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Syntheses and Structural Characterizations of Vanada- and Niobatricarbadecaboranyl Monohalide Complexes

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The syntheses and structural characterizations of the vanadium and niobium monohalide tricarbadecaboranyl complexes 1-(η^5-C_5H_5)-1-Br-2-Ph-1,2,3,4-$VC_3B_7H_9$ (**1**), [1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Ph-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$ (**2**), [1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Me-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$ (**3**), and *commo-Nb*-1-Cl-(4-Me-1,2,3,4-$NbC_3B_7H_9$)$_2$ (**4**) are described. X-ray crystallographic studies of **1**, **3**, and **4** confirmed that they are monohalide complexes in which the V^{3+} and Nb^{3+} ions are sandwiched between cyclopentadienyl and/or tricarbadecaboranyl monoanions. These compounds are analogues of (η^5-C_5H_5)$_2$VX and (η^5-C_5H_5)$_2$NbX but, unlike their metallocene counterparts, are air- and water-stable, further illustrating the unique ability of the tricarbadecaboranyl ligand to stabilize complexes with the metals in lower oxidation states.

Introduction

As part of our interest in the design of new metallapolyborane analogues of metallocene antitumor agents,[3] we have been investigating the syntheses[4] and bioactivity properties[5] of metallatricarbadecaboranyl complexes. Because of their equivalent charges and formal electron-donating abilities, the coordination properties of tricarbadecaboranyl and the cyclopentadienyl monoanions are in many ways similar, but in comparison to their cyclopentadienyl counterparts, the tricarbadecaboranyl ligands have an unusual ability to stabilize complexes with the metals in lower oxidation states. As a further illustration of this important difference, we report here the syntheses and structural characterizations of a series of V(III) and Nb(III) monohalide complexes: 1-(η^5-C_5H_5)-1-Br-2-Ph-1,2,3,4-$VC_3B_7H_9$ (**1**), [1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Ph-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$ (**2**), [1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Me-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$ (**3**), and *commo-Nb*-1-Cl-(4-Me-1,2,3,4-$NbC_3B_7H_9$)$_2$ (**4**). Unlike their (η^5-C_5H_5)$_2$MX (M = V, Nb) metallocene analogues, these new complexes are air- and water-stable and several of these complexes have now been shown to exhibit significant cytotoxic properties.[5c]

Experimental Section

General Synthetic Procedures and Materials. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under nitrogen or argon atmospheres using the high-vacuum or inert-atmosphere techniques described by Shriver.[6] Solutions of Li^+(6-Me-*nido*-5,6,9-$C_3B_7H_9^-$)[4h,7] and Li^+(6-Ph-*nido*-5,6,9-$C_3B_7H_9^-$)[4j] in toluene were prepared by the reported methods. LiH, PhCN, (η^5-C_5H_5)V(CO)$_4$, Br_2, and $NbCl_4(THF)_2$ were purchased from Strem or Aldrich and used as received. Spectrochemical grade glyme, toluene, CH_3CN, THF, and hexanes were purchased from Fisher or EM Science. Glyme, THF, toluene, and hexanes were freshly distilled from sodium−benzophenone ketyl prior to use. Acetonitrile was dried over P_2O_5, transferred onto activated 4 Å molecular sieves, and stored under vacuum. All other solvents were used as received unless noted otherwise.

Celite was purchased from Fisher Scientific and was evacuated and then purged with Ar before use. The yields of all metallatricarbaborane products are calculated on the basis of starting metal reagents.

Physical Methods. The ^{11}B NMR spectra at 64.2 MHz and ^1H NMR spectra at 200.1 MHz were obtained on a Bruker AC 200 Fourier transform spectrometer equipped with appropriate decoupling accessories. ^{11}B NMR spectra at 160.5 MHz and

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^{1}H NMR spectra at 500.1 MHz were obtained on a Bruker AM-500 spectrometer equipped with the appropriate decoupling accessories. All ^{11}B chemical shifts are referenced to $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm), with a negative sign indicating an upfield shift.

All proton chemical shifts were measured relative to internal residual protons from lock solvents (99.5% C_6D_6 and 99.9% CD_2Cl_2) and then referenced to $(CH_3)_4Si$ (0.0 ppm). High- and low-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer. IR spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analyses were performed at the University of Pennsylvania microanalysis facility. Melting points were determined using a standard melting point apparatus and are uncorrected.

