-$C_3B_7H_9$), $R_f = 0.39$, 0.0083 g (0.03 mmol, 2%), emerald green; mp 169 °C; $\mu = 1.47{-}1.7\ \mu B$; HRMS calcd for $^{12}C_8{}^1H_{24}{}^{11}B_{14}{}^{51}V_1$ 325.2620, found 325.2621; IR (KBr, cm^{-1}) 3051 (m), 3022 (w), 2930 (w), 2861 (w), 2602 (m), 2557 (s), 1541 (w), 1444 (w), 1382 (w), 1159 (w), 1040 (w), 921 (w), 854 (w), 720 (m), 669 (s), 650 (m). Anal. Calcd for $C_8H_{24}B_{14}V$: C, 29.79; H, 7.50. Found: C, 30.23; H, 7.58.

For **4**: *commo*-*V*-(1-V-5′-CH_3-2′,3′,5′-$C_3B_7H_9$)(1-V-2-CH_3-2,3,4-$C_3B_7H_9$), $R_f = 0.34$, 0.015 g (0.05 mmol, 3%), light green; mp 195−196 °C; $\mu = 1.49\ \mu B$; HRMS calcd for $^{12}C_8{}^1H_{24}{}^{11}B_{14}{}^{51}V_1$ 325.2620, found 325.2633; IR (KBr, cm^{-1}) 3047 (m), 3044 (m), 3025 (w), 2932 (w), 2862 (w), 2602 (s), 2561 (vs), 2539 (s), 1444 (m), 1384 (m), 1122 (w), 1043 (w), 992 (w), 956 (w), 930 (w), 858 (w), 719 (m), 668 (w), 652 (w). Anal. Calcd for $C_8H_{24}B_{14}V$: C, 29.79; H, 7.50. Found: C, 29.62; H, 7.56.

For **5**: *commo*-*V*-(1-V-2-CH_3-2,3,4-$C_3B_7H_9$)$_2$, $R_f = 0.15$, 0.016 g (0.05 mmol, 3%), gray; mp 166 °C; $\mu = 1.48\ \mu B$; HRMS calcd for $^{12}C_8{}^1H_{24}{}^{11}B_{14}{}^{51}V_1$ 325.2620, found 325.2611; IR (KBr, cm^{-1}) 2956 (w), 2561 (s), 2503 (m), 1445 (m), 1192 (m), 982 (m), 883 (w), 731 (m), 644 (w), 548 (w). Anal. Calcd for $C_8H_{24}B_{14}V$: C, 30.07; H, 7.57. Found: C, 29.68; H, 7.57.

For **6**: *commo*-*V*-(1-V-CH_3-$C_3B_7H_9$)(1-V-CH_3-$C_3B_7H_9$), $R_f = 0.27$, 0.011 g (0.03 mmol, 2%), brown green; mp 172 °C; $\mu = 1.45\ \mu B$; HRMS calcd for $^{12}C_8{}^1H_{24}{}^{11}B_{14}{}^{51}V_1$ 325.2620, found 325.2628; IR (KBr, cm^{-1}) 3047 (m), 3044 (m), 3024 (m), 2932 (w), 2860 (w), 2561 (vs), 2357 (w), 2259 (w), 1438 (m), 1383 (m), 1194 (m), 1042 (w), 717 (w), 648 (w), 547 (w). Anal. Calcd for $C_8H_{24}B_{14}V$: C, 29.79; H, 7.50. Found: C, 29.81; H, 7.55.

Reaction of 1 with VBr_2. A toluene solution of **1** (6.84 mL of 0.5 M, 3.4 mmol) was added dropwise to a stirring solution of VBr_2 (0.32 g, 1.5 mmol) in toluene (35 mL), resulting in a dark green solution.

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After being stirred for 36 h at reflux, the reaction was worked up as described above to give five compounds in an overall yield of 47% (0.23 g, 0.70 mmol): **2**, 0.082 g, 0.25 mmol, 17%; **3**, 0.019 g, 0.06 mmol, 4%; **4**, 0.048 g, 0.15 mmol, 10%; **5**, 0.037 g, 0.11 mmol, 7.6%; **6**, 0.047 g, 0.15 mmol, 9.8%.

Reaction of 1 with VCl_3. A toluene solution of **1** (5.85 mL of 0.5 M, 3.0 mmol) was added dropwise to a stirring solution of VCl_3 (0.25 g, 1.58 mmol) in toluene (35 mL), resulting in a dark green solution. After being stirred for 36 h at reflux, the reaction was worked up as described above to give the five compounds in an overall yield of 27% (0.138 g, 0.42 mmol): **2**, 0.055 g, 0.17 mmol, 11%; **3**, 0.011 g, 0.03 mmol, 2%; **4**, 0.020 g, 0.06 mmol, 4%; **5**, 0.032 g, 0.10 mmol, 6%; **6**, 0.021 g, 0.07 mmol, 4%.

Reaction of 1 with VBr_2 and $Na^+(C_5H_5^-)$. A toluene solution of **1** (3.04 mL of 0.5 M, 1.5 mmol) and a THF solution of $Na^+(C_5H_5^-)$ (0.76 mL of 2.0 M, 1.5 mmol) were added dropwise to a stirring solution of VBr_2 (0.28 g, 1.3 mmol) in toluene (35 mL), resulting in a green solution. After being stirred for 36 h at reflux, the reaction was worked up as described above to give the five compounds in an overall yield of 27% (0.114 g, 0.35 mmol): **2**, 0.037 g, 0.11 mmol, 9%; **3**, 0.013 g, 0.04 mmol, 3%; **4**, 0.023 g, 0.07 mmol, 5%; **5**, 0.017 g, 0.05 mmol, 4%; **6**, 0.024 g, 0.07 mmol, 6%.

Reactions of 2 and 4 with Oxidizing Agents. The oxidations of complexes **2** and **4** were attempted via various methods. A typical experiment was carried out in a one-neck 10-mL round-bottom flask containing a stirbar and either complex **2** or **4** (0.01 g, 0.03 mmol) dissolved in CH_2Cl_2. A sample of Br_2 (3.09 μL, 0.06 mmol) in CH_2Cl_2 was added dropwise. There was no evidence of reaction after stirring overnight. Additional attempts at oxidation with $Ag^+AsF_6^-/(CH_3CH_2)_2O$ and $Ag^+SbF_6^-/(CH_3CH_2)_2O$ were also unsuccessful.

Crystallographic Data. Single crystals of $[Li(CH_3CN)_2^+](6\text{-}CH_3\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-)$ (**1**, UPenn #3092) were grown in an inert atmosphere at 0 °C from toluene. The air-sensitive crystals were removed from the flask in a drybox under nitrogen and covered with silicon oil for mounting. Single crystals of **2** (UPenn #3115), **3** (UPenn #3116), **4** (UPenn #3119), and **5** (UPenn #3083) were grown via slow evaporation from hexanes or a 50:50 hexanes/methylene chloride mixture in air.

Collection and Reduction of the Data. X-ray intensity data were collected on a Rigaku R-AXIS IIc area detector employing graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Indexing was performed from a series of oscillation images. A hemisphere of data was collected using 8° oscillation angles for **1**, **3**, **4**, and **5**, 10° oscillation angles for **2**, and a crystal-to-detector distance of 82 mm. Oscillation images were processed using bioteX,[10] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the teXsan[11] program package for further processing and structure solution on a Silicon Graphics Indigo R4000 computer. The intensity data were corrected for Lorentz and polarization effects, but not for absorption.

Solution and Refinement of the Structures. The structures were solved by direct methods (SIR92).[12] Refinement was by full-matrix least-squares based on F^2 using SHELXL-93.[13] All reflections were used during refinement (F^2's that were experimentally negative were replaced by $F^2 = 0$). The weighting schemes were as follow: for **1**, $w = 1/[\sigma^2(F_o^2) + 0.0490P^2 + 1.5402P]$; for **2**, $w = 1/[\sigma^2(F_o^2) + 0.0580P^2 + 14.0764P]$; for **3**, $w = 1/[\sigma^2(F_o^2) + 0.0490P^2 + 1.5402P]$; for **4**, $w = 1/[\sigma^2(F_o^2) + 0.0544P^2 + 1.3896P]$; and for **5**, $w = 1/[\sigma^2(F_o^2) + 0.0000P^2 + 5.2400P]$, where $P = (F_o^2 + 2F_c^2)/3$.

For **1**, **2**, **3**, and **5**, hydrogen atoms were included as constant contributions to the structure factors and were not refined. For **4**, the hydrogens were refined isotropically. Crystal and refinement data are given in Table 1.

Results and Discussion

Improved Synthesis of the Tricarbadecaboranyl Anion and Structural Characterization of $[Li(CH_3CN)_2^+](6\text{-}CH_3\text{-}$*nido*$\text{-}5,6,9\text{-}C_3B_7H_9^-)$. The original synthesis[4] of the $6\text{-}CH_3\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-$ tricarbadecaboranyl monoanion involved the reaction of CH_3CN with $Na^+(arachno\text{-}4,6\text{-}C_2B_7H_{12}^-)$ in ethereal solvents and was proposed to occur by the reaction sequence shown in Figure 2. This sequence involves the initial nucleophilic attack of the *arachno*-$4,6\text{-}C_2B_7H_{12}^-$ anion at the positively charged cyano carbon of the acetonitrile, reduction of the cyano group, and then deammination and insertion of the acetonitrile CH_3C- group into the cage framework. The initially reported multistep synthesis took 2 weeks for completion. Plumb et al.[5a] improved upon the synthesis by optimizing the reactant ratios and using acetonitrile as the solvent for both reaction steps. These changes shortened the reaction time to 4 days.

We have now found that in reactions employing only 0.95 equiv[5a] of LiH as the deprotonating agent and acetonitrile as the solvent, the reaction times are further decreased. Thus, 10−15 mmol scale reactions are complete in only 2 days and give typical isolated yields of 85% based on the starting *arachno*-$4,6\text{-}C_2B_7H_{13}$. It is also significant that the resulting solvated salt $[Li(CH_3CN)_2^+](6\text{-}CH_3\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-)$ (**1**), unlike the previous $Na^+(6\text{-}CH_3\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-)$ salt, has reasonable solubility in toluene. This is important since it allows subsequent reactions with metal reagents to be carried out in nonethereal solvents, thereby reducing cage fragmentation products. The $[Li(CH_3CN)_2^+](6\text{-}CH_3\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-)$ salt (**1**) can also be isolated as a crystalline solid. This has allowed the first X-ray crystallographic confirmation of the structure of the tricarbadecaboranyl anion.

As can be seen in the ORTEP representation given in Figure 3, the observed structure of $[Li(CH_3CN)_2^+](6\text{-}CH_3\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-)$ is clearly in agreement with the previously proposed[4] reaction sequence in Figure 2, confirming that the insertion of the CH_3C group in the reaction of *arachno*-$4,6\text{-}C_2B_7H_{12}^-$ with CH_3CN has occurred at a position adjacent to one of the original *arachno*-$4,6\text{-}C_2B_7H_{12}^-$ cage carbons to produce the new tricarbadecaboranyl framework.