1-(η^5-C_5H_5)-1-Br-2-Ph-1,2,3,4-$VC_3B_7H_9$ (1). Inside a glovebag, 0.23 mmol (0.083 g) of (η^5-C_5H_5)VBr_3 (prepared by the reaction of (η^5-C_5H_5)$V(CO)_4$ with Br_2)[8] was dissolved in freshly distilled toluene in a 100 mL two-neck round-bottom flask equipped with a stirbar, septum, and vacuum stopcock to give a dark green solution. A 0.23 mmol sample of Li^+(6-Ph-*nido*-5,6,9-$C_3B_7H_9^-$) (0.46 mL of a 0.5 M stock solution) was syringed in, and the reaction mixture was stirred overnight at room temperature. The resulting dark red-brown solution was filtered through a Celite plug inside the glovebag. Vacuum evaporation of the volatiles from the filtrate gave a dark-colored residue. Initial washings of the residue with toluene were green (unreacted (η^5-C_5H_5)VBr_3), but subsequent washings with toluene were orange-brown. Vacuum evaporation of the solvent from the orange-brown washings yielded 0.012 g (0.03 mmol, 13% yield) of pure orange-brown 1-(η^5-C_5H_5)-1-Br-2-Ph-1,2,3,4-$VC_3B_7H_9$ (**1**). For **1**: mp ~170 °C dec. Anal. Calcd: C, 42.70; H, 4.86. Found: C, 42.47; H, 4.42. HRMS (*m*/*e*): calcd for $^{12}C_{14}{}^1H_{19}{}^{11}B_7{}^{80}Br^{51}V$, 394.0761; found, 394.0761. IR (KBr, cm^{-1}): 3124 (s), 3032 (s), 2619 (s), 2561 (s), 2532 (s), 2348 (m), 1951 (m), 1591 (s), 1347 (s), 1028 (w), 846 (s), 760 (m), 695 (s), 665 (w), 521 (w), 474 (w).

[1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Ph-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$ (2) and [1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Me-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$ (3). Inside a glovebag, 1.40 mmol (0.420 g) of (η^5-C_5H_5)$NbCl_4$ was dissolved in freshly distilled toluene in a 100 mL two-neck round-bottom flask equipped with a stirbar, septum, and vacuum stopcock. A 2.80 mmol sample of Li^+(6-Ph-*nido*-5,6,9-$C_3B_7H_9^-$) (5.60 mL of a 0.5 M stock solution) was syringed in, and the reaction mixture was stirred overnight at room temperature. Vacuum evaporation of the solvent from the resulting dark red solution yielded a dark residue that was then extracted with toluene. The toluene extract was filtered through a Celite plug inside the glovebag and the filtrate then concentrated by vacuum evaporation. Addition of hexanes to the concentrated toluene extract then resulted in the precipitation of 0.066 g (0.08 mmol, 12% yield) of brown [1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Ph-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$ (**2**). For **2**: mp 160−162 °C. Anal. Calcd for {[1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Ph-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$}{$CH_3C_6H_5$}$_{0.6}$: C, 46.15; H, 5.15. Found: C, 46.33; H, 5.48. HRMS (*m*/*e*): calcd for $^1/_2$($^{12}C_{28}{}^1H_{38}{}^{11}B_{14}{}^{35}Cl_2{}^{93}Nb_2$), 392.0890; found, 392.0911. IR (KBr, cm^{-1}): 3234 (m), 3112 (s), 3055 (s), 3033 (s), 2594 (s), 2552 (s), 2262 (m), 1951 (m), 1876 (w), 1866 (w), 1595 (s), 1490 (s), 1444 (m), 1101 (w), 1021 (w), 911 (m), 837 (w), 788 (w), 759 (m).

Using similar procedures, 1.91 mmol (0.573 g) of (η^5-C_5H_5)$NbCl_4$ was reacted with 3.8 mmol of Li^+(6-Me-*nido*-5,6,9-$C_3B_7H_9^-$) (7.6 mL of a 0.5 M stock solution) to give 0.16 g (0.24 mmol, 25% yield) of yellow-orange [1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Me-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$ (**3**). For **3**: mp 168−170 °C. Anal. Calcd: C, 32.83; H, 5.20. Found: C, 33.17; H, 5.10. HRMS (*m*/*e*): calcd for $^1/_2$($^{12}C_{18}{}^1H_{34}{}^{11}B_{14}{}^{35}Cl_2{}^{93}Nb_2$), 330.0734; found 330.0761. IR (toluene, cm^{-1}): 2583 (s).

***commo-Nb*-1-Cl-(4-Me-1,2,3,4-$NbC_3B_7H_9$)$_2$ (4).** Inside a glovebag, 0.33 mmol (0.125 g) of $NbCl_4(THF)_2$ was dissolved in freshly distilled THF in a 100 mL two-neck round-bottom flask equipped with a stirbar, septum, and vacuum stopcock. A 0.66 mmol sample of Li^+(6-Me-*nido*-5,6,9-$C_3B_7H_9^-$) (1.32 mL of a 0.5 M stock solution) was syringed in, and the reaction mixture was stirred overnight at room temperature. Vacuum evaporation of the solvent from the resulting dark red solution yielded a dark residue that was then extracted with toluene. The toluene extract was filtered through a Celite plug inside the glovebag and the filtrate then concentrated by vacuum evaporation. Addition of ~3 mL of hexanes resulted in the precipitation of a brown solid, which was then filtered inside the glovebag and washed with hexanes to give 0.0133 g (0.033 mmol, 10% yield) of pure brown *commo-Nb*-1-Cl-(4-Me-1,2,3,4-$NbC_3B_7H_9$)$_2$ (**4**). For **4**: mp ~157 °C dec. Anal. Calcd: C, 24.02; H, 6.05. Found: C, 23.89; H, 5.86. HRMS (*m*/*e*): calcd for $^{12}C_8{}^1H_{24}{}^{11}B_{14}{}^{35}Cl^{93}Nb$, 402.1933; found, 402.1929. IR (KBr, cm^{-1}) 3206 (s), 2571 (s), 2343 (s), 2259 (s), 1700 (w), 1684 (w), 1653 (w), 1558 (m), 1457 (w), 1193 (s), 1060 (m), 789 (m).

Crystallographic Data for 1, 3, and 4. Single crystals of 1-(η^5-C_5H_5)-1-Br-2-Ph-1,2,3,4-$VC_3B_7H_9$ (**1**; Upenn #3170) and [1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Me-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$ (**3**; Upenn #3105) were grown from toluene solutions at 0 °C, while those of *commo-Nb*-1-Cl-(4-Me-1,2,3,4-$NbC_3B_7H_9$)$_2$, (**4**; Upenn #3148) were grown via slow evaporation from CH_2Cl_2.

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. Indexing was performed from a series of oscillation angles. A hemisphere of data was collected using oscillation angles of 3° for **1**, 10° for **3**, and 4° for **4** and a crystal-to-detector distance of 82 mm. Oscillation images were processed using bioteX,[9] producing a listing of unaveraged F and $\sigma(F)$ values which were then passed to the teXsan[10] 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 structure was solved by direct methods (SIR92).[11] During solution of the structure of **3**, Fourier electron density maps revealed that there was an area of disordered toluene solvent. The data were then corrected for the presence of disordered solvent by using SQUEEZE.[12] Refinements were by full-matrix least squares based on F^2 using SHELXL-93.[13] All reflections were used during refinement, and F^2 values that were experimentally negative were replaced by $F^2 = 0$.

Results and Discussion

The compositions of all compounds were established by mass spectrometry and/or elemental analyses. The proposed structures are supported by the NMR data given in Table 1, with the structures of compounds **1**, **3**, and **4** being further confirmed by crystallographic determinations.

The reaction of cyclopentadienyl vanadium(IV) trihalides with MCp′ (M = Li, Na, Tl, etc.) has been shown to be an efficient route to mixed-ring $CpCp'VX_2$ com-

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Table 1. NMR Data

compd	nucleus	δ (multiplicity, assignment, J (Hz))
1	$^{11}B^{a,b}$	10.3 (d, 1B, J_{BH} 153), 7.6 (d, 1B, J_{BH} 159), 6.3 (d, 1B, J_{BH} 176), 4.7 (d, 1B, J_{BH} 154), −4.4 (d, 1B, J_{BH} 162), −22.8 (d, 1B, J_{BH} 147), −27.9 (d, 1B, J_{BH} 152)
	$^1H\{^{11}B\}^{a,c}$	7.28 (Ph), 6.96 (Ph), 6.88 (Ph), 6.25 (s, C3H), 5.68 (s, Cp), 4.43 (s, C4H)
2	$^{11}B^{a,b}$	7.5 (d, 1B, J_{BH} 167), 5.5 (d, 1B, J_{BH} 162), 2.6 (d, 1B, J_{BH} 142), −1.7 (d, 1B, J_{BH} 146), −9.0 (d, 1B, J_{BH} 161), −24.4 (d, 1B, J_{BH} 152), −28.5 (d, 1B, J_{BH} 166)
	$^1H\{^{11}B\}^{a,d}$	7.25−6.96 (Ph), 6.35 (s, C3H), 5.32 (s, Cp), 2.82 (s, C4H)
3	$^{11}B^{a,e}$	3.3 (d, 1B, J_{BH} ~200), −1.0 (d, 2B^f), −3.7 (d, 1B, J_{BH} 158), −13.2 (d, 1B, J_{BH} 161), −28.0 (d, 1B, J_{BH} 146), −33.1 (d, 1B, J_{BH} 162)
	$^1H\{^{11}B\}^{a,d}$	6.24 (s, C3H), 5.38 (s, Cp), 2.21 (s, C4H), 2.13 (s, Me)
4	$^{11}B^{a,b}$	4.0 (d, 1B, J_{BH} 74), 3.5 (d, 1B, J_{BH} 90), 2.3 (d, 1B, J_{BH} 210), 0.9 (d, 1B, J_{BH} 215), −6.9 (d, 1B, J_{BH} 165), −9.6 (d, 1B, J_{BH} 157), −13.8 (d, 1B, J_{BH} 149)
	$^1H\{^{11}B\}^{a,c}$	7.49 (s, C2H), 5.94 (s, C3H), 1.37 (s, Me)