In agreement with its 24-skeletal-electron count,[14] the tricarbadecaboranyl anion adopts an open, *nido*-cage geometry based on an octadecahedron from which the unique six-coordinate vertex has been removed. The resulting six-membered open face is puckered, with two of the cage carbons (C6 and C9) occupying the low-coordinate cage positions above the plane of the four remaining atoms (C5, B7, B8, and B10). The C5−C6 distance (1.495(7) Å) and the B−C and B−B distances in the cage (Table 2) are all in the normal ranges observed in carbaborane clusters. The Li^+ ion is centered over the six-membered open face and is solvated by two acetonitrile molecules. The distances from the Li^+ to the four-coordinated carbons C6 (2.272(6) Å) and C9 (2.151(6) Å) are much shorter than the distances to the other four atoms, Li^+−C5 (2.689(9) Å), Li^+−B7 (2.682(9) Å), Li^+−B8 (2.619(9) Å), and Li^+−B10 (2.616(9) Å). The Li^+−C6 and Li^+−C9 bond distances are somewhat shorter than those that have been found in other

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Table 1. Crystallographic Data Collection and Structure Refinement Information

compound	**1**	**2**	**3**	**4**	**5**
formula	$LiC_8B_7H_{18}N_2$	$VC_8B_{14}H_{24}$	$VC_8B_{14}H_{24}$	$VC_8B_{14}H_{24}$	$VC_8B_{14}H_{24}$
formula weight	224.85	322.55	322.55	322.55	322.55
crystal class	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	*Aba*2 (No. 41)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	*Pnna* (No. 52)
Z	8	4	4	4	4
cell constants					
a (Å)	13.7522(4)	18.260(2)	7.8016(3)	17.9968(3)	13.2530(8)
b (Å)	16.1748(5)	7.8315(10)	24.0340(12)	7.8842(2)	12.5390(7)
c (Å)	13.2421(4)	12.751(2)	9.7784(4)	12.5502(3)	10.4840(6)
β (deg)		105.480(9)	108.270(3)	105.730(2)	
V (Å^3)	2945.6(2)	1757.3(4)	1741.06(13)	1714.06(7)	1742.2(2)
μ (cm^{-1})	0.52	5.46	5.51	5.60	5.51
crystal size, mm	0.42 × 0.30 × 0.05	0.50 × 0.25 × 0.03	0.42 × 0.14 × 0.08	0.45 × 0.35 × 0.075	0.20 × 0.03 × 0.03
D_{calc} (g/cm^3)	1.014	1.219	1.231	1.250	1.230
F(000)	944	660	660	660	154
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
λ (Å)	0.71069	0.71069	0.71069	0.71069	0.71069
2θ range (deg)	5.04−49.62	6.16−50.70	5.50−50.68	5.68−50.78	4.96−49.62
temperature, K	233	203	209	210	233
hkl collected	$-15 \le h \le 16$ $-19 \le k \le 18$ $-15 \le l \le 15$	$-18 \le h \le 21$ $-9 \le k \le 9$ $-14 \le l \le 12$	$0 \le h \le 9$ $-28 \le k \le 28$ $-11 \le l \le 11$	$-19 \le h \le 21$ $-9 \le k \le 9$ $-14 \le l \le 15$	$-15 \le h \le 14$ $-14 < k \le 14$ $-12 \le l \le 12$
no. reflns measd	15 296	9311	14 110	13 998	8341
no. unique reflns	2537	2885	3163	2946	1497
R_{int}	0.0575	0.0793	0.0416	0.0349	0.1066
no. obsd reflns ($F > 4\sigma$)	2332	2624	2823	2780	1317
no. reflns used in refinement	2537	2885	3163	2946	1497
no. parameters	163	209	304	305	154
R indices ($F > 4\sigma$)^a	$R_1 = 0.0765$ $wR_2 = 0.1662$	$R_1 = 0.0999$ $wR_2 = 0.2564$	$R_1 = 0.0443$ $wR_2 = 0.1044$	$R_1 = 0.0448$ $wR_2 = 0.1087$	$R_1 = 0.1154$ $wR_2 = 0.1679$
R indices (all data)^a	$R_1 = 0.0841$ $wR_2 = 0.1709$	$R_1 = 0.1081$ $wR_2 = 0.2614$	$R_1 = 0.0525$ $wR_2 = 0.1096$	$R_1 = 0.0496$ $wR_2 = 0.1122$	$R_1 = 0.1347$ $wR_2 = 0.1742$
GOF	1.203	1.158	1.011	1.10	1.389
final difference peaks, e/Å^3	+0.135, −0.175	+0.878, −0.648	+0.215, −0.461	+0.288, −0.312	+0.247, −0.495

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

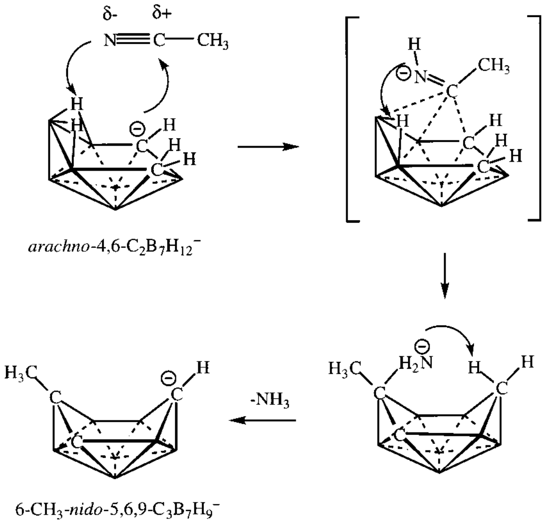

Figure 2. Previously proposed reaction sequence for the synthesis of 6-CH_3-*nido*-5,6,9-$C_3B_7H_9^-$ from the reaction of *arachno*-4,6-$C_2B_7H_{12}^-$ with CH_3CN.