[a] In C_6D_6. [b] 160.5 MHz. [c] 500.2 MHz. [d] 200.1 MHz. [e] 64.2 MHz. [f] Overlapping resonances; coupling contants could not be accurately measured.

plexes.[14] Accordingly, the reaction of cyclopentadienyl vanadium(IV) tribromide with $Li^+(6\text{-Ph-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-)$ was expected to yield the mixed-ligand vanadium dibromide sandwich complex $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1,1\text{-}Br_2\text{-}2\text{-Ph-}closo\text{-}1,2,3,4\text{-}VC_3B_7H_9$, according to eq 1.

$$(\eta^5\text{-}C_5H_5)VBr_3 + Li^+(6\text{-Ph-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-) \xrightarrow{X} 1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1,1\text{-}Br_2\text{-}2\text{-Ph-}closo\text{-}1,2,3,4\text{-}VC_3B_7H_9 + LiBr \quad (1)$$

$$(\eta^5\text{-}C_5H_5)VBr_3 + Li^+(6\text{-Ph-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-) \xrightarrow{\text{reduction}} \underset{\mathbf{1}}{1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1\text{-Br-}2\text{-Ph-}1,2,3,4\text{-}VC_3B_7H_9} \quad (2)$$

The reaction instead yielded the vanadium monobromide complex $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1\text{-Br-}2\text{-Ph-}1,2,3,4\text{-}VC_3B_7H_9$ (**1**) (eq 2), in which the vanadium had been reduced to a formal +3 oxidation state. Previous[4h] attempts to synthesize $(MeC_3B_7H_9)_2VX_2$ analogues of vanadocene dihalide by reacting VX_4 (X = Cl, Br) with $6\text{-Me-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-$ had also failed, yielding instead *commo*-*V*-$(1\text{-V-Me-}2,3{-}4\text{-}C_3B_7H_9)_2$ analogues of vanadocene where reduction to V^{2+} had occurred.

Likewise, instead of producing the expected $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1\text{-}Cl_2\text{-}2\text{-R-}closo\text{-}1,2,3,4\text{-}NbC_3B_7H_9$ complexes analogous to $(\eta^5\text{-}C_5H_5)_2NbCl_2$,[15] the reactions of $(\eta^5\text{-}C_5H_5)NbCl_4$ with $Li^+(6\text{-Ph-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-)$ and $Li^+(6\text{-Me-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-)$ yielded the dimeric monohalide complexes **2** and **3** (eq 3), in which the niobium has been reduced from +5 to +3.

$$(\eta^5\text{-}C_5H_5)NbCl_4 + Li^+(6\text{-R-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-) \xrightarrow{\text{reduction}} [1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1,1'\text{-}\mu\text{-Cl-}2\text{-Ph-}closo\text{-}1,2,3,4\text{-}NbC_3B_7H_9]_2 \quad R = Ph\ (\mathbf{2}),\ Me\ (\mathbf{3}) \quad (3)$$

Reactive borane fragments derived from cage decomposition are the likely reducing agents in these reactions. Indeed, the reaction of $(\eta^5\text{-}C_5H_5)_2NbCl_2$ with borohydride ion has been shown to lead to reduction and the formation of $(\eta^5\text{-}C_5H_5)_2NbCl$.[16]

The above results are consistent with the previous electrochemical studies of metallatricarbadecaboranyl complexes,[4a,h,i] showing that the strong electron-withdrawing capacity of the tricarbadecaboranyl ligand allows it to stabilize metals in low oxidation states. For example, whereas the one-electron oxidation of vanadocene to form $(\eta^5\text{-}C_5H_5)_2V^+$ is extremely facile, the oxidation of the bis-cage *commo*-*V*-$(1\text{-V-Me-}2,3\text{-}4\text{-}C_3B_7H_9)_2$ complexes requires a potential that is ~2.2 V more positive.[4h]

The ^{11}B NMR spectra obtained for **1**−**3** are each consistent with C_1 cage symmetries and are similar to those reported for $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-R-}closo\text{-}1,2,3,4\text{-}FeC_3B_7H_9$ (R = Me, Ph).[4a,i,j] The ^1H NMR spectra for these compounds are likewise similar to those of the ferratricarbadecaboranyl complexes, each showing, in addition to the appropriate Ph or Me resonances, two C−H resonances with one occurring at a low-field shift (6.35−6.24 ppm) characteristic of the proton attached to the low-coordinate C3 carbon which is adjacent to the metal and the other at a high-field shift (4.43−2.21 ppm) characteristic of the C4H proton.

In agreement with the spectroscopic data, crystallographic determinations confirmed that **1** and **3** (Figures 1 and 2; crystal data and structure determination parameters are given in Table 2) are monohalide complexes in which the V^{3+} and Nb^{3+} ions are sandwiched between tricarbadecaboranyl and cyclopentadienyl monoanions. The metals are η^6-coordinated to the puckered six-membered face of the tricarbadecaboranyl cage with the Ph and Me groups bonded to the C2 cage carbon adjacent to the metal.