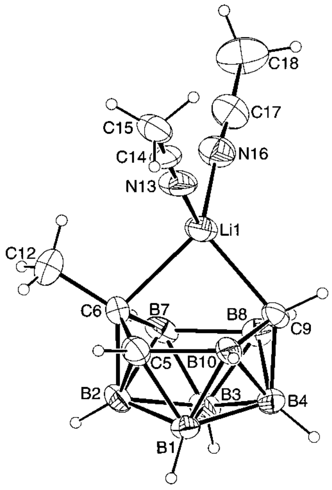

Figure 3. ORTEP drawing of the structure of $[Li(CH_3CN)_2^+](6\text{-}CH_3\text{-}$*nido*-5,6,9-$C_3B_7H_9^-)$ (**1**).

lithiocarbaboranes, while those between Li^+−C5, Li^+−B7, Li^+−B8, and Li^+−B10 are longer. For example, in the compound *closo-exo*-4,5-{(μ-H)$_2$Li[$(CH_3)_2NCH_2)_2$]}-1-Li[$(CH_3)_2NCH_2)_2$]-2,3-$(Si(CH_3)_2$-2,3-$C_2B_4H_4$, the Li to cage carbon distances are 2.367(9) and 2.296(9) Å.[15]

Syntheses and Structural Characterizations of Vanadatricarbadecaboranyl Complexes. Attempts were made to synthesize the tricarbadecaboranyl analogues, i.e., $(CH_3\text{-}C_3B_7H_9)_2V$, $(CH_3\text{-}C_3B_7H_9)_2VX$, and $(CH_3\text{-}C_3B_7H_9)_2VX_2$, of vanadocene $(\eta^5\text{-}C_5H_5)_2V$ and the vanadocene halides $(\eta^5\text{-}C_5H_5)_2VX$ and $(\eta^5\text{-}C_5H_5)_2VX_2$.[16] Reactions of the 6-CH_3-*nido*-5,6,9-$C_3B_7H_9^-$ anion with the vanadium halides VBr_2, VCl_3, and VCl_4 were examined. However, regardless of the reaction stoichiometry and particular metal halide employed, only $(CH_3\text{-}C_3B_7H_9)_2V$ complexes were obtained. Likewise, reactions of VBr_2 with mixtures of the 6-CH_3-*nido*-5,6,9-$C_3B_7H_9^-$ and $C_5H_5^-$ anions gave only $(CH_3\text{-}C_3B_7H_9)_2V$ complexes. Best

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Table 2. Comparison of Intramolecular Distances (Å) in Compounds **1**, **2**, **3**, **4**, and **5**

1	bond	**2**	**3**	**4**	**5**
2.272(6)	V−C2	2.073(8)	2.048(2)	2.070(2)	2.063(6)
Li^+−C6		2.064(8)	2.031(2)	2.053(3)	
2.151(6)	V−C3	2.024(7)	2.028(2)	2.022(2)	2.042(7)
Li^+−C9		2.051(7)	2.036(3)	2.043(3)	
2.689(9)	V−C4 or	2.343(8)	2.383(2)	2.337(2)	2.352(7)
Li^+−C5	(V−C5′)	2.391(8)	2.373(2)	2.401(2)	
2.682(9)	V−B5 or	2.411(8)	2.391(3)	2.389(3)	2.391(7)
Li^+−B7	(V−B7′)	2.442(9)	2.414(3)	2.424(3)	
2.619(9)	V−B6 or	2.380(8)	2.409(3)	2.387(3)	2.379(7)
Li^+−B8	(V−B4′)	2.434(9)	2.398(3)	2.419(3)	
2.616(9)	V−B7 or	2.363(8)	2.368(3)	2.351(3)	2.375(10)
Li^+−B10	(V−B6′)	2.390(9)	2.352(3)	2.370(3)	
1.495(7)	C2−C4 or	1.542(10)	1.520(4)	1.533(3)	1.509(9)
C5−C6	(C2′-C5′)	1.544(11)	1.521(3)	1.507(4)	
1.468(8)	C2−B5 or	1.601(11)	1.577(4)	1.591(4)	1.584(9)
C6−B7	(C2′-B4′)	1.576(12)	1.581(4)	1.573(4)	
1.782(7)	C4−B7 or	1.730(11)	1.743(4)	1.718(4)	1.705(12)
C5−B10	(C5′-B6′)	1.742(12)	1.732(4)	1.744(4)	
1.844(8)	B5−B6 or	1.854(12)	1.842(4)	1.844(4)	1.844(11)
B7−B8	(B4′-B7′)	1.854(14)	1.841(4)	1.846(5)	
1.545(7)	C3−B6 or	1.585(11)	1.589(4)	1.588(4)	1.596(10)
C9−B8	(C3′-B7′)	1.568(12)	1.588(4)	1.582(4)	
1.505(7)	C3−B7 or	1.594(11)	1.591(4)	1.596(4)	1.575(11)
C9−B10	(C3′-B6′)	1.592(12)	1.588(4)	1.589(4)	