Selected bond distances are given in the figure captions. In both compounds, the metals are approximately centered over the six-membered open face with the closest metal−cage interactions being with the two carbons C2 and C3, which are puckered out of the ring. Longer and approximately equivalent bond lengths are observed between the metals and the remaining four atoms (C4, B5, B6, and B7) on the tricarbadecaboranyl bonding face. For **1**, the V−C2 (2.043(5) Å) and V−C3 (2.023(6) Å) bond lengths are similar to those previously reported for the comparable distances in the *commo*-*V*-$(1\text{-V-Me-}2,3,4\text{-}C_3B_7H_9)_2$ (V^{2+}) complexes.[4h] The M−C2 and M−C3 distances in both compounds are also significantly shorter than the distances found from the

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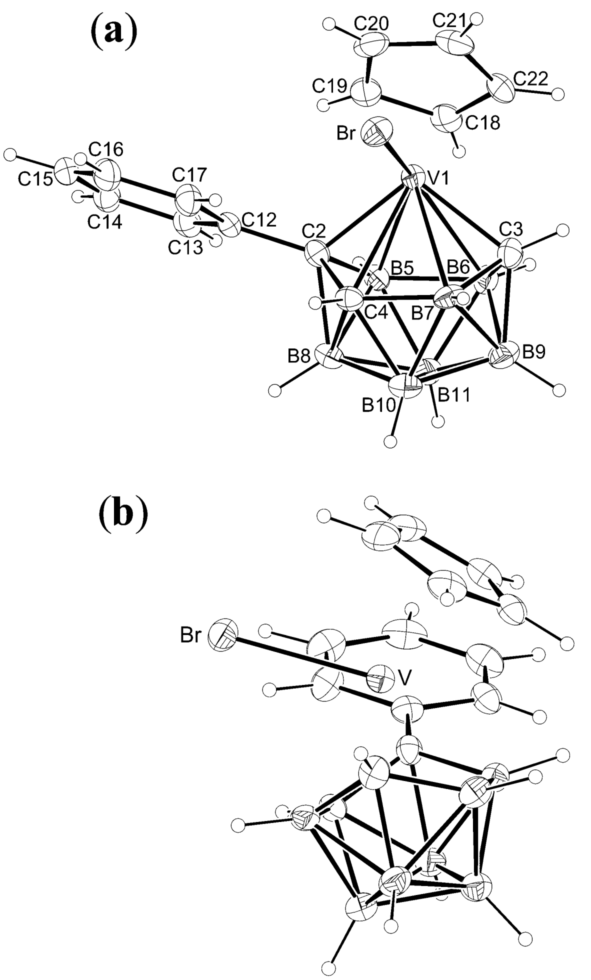

Figure 1. ORTEP drawings showing two views of the structure of one of the two independent molecules in the unit cell of 1-(η^5-C_5H_5)-1-Br-2-Ph-1,2,3,4-$VC_3B_7H_9$ (**1**). Selected distances (Å) and angles (deg): V1−Br, 2.4827(10); V1−C2, 2.043(5); V1−C3, 2.023(6); V1−C4, 2.368(5); V1−B5, 2.397(6); V1−B6, 2.408(6); V1−B7, 2.393(6); C2−C12, 1.509(7); C2−C4, 1.515(7); C4−B7, 1.694(8); B7−C3, 1.601(9); C3−B6, 1.614(8); B6−B5, 1.822(9); B5−C2, 1.609(8); C2−V1−C3, 104.6(2); Br−V1−C2, 101.06(14); Br−V1−C3, 105.3(2); Br−V1−C4, 80.74(14); Br−V1−B7, 79.2(2); V1−C2−C12, 123.3(4).

metals to the carbons of their cyclopentadienyl ring (average 2.300 Å (**1**), 2.418 Å (**3**)).

While they are both monohalide complexes, the structures of **1** and **3** differ in the solid state, since **1**, like (η^5-C_5H_5)$_2$VCl,[17] is a monomeric 16-electron complex containing only a single bromide bonded to the vanadium, whereas **3** achieves an 18-electron configuration by forming a dimeric structure in which the two [1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-$NbC_3B_7H_9$] units are bridged by two chlorines. The two chlorines in **3** are reasonably symmetrically oriented, and the observed structure and Nb−Cl bond distances are quite similar to those found for the [(η^5-$Me_3SiC_5H_4$)NbCl]$_2$[18] metallocene. Consistent with the lower Nb^{3+} oxidation state, the Nb−Cl distances in **3** are ~0.15 Å longer than those found in the (η^5-C_5H_5)$_2$$NbCl_2$ complex (Nb^{4+}).[19]