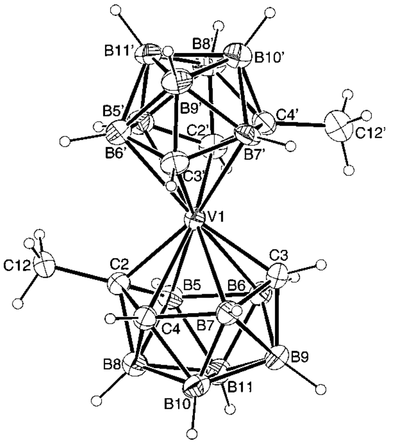


Figure 4. ORTEP drawing of the structure of *commo-V*-(1-V-4′-CH_3-2′,3′,4′-$C_3B_7H_9$)(1-V-2-CH_3-2,3,4-$C_3B_7H_9$) (**2**).

yields (48% total isolated yields) of the $(CH_3\text{-}C_3B_7H_9)_2V$ complexes were obtained in the reactions with VBr_2 (eq 1).

$$2Li^+(6\text{-}CH_3\text{-}\mathit{nido}\text{-}5,6,9\text{-}C_3B_7H_9)^- + VBr_2 \xrightarrow[\text{toluene}]{\Delta} (CH_3\text{-}C_3B_7H_9)_2V + 2LiBr \quad (1)$$

$$\mathbf{2{-}6}$$

Separation of the products was accomplished via preparative TLC (silica gel plates/hexane eluent) and resulted in the isolation of five air- and moisture-stable products. Mass spectrometry and elemental analyses established that all compounds had the $(CH_3\text{-}C_3B_7H_9)_2V$ composition. Evan's method[9] measurements of magnetic moments indicated that the complexes have one unpaired electron. Vanadocene is a 15-electron, high-spin complex with three unpaired electrons in an $e_{2g}{}^2a^n{}_{1g}{}^1$ configuration.[16] Because of the lower symmetry of the vanadatricarbadecaboranes, the molecular orbital diagram for vanadocene cannot be directly applied. However, the fact that the vanadatricarbadecaboranes have only one unpaired electron is consistent with a low-spin configuration resulting from a stronger bonding interaction of the vanadium with the tricarbadecaboranyl compared to the cyclopentadienyl ligand.

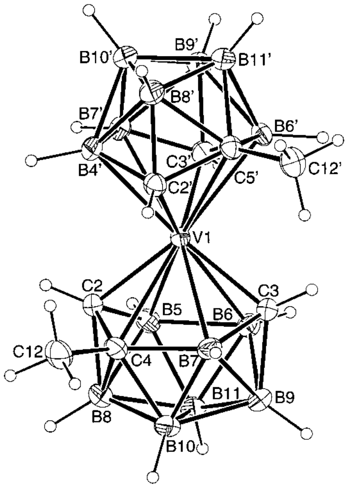


Figure 5. ORTEP drawing of the structure of *commo-V*-(1-V-5′-CH_3-2′,3′,5′-$C_3B_7H_9$)(1-V-4-CH_3-2,3,4-$C_3B_7H_9$) (**3**).

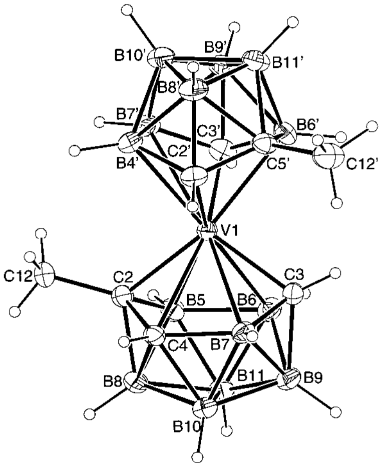


Figure 6. ORTEP drawing of the structure of *commo-V*-(1-V-5′-CH_3-2′,3′,5′-$C_3B_7H_9$)(1-V-2-CH_3-2,3,4-$C_3B_7H_9$) (**4**).

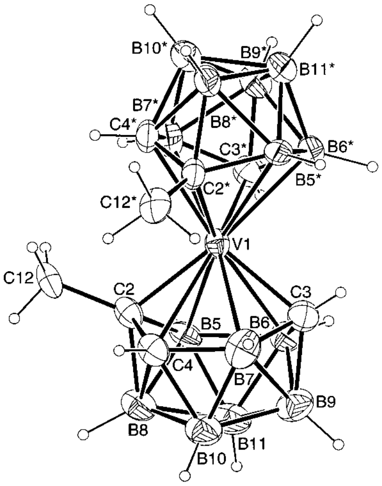


Figure 7. ORTEP drawing of the structure of *commo-V*-(1-V-2-CH_3-2,3,4-$C_3B_7H_9$)$_2$ (**5**).

Since the products were paramagnetic, they could not be characterized via NMR. However, it was possible to establish the structures of compounds **2**−**5** by crystallographic determinations as *commo-V*-(1-V-4′-CH_3-2′,3′,4′-$C_3B_7H_9$)(1-V-2-CH_3-2,3,4-$C_3B_7H_9$) (**2**), *commo-V*-(1-V-5′-CH_3-2′,3′,5′-$C_3B_7H_9$)(1-V-4-CH_3-2,3,4-$C_3B_7H_9$) (**3**), *commo-V*-(1-V-5′-CH_3-2′,3′,5′-

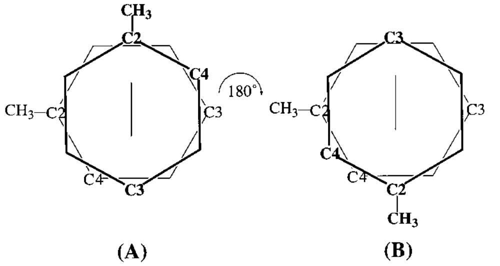
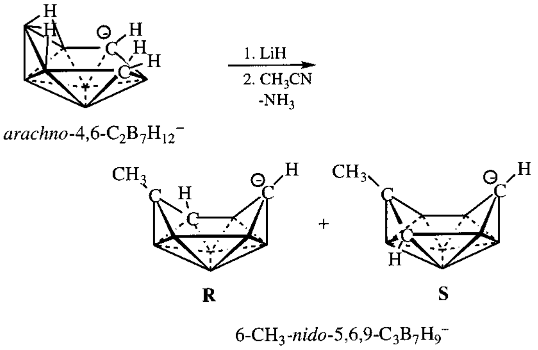


Figure 8. The two possible twist orientations of the two cages.

$C_3B_7H_9$)(1-V-2-CH_3-2,3,4-$C_3B_7H_9$) (**4**), and *commo*-*V*-(1-V-2-CH_3-2,3,4-$C_3B_7H_9$)2 (**5**).

As can be seen from the ORTEP drawings in Figures 4−7, the complexes can be considered analogues of vanadocene, (η^5-C_5H_5)$_2$V, in which the vanadium is sandwiched between the two tricarbadecaboranyl monoanions. The vanadium is centered over the six-membered, puckered open faces of the two cages. The planes containing three boron (B5, B6, B7) atoms and one carbon (C4) atom on the six-membered open faces of each of the two cages are approximately parallel: dihedral angles **2**, 4(2)°; **3**, 6(1)°; **4**, 4(1)°; **5**, 7.7°(2). The two cages in each complex are aligned ~90° to one another, as measured by the dihedral angle between the C2−V1−C3 and C2′−V1−C3′ planes: **2**, 89.6(2)°; **3**, 88.18(4)°; **4**, 89.81(7)°; **5**, 87.2(2)°. Several isomeric products are produced in these reactions. This is the result of three factors. First, as shown in eq 2, the anion is synthesized as a racemic mixture.



(2)

Thus, when a bis-cage complex is formed, two types of isomeric complexes must result: (1) complexes such as **2** and **5**, in which the two cages are of the same enantiomeric type, S−V−S or R−V−R, or (2) complexes that have two different enantiomeric forms of the anion, resulting in R−V−S complexes (compounds **3** and **4**). Second, as previously demonstrated,[5,17] cage rearrangements can readily occur in these complexes to produce isomers in which one (compounds **2** and **4**) or both (compound **3**) of the methyl substituents originally present at the 2 cage positions (as in compound **5**) have migrated to the 4 (or 5) cage position. Finally, as illustrated in Figure 8, two different twist orientations of the two cages are possible. Thus, configuration **A**, in which the C4 (C5′) carbons of both cages are located on opposite sides of the C2−V−C3 planes, is found in **2**, while configuration **B**, having the C4 (C5′) carbons on the same side of the C2−V−C3 planes, is found in **3**, **4**, and **5**.

Selected bond distances for **1** and complexes **2**−**5** are compared in Table 2. The shortest distances (2.02−2.07 Å) between the vanadium and the tricarbadecaboranyl ligand are those with the two carbons, C2 and C3, puckered out of the six-membered face. The distances to the other four atoms on the face, C4, B5, B6, and B7, are longer, 2.34−2.44 Å. As pointed out previously,[18] the orbitals extending from the open face of even a planar polyhedral cluster are orientated more directly toward the metal than in a cyclopentadienyl ring. This enhances the overlap of the metal and ligand orbitals and strengthens the bonding. In the case of the tricarbadecaboranes, even stronger interactions are possible because the puckered ring structure allows close approach of the metal to the C2 and C3 carbons.

When the methyl group is present at the C2 carbon, the V−C2 distance is found to be considerably lengthened compared to the V−C3 distance in the same cage. For example, in **2** the V−C2 distance is 2.073(8) Å, whereas V−C3 is 2.024(7) Å, and in **4**, V−C2 is 2.070(2) Å versus V−C3, 2.022(2) Å. These differences can most likely be attributed to steric interactions of the methyl group with the opposite cage. For those cages in which the methyl is attached to C4, the V−C2 and V−C3 distances are approximately equal. The V−C2 and V−C3 bond lengths in **2**−**5** are significantly shorter than the V−C bond lengths in either vanadocene,[19] (η^5-C_5H_5)$_2$V (2.269(6) Å), or the vanadadicarbaborane,[20] 1-(η^8-C_8H_8)V-[2,3-(C_2H_5)$_2C_2B_4H_4$], V−C2 (2.269(10) Å) and V−C3 (2.190(9) Å).

Vanadocene readily reacts with π-acceptor ligands, such as isocyanides, to form adducts of the formula (η^5-C_5H_5)$_2$V(CNR), but it was found that the vanadatricarbadecaboranes do not react with Bu^{t}NC.[21] This difference may be a consequence of the fact that the vanadium in vanadocene is considerably more accessible to incoming ligands than the vanadatricarbadecaboranes. The two parallel cyclopentadienyl ligands of vanadocene can readily bend back to open a coordination site for an incoming ligand.[16] However, because of the twist orientation of the two cages in the vanadatricarbadecaboranes, the vanadium is almost totally encapsulated, preventing attack by a Lewis base. Likewise, because of the interlocked orientation of the two cages, there is no simple movement, such as cyclopentadienyl bending, of the two cages that will open a coordination site.