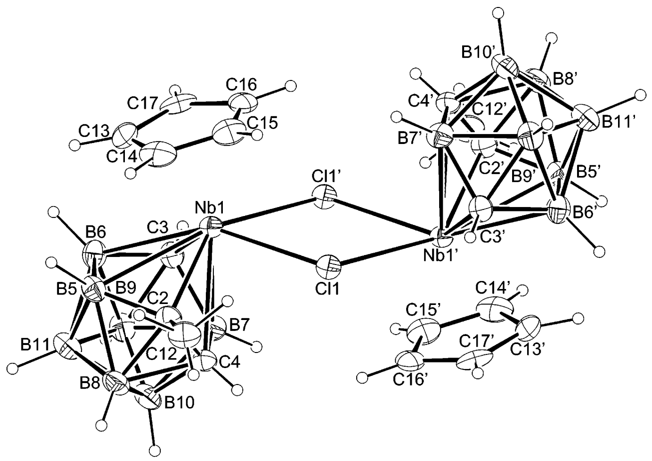

Figure 2. ORTEP drawing of the structure of [1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Me-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$ (**3**). Selected distances (Å) and angles (deg): Nb1−Cl1, 2.5967(14); Nb1−Cl1′, 2.6791(14); Nb1−C2, 2.167(6); Nb1−C3, 2.153(5); Nb1−C4, 2.475(5); Nb1−B5, 2.505(6); Nb1−B6, 2.533(7); Nb1−B7, 2.469(6); Nb1−Nb1′, 4.277(1); C2−C12, 1.509(7); C2−C4, 1.534(8); C4−B7, 1.683(8); B7−C3, 1.587(9); C3−B6, 1.610(8); B6−B5, 1.818(9); B5−C2, 1.611(9); C2−Nb1−C3, 98.5(2); Cl1−Nb1−Cl1′, 71.7(2); Cl1−Nb1−C2, 81.1(2); Cl1−Nb1−C3, 129.9(2); Cl1−Nb1−C4, 76.47(13); Cl1−Nb1−B7, 94.7(2); Cl1′-Nb1−C3, 77.2(1); Cl1′-Nb1−C2, 138.3(1); Nb1−Cl1−Nb1′, 108.33(5); Nb1−C2−C12, 124.7(4).

In both **1** and **3**, the cyclopentadienyl ring and the C4−B5−B6−B7 plane of the tricarbadecaboranyl ligand are not parallel but are tilted to open coordination sites for the halogens. The dihedral angles between these planes in **1** (41.6(3)°) and **3** (48.0(3)°) are similar to the wedge angles found between the two cyclopentadienyl rings in the (η^5-C_5H_5)$_2$VCl[16] (48.3(4)°) and (η^5-C_5H_5)$_2$-$NbCl_2$ (49.1°)[19] complexes.

As in the reactions discussed above, instead of yielding a bis(tricarbadecaboranyl) niobium dihalide complex, the reaction of $NbCl_4(THF)_2$ with 2 equiv of Li^+(6-Me-*nido*-5,6,9-$C_3B_7H_9^-$) yielded the monohalide complex **4** shown in eq 4, in which the niobium has been reduced from +4 to +3.

$$\begin{aligned}&NbCl_4(THF)_2 + \\ &\qquad 2Li^+(6\text{-Me-}nido\text{-}5,6,9\text{-}C_3B_7H_9^-) \xrightarrow{\text{reduction}} \\ &\qquad commo\text{-}Nb\text{-}1\text{-Cl-}(4\text{-Me-}1,2,3,4\text{-}NbC_3B_7H_9)_2 \quad (4) \\ &\qquad\qquad\qquad\qquad\quad \mathbf{4}\end{aligned}$$

The ^{11}B NMR spectrum of **4** is similar to those of **1**−**3**, indicating that the two cages in **4** are symmetry related. Thus, there are only 7 equal intensity doublets in the ^{11}B NMR spectrum, instead of the 14 lines that would be expected if the two cages are inequivalent. The ^1H NMR spectrum shows a single resonance for the two Me groups, confirming the equivalence of the two cages. There are two C−H resonances (7.49 and 5.94 ppm) in the low-field range indicative of protons attached to the low-coordinate C2 and C3 carbons that are adjacent to the metal. This observation indicates that, unlike in complexes **1**−**3** where the Me or Ph substituents are bonded to the C2 carbon adjacent to the metal, in **4** the

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Table 2. Crystallographic Data Collection and Structure Refinement Information