The VC_3B_7 cage fragments show no significant distortions from an octadecahedral cluster geometry. This is perhaps surprising given that, according to skeletal electron counting methods,[14] each VC_3B_7 fragment has only 21 skeletal electrons instead of the 24 electrons normally associated with an 11-vertex *closo*-octadecahedral geometry, such as that found for *closo*-1-(η^5-C_5H_5)Fe-2-CH_3-2,3,4-$C_3B_7H_9$.[5a] However, Wade and coworkers[22] have pointed out that 11-vertex clusters are unique in their ability to accommodate various electron counts without undergoing cage distortion. Most *closo*-polyhedral clusters have degenerate HOMO and LUMO orbitals, so if electrons are added to or removed from the cluster, the resulting unequal occupancy of these levels causes a Jahn−Teller distortion. The 11-vertex *closo*-clusters are unique in that the HOMO and LUMO orbitals do not have degenerate levels. So, if an electron is added to or

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Table 3. Redox Potentials ($E_{1/2}$, V vs Ferrocene)[a] for Metallatricarbadecaboranyl Complexes and Relevant Analogues

complex	0/1+	1+/2+	0/1−	1−/2−	ref
$(MeC_3B_7H_9)_2V$ (**2**)	1.1[b]		−0.41	−2.14[c]	this work
Cp_2V	−1.11	0.03[b]	−3.30		*d*
$(2,3,4\text{-}MeC_3B_7H_9)FeCp$ (**7**)	0.39		−1.74		this work
Cp_2Fe	0		−3.4		*e*
$(C_2B_4H_6)FeCp$	−0.92	0.80			*f*

[a] Unless noted, $E_{1/2}$ values were obtained as an average of E_{pa} and E_{pc} for chemically reversible couples. [b] Chemically irreversible oxidation, E_{pa} listed. [c] Quasi-Nernstian system, average of E_{pa} and E_{pc} listed. [d] Reference 23, converted to Fc reference potential. [e] Ito, N.; Saji, T.; Aoyagui, S. *J. Organomet. Chem.* **1983**, *247*, 301. [f] Geiger, W. E.; Brennan, D. E. *Inorg. Chem.* **1982**, *21*, 1963−1966.

removed from these systems, there is no Jahn−Teller effect to cause a cage opening. As a result, 11-vertex clusters can have a variety of skeletal electron counts with retention of the normal *closo*-octadecahedral geometry.

Electrochemical Studies

The capacity of the tricarbadecaboranyl ligand to accept additional electrons may also help explain its ability to stabilize metals in low oxidation states. Since the original tricarbadecaboranyl ligand has a −1 charge, the vanadium in complexes **2**−**6** has, like vanadocene, a formal +2 charge. However, while vanadocene is readily air-oxidized, complexes **2**−**6** are air-stable and unreactive toward Br_2 or Ag^+ oxidation. These differences are consistent with previous electrochemical and infrared studies[5] that have shown both that the tricarbadecaboranyl ligand is much more strongly electron-withdrawing than a cyclopentadienyl ligand and that it greatly stabilizes metals in low oxidation states. For example, the ferratricarbadecaboranyl analogues of ferrocene, *closo*-1-(η^5-C_5H_5)Fe-2-CH_3-2,3,4-$C_3B_7H_9$[5a] (**7**) and *commo-Fe*-(1-Fe-2′-CH_3-2′,3′,4′-$C_3B_7H_9$)(1-Fe-2-CH_3-2,3,4-$C_3B_7H_9$),[5b] were found earlier to undergo oxidation at considerably higher potentials, 0.79 and 1.28 V vs the SCE, respectively, than ferrocene, 0.41 V. Electochemical studies of compound **2** were also undertaken.

Initially, the iron(II) complex *closo*-1-(η^5-C_5H_5)Fe-2-CH_3-2,3,4-$C_3B_7H_9$ (**7**), the oxidation of which in CH_3CN was previously reported,[5a] was reinvestigated under the present conditions to facilitate comparison with the behavior of the V(II) complex **2**. In THF, complex **7** undergoes both a one-electron oxidation to the Fe(III) complex $\mathbf{7}^+$ ($E_{1/2} = 0.39$ V vs Fc) and a one-electron reduction to the formal Fe(I) complex $\mathbf{7}^-$ ($E_{1/2} = -1.74$ V vs Fc) (Table 3). Cyclic voltammetry (CV) measurements using scan rates between 0.1 and 5 V/s show that both the $\mathbf{7}/\mathbf{7}^+$ and $\mathbf{7}/\mathbf{7}^-$ couples are fully reversible (Figure SM 1, Supporting Information). Evidence of the (quasi-Nernstian) electrochemical reversibilities was taken from the similarities of the ΔE_p values of **7** to those of approximately equal concentrations of ferrocene (e.g., ca. 83 mV for **7** vs 80 mV for $Cp_2Fe^{0/+}$ at a CV scan rate of 0.2 V/s). Bulk coulometric oxidation at $E_{appl} = 1.0$ V of 0.5 mM **7** (1.0 F/equiv) confirmed the one-electron oxidation reaction and the long-term stability of the monocation $\mathbf{7}^+$. Bulk reduction of **7** was not attempted.