	1	3	4
empirical formula	$VC_{14}B_7H_{19}Br$	$C_{18}B_{14}H_{34}Cl_2Nb_2{\cdot}C_7H_8$	$NbC_8B_{14}H_{24}Cl$
formula wt	393.81	750.65	399.97
cryst class	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	*Pnma* (No. 62)
Z	8	2	8
a, Å	16.9853(5)	7.7853(3)	13.6238(13)
b, Å	23.0474(7)	16.9280(10)	19.604(2)
c, Å	8.5371(2)	12.7210(6)	13.6755(7)
α, deg			
β, deg	91.152(2)	101.440(2)	
γ, deg			
V, Å^3	3341.3(2)	1643.19(14)	3652.4(5)
μ, cm^{-1}	29.73	8.79	7.90
cryst size, mm	0.32 × 0.13 × 0.04	0.22 × 0.18 × 0.12	0.27 × 0.12 × 0.02
D_{calcd}, g/cm^3	1.566	1.517	1.455
$F(000)$	1568	756	1600
radiation	Mo Kα	Mo Kα	Mo Kα
2θ angle, deg	5.58−50.9	4.06−50.68	5.92−50.68
temp, K	210	233	180
hkl collected	$-19 \le h \le 20$	$-9 \le h \le 8$	$-16 \le h \le 13$
	$-27 \le k \le 27$	$-19 \le k \le 20$	$-23 \le k \le 21$
	$-15 \le l \le 9$	$-15 \le l \le 15$	$-15 \le l \le 14$
no. of rflns measd	23016	10254	8872
no. of unique rflns	5801 ($R_{int} = 0.0652$)	2975 ($R_{int} = 0.0589$)	3191 ($R_{int} = 0.0708$)
no. of obsd rflns, ($F > 4\sigma$)	5250	2457	2699
no. of rflns used in refinement	5801	2975	3191
no. of params	567	164	224
R^a indices ($F > 4\sigma$)	R1 = 0.0596	R1 = 0.0553	R1 = 0.1056
	wR2 = 0.1275	wR2 = 0.1304	wR2 = 0.2365
R^a indices (all data)	R1 = 0.0684	R1 = 0.0699	R1 = 0.1232
	wR2 = 0.1326	wR2 = 0.1385	wR2 = 0.2516
GOF^b	1.187	1.069	1.144
final diff peaks, e/Å^3	+0.474, −0.772	+0.765, −0.566	+1.310, −1.589

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. [b] $GOF = \{\sum w(F_o^2 - F_c^2)^2/(n - p)\}^{1/2}$, where n = no. of reflections and p = no. of parameters refined.

methyl group is attached at the C4 carbons of both cages. Similar rearrangements have previously been observed in a variety of tricarbadecaboranyl complexes derived from reactions with the 6-Me-*nido*-5,6,9-$C_3B_7H_9^-$ anion.[4,20]

As shown in Figure 3, the crystallographically determined structure of **4** is in agreement with the spectroscopic data discussed above. The Me groups on both cages are bonded at the C4 carbon, and a single chlorine atom is directly bonded to the metal. A mirror plane containing the Nb−Cl bond accounts for the equivalence of the two cages observed in the NMR spectra of **4**.

As discussed previously,[4b,h] because the 6-Me-*nido*-5,6,9-$C_3B_7H_9^-$ anion is synthesized as a racemic mixture, a bis-cage complex may be formed containing either two cages of the same enantiomer (*R*−M−*R* or *S*−M−*S*) or two different cage enantiomers (*R*−M−*S*). As can be seen in Figure 3, **4** is the *R*−M−*S* isomer, containing the two different enantiomeric forms of the 6-Me-*nido*-5,6,9-$C_3B_7H_9^-$ cage. Since **4** was isolated from the product mixture by crystallization, it is reasonable that the *R*−M−*R* and *S*−M−*S* isomers were also produced in the reaction but not isolated.

Although a number of bis-cage complexes containing two η^6-coordinated $RC_3B_7H_9^-$ ligands have now been synthesized,[4] **4** is the first such complex to have another ligand bonded to the metal. As shown in Figure 3b, while remaining η^6 coordinated, the two cages in **4** are tilted away from each other on the C4-Me side to form the wedge-type structure (40.3(3)° dihedral angle between the B5a−B6a−B7a−C4a and B5a′−B6a′−B7a′−C4a′ planes) needed to accommodate the chlorine. The cages are also twisted with respect to each other, as indicated by the 39.2(5)° dihedral angle between the C2a−C3a−B8a−B9a and C2a′−C3a′−B8a′−B9a′ planes.

Selected bond distances are presented in the Figure 3 caption. As was the case for **1** and **3**, the Nb is approximately centered over the six-membered open faces of the two cages in **4**, with the shortest metal−cage distances being between the metal and the two carbons, C2a/C2a′ and C3a/C3a′, on each face that are puckered toward the metal. The distances from the niobium to the atoms on the faces of the two tricarbadecaboranyl cages, as well as the Nb1a−Cla distance, are generally about 0.1 Å longer than the comparable distances in **3**, perhaps reflecting the greater steric interactions of the two cages in **4**.

It should also be noted that the $MC_3B_7H_9$ (M = V, Nb) cage fragments in **1** and **4** show no significant distortions from octadecahedral cluster geometries. This is perhaps surprising, since according to skeletal electron counting rules,[21] each $MC_3B_7H_9$ cluster has only 22 skeleton electrons instead of the 24 electrons normally associated with an 11-vertex *closo*-octadecahedral geometry (such as that found for 1-(η^5-C_5H_5)-2-Me-*closo*-1,2,3,4-$FeC_3B_7H_9$[2a] and **3**). However, Wade[22] and coworkers have pointed out that 11-vertex clusters are unique, since unlike most *closo*-polyhedral clusters,

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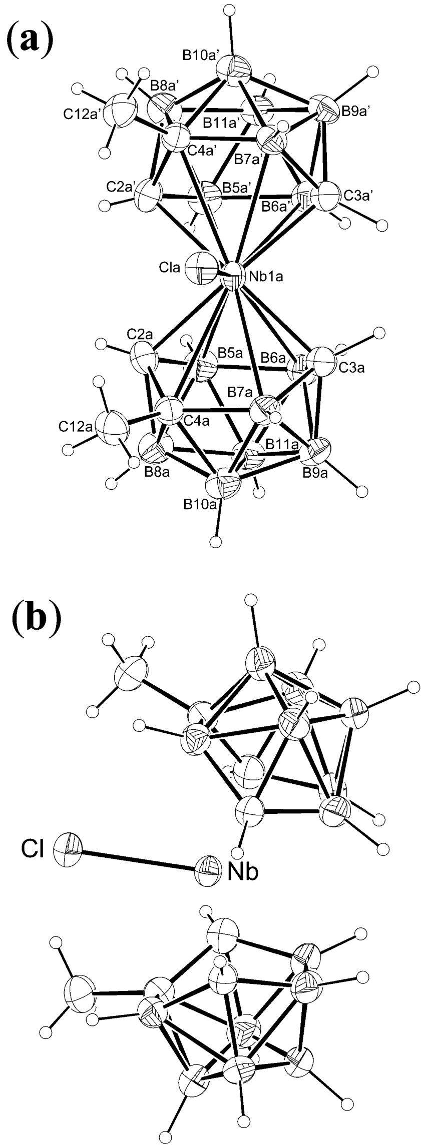

Figure 3. ORTEP drawings showing two views of the structure of one of the two independent molecules in the unit cell of *commo-Nb*-1-Cl-(4-Me-1,2,3,4-$\mathrm{NbC_3B_7H_9}$)$_2$ (**4**). Selected distances (Å) and angles (deg): Nb1a−Cla, 2.388(4); Nb1a−C2a, 2.266(11); Nb1a−C3a, 2.179(11); Nb1a−C4a, 2.646(11); Nb1a−B5a, 2.596(13); Nb1a−B6a, 2.603(13); Nb1a−B7a, 2.575(13); C4a−C12a, 1.52(2); C2a−C4a, 1.52(2); C4a−B7a, 1.77(2); B7a−C3a, 1.60(2); C3a−B6a, 1.59(2); B6a−B5a, 1.85(2); B5a−C2a, 1.58(2); C2a−Nb1a−C3a, 93.2(4); Cla−Nb1a−C3a, 103.1(3); Cla−Nb1a−C2a, 101.9(3); Cla−Nb1a−C4a, 79.8(2); Cla−Nb1a−B7a, 77.1(3); Nb1a−C4a−C12a, 124.0(7); C2a−Nb1a−C3a′, 154.9(4).

their HOMO and LUMO orbitals do not have degenerate levels. If an electron is added or removed from these systems, there are no Jahn−Teller distortions to cause a cage opening. As a result, 11-vertex clusters can accommodate a variety of skeletal electron counts while retaining the normal *closo*-octadecahedral cage geometry.

Because of their abilities to directly bind to biomolecules, many early-metal metallocene dihalide complexes (η^5-$\mathrm{C_5H_5}$)$_2$$\mathrm{MX_2}$ (M = Ti, V, Nb, Mo, W) have potent antitumor properties.[3] For example, the (η^5-$\mathrm{C_5H_5}$)$_2$$\mathrm{MX_2}$ (M = Nb, V) complexes have proven active in vivo against Ehrlich ascites carcinoma growth in mice and against breast cancer.[23] The monohalide cyclopentadienyl complexes (η^5-$\mathrm{C_5H_5}$)$_2$MX, (M = V,[17,24] Nb;[18,25] X = Cl, Br) are extremely reactive toward both air and moisture. As a result, they are unsuitable for bioapplications. The remarkable air and water stability of the vanada (**1**) and nioba (**2**−**4**) tricarbadecaboranyl monohalide complexes suggested that their potentially useful bioactivity properties could be exploited. We have in fact recently reported[5c] that **1** and **4** are potent cytotoxic agents against murine and human leukemia and lymphoma growth, as well as HeLa suspended uterine carcinomas. Most significantly, **1** inhibited the growth of cultured human solid tumors, which is an activity that had not been previously observed for other metallatricarbadecaboranyl complexes. These results suggest that the stabilizing effect of the tricarbadecaboranyl ligand may enable the generation of a wide variety of early-metal monohalide complexes with properties compatible with bioapplications. As has been the case for the metallocene dihalides,[3] second-generation tricarbadecaboranyl monohalide complexes containing functional groups with more specific binding properties may provide even greater potencies.

Acknowledgment. We thank the National Science Foundation for the support of this research.

Supporting Information Available: CIF files, giving X-ray crystallographic data for the structure determinations of compounds **1**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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