Oxidation of the V(II) complex **2** was sharply dissimilar to that of **7**. Two poorly reproducible irreversible anodic waves were observed, having potentials (ca. 1.1 and 1.35 V vs Fc, Table 3) and breadths which varied with the CV scan rate, the nature of the solid working electrode and its pretreatment, and the number of scans made. Bulk electrolysis at $E_{appl} = 1.2$ V passed 1 equiv of charge, suggesting that the first of these waves is a one-electron process. No voltammetric waves were observed after electrolysis, indicating that the oxidation of **2** results in nonelectroactive products. Although these results allow only an estimate of the thermodynamic potential for the oxidation of **2** (ca. 1.1 V vs Fc), they are consistent with the observed lack of reactivity of this compound with strong oxidizing agents (vide ante).

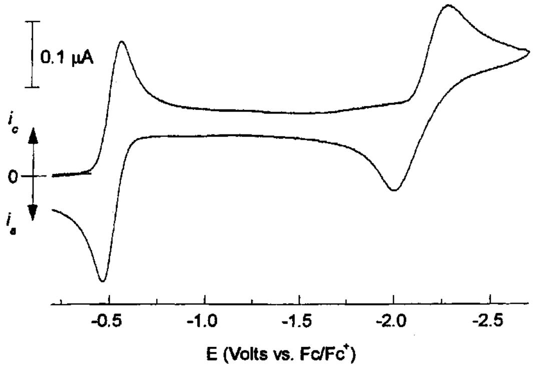

Figure 9. Cyclic voltammogram of reductions of 0.45 mM **2** in THF/0.1 M $[NBu_4][PF_6]$, 250 μm Pt electrode, scan rate 0.2 V/s, ambient temperature.

In contrast, complex **2** undergoes a well-behaved, reversible, one-electron reduction to $\mathbf{2}^-$ at $E_{1/2}(0/1^-) = -0.41$ V. A bulk electrolysis at $E_{appl} = -0.7$ V produced the monoanion $\mathbf{2}^-$ in at least 80% yield after passage of 1.0 F/equiv. A second, apparently chemically reversible, one-electron reduction was also observed for this complex (Figure 9). In this case, the potential separations (e.g., 250 mV at $\nu = 0.2$ V/s) and shapes of the cathodic and anodic waves suggest a diminished electron-transfer rate for the $\mathbf{2}^-/\mathbf{2}^{2-}$ process. An estimated $E_{1/2}$ value for the $(1^-/2^-)$ couple, −2.14 V, is obtained from the average of E_{pc} and E_{pa} at slow scan rates. Bulk reduction at $E_{appl} = -2.4$ V gave waves only for the oxidation of unspecified products. The overall electron-transfer properties of **2** are best defined by equations 3−5, which specify the known one-electron reactions and the occurrence of follow-up reactions when noted.

$$\mathbf{2} \rightleftharpoons \mathbf{2}^+ + e^- \qquad E_{1/2}(0/+) \approx 1.1\text{ V} \tag{3}$$

$$\mathbf{2}^+ \rightarrow \text{product(s) formed within CV time scale} \tag{3a}$$

$$\mathbf{2} + e^- \rightleftharpoons \mathbf{2}^- \qquad E_{1/2}(0/1-) = -0.41\text{ V} \tag{4}$$

$$\mathbf{2}^- + e^- \rightleftharpoons \mathbf{2}^{2-} \qquad E_{1/2}(1-/2-) = -2.14\text{ V} \tag{5}$$

$$\mathbf{2}^{2-} \rightarrow \text{product(s) formed over bulk electrolysis time scale} \tag{5a}$$

These results are in agreement with the earlier evidence,[5] discussed above, that the strong electron-withdrawing capacity of the tricarbadecaboranyl ligand allows it to stabilize metals in low oxidation states. The degree of this stabilization is demonstrated when comparing the redox potentials of **2** with those of vanadocene, Cp_2V, which also has a formal V(II) oxidation state. Whereas the one-electron oxidation of vanadocene to form Cp_2V^+ is extremely facile ($E_{1/2} = -1.11$ V vs Fc),[23] the oxidation of **2** requires a potential that is about *2.2 V more positive*. This large difference in potentials rationalizes the fact that, while vanadocene is readily air-oxidized, complexes **2**−**6** are air-stable and unreactive toward oxidation by either Br_2 or Ag^+.

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(23) Holloway, J. D. L.; Geiger, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 2038−2044.

A similar electronic trend is observed in comparing the one-electron *reduction* of **2** with that of vanadocene. The potential of the one-electron reduction of **2** to **2** $^-$ is a remarkable *2.9 V positive* of that necessary for the reduction of Cp_2V to Cp_2V^-.[23] This trend is underscored in the redox potentials of the iron complex **7** with ferrocene. In this case, only one tricarbadecaboranyl ligand is substituted for a Cp ligand. The potential of the reversible one-electron oxidation of **7** is about 0.4 V positive of that of Cp_2Fe. As in the case of the vanadium analogues, the degree of this positive potential shift increases significantly (to about 1.7 V) when comparing the one-electron *reductions* of **7** and Cp_2Fe (Table 3).

These results suggest that although the vanadium in complexes **2**−**6** has a formal +2 charge, metal-to-ligand charge transfer may result in the delocalization of additional metal electrons in the VC_3B_7 fragment. This, in effect, oxidizes the metal. Thus, the vanadium could have a higher effective oxidation state, making it, as observed, much more resistant to further oxidation than a normal V(II).

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Supporting Information Available: Tables listing refined positional and thermal parameters, bond distances, and bond angles for compounds **1**−**5**; figures showing the cyclic voltammograms of the oxidations of **7** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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