



Synthesis and structural characterizations of *ansa*-vanadabis(tricarbadeboranyl) sandwich complexes

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Dedicated to our friends Nancy and Russ Grimes on the occasion of Russ's 80th birthday.

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ABSTRACT

A new linked bis(tricarbadeboranyl) dianion has been used to form the first examples of *ansa*-vanadabis(tricarbadeboranyl) complexes. The $\text{Li}_2[6,6-(\text{CH}_2)_4\text{-nido-(5,6,9-C}_3\text{B}_7\text{H}_9)_2]^{2-}$ (**1**) dianion was produced by a carbon-insertion route involving the reaction of two equivalents of *arachno*-4,6- $\text{C}_2\text{B}_7\text{H}_{12}$ with adiponitrile. The reaction of **1** with $\text{VCl}_3 \cdot \text{THF}$ produced two isomeric *ansa*-vanadabis(tricarbadeboranyl) complexes, *ansa*-(2',4-(CH_2)₄-)*commo*-V-(1'-V-2',3',5'- $\text{C}_3\text{B}_7\text{H}_9$)(1-V-2,3,4- $\text{C}_3\text{B}_7\text{H}_9$) (**2**) and *ansa*-(2',4-(CH_2)₄-)*commo*-V-(1'-V-2',3',4'- $\text{C}_3\text{B}_7\text{H}_9$)(1-V-2,3,4- $\text{C}_3\text{B}_7\text{H}_9$) (**3**). Crystallographic determinations showed that in both complexes a formal V^{2+} ion is sandwiched between two tricarbadeboranyl cages that are linked by the *ansa*-(CH_2)₄- group, but that the points of linker-attachment on the two cages are different. One cage of each complex has the linkage attached to the C2 cage-carbon, but in the other cage, a cage-atom rearrangement moved the C2 cage-carbon along with its attached $-(\text{CH}_2)_4-$ linker to an adjacent 4-position. This rearrangement along with the long flexible $-(\text{CH}_2)_4-$ linker enables the two cages in each complex to rotate into a perpendicular interlocking configuration that maximizes the bonding interaction with the metal, reduces unfavorable steric interactions between the two linked cages and encapsulates the vanadium inhibiting its interactions with other potential ligands. The isomeric structures of **2** and **3** differ as a result of their being formed from different combinations of the enantiomeric forms of the $-(\text{CH}_2)_4-\text{C}_3\text{B}_7\text{H}_9$ cages, with the C4 and C5' carbons on opposite sides of the tether in **2**, whereas in **3** the C4 and C4' carbons are on the same side.

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Introduction

Although the first tricarbaboranes [1], $\text{Me-C}_3\text{B}_3\text{H}_6$ and $\text{Me}_2\text{-C}_3\text{B}_3\text{H}_5$, and metallatricarbaborane complex [2], $(\text{Me-C}_3\text{B}_3\text{H}_6)\text{Mn}(\text{CO})_3$, were reported in seminal work by Grimes in 1966 and 1969, it took over 20 more years to develop the efficient methods for the syntheses of the larger cage C_3B_7 [3] and C_3B_8 tricarbaboranes [4] that have now enabled the extensive and growing investigations of metallatricarbaborane chemistry [5]. Our work in this area has demonstrated that the 6-R-5,6,9-*nido*- $\text{C}_3\text{B}_7\text{H}_9$ (R = Me or Ph) [3,6] tricarbadeboranyl anions can function as cyclopentadienyl analogs with the tricarbadeboranyl sandwich complexes exhibiting properties that are complimentary to their metallocene cousins [7]. For example, we synthesized [8] a range of

different $\text{V}(\text{Me-C}_3\text{B}_7\text{H}_9)_2$ vanadabis(tricarbadeboranyl) sandwich complexes and demonstrated that, unlike the Cp_2V [9] and Cp^*_2V [10] vanadocenes, the vanadabis(tricarbadeboranes) are both air and water stable, as well as unreactive toward coordination with additional ligands. In light of the unique properties imparted by tricarbadeboranyl ligands, we have continued to explore the syntheses and properties of the tricarbadeboranyl equivalents of other important classes of metallocene structure types.

Ansa-ligated metallocene [11] and metallacarboranyl complexes [12] are new and growing classes of stabilized sandwich complexes with constrained geometries that have found increasing uses as, for example, stereo-selective catalysts, chelating agents for metal separations and biomedical reagents. We recently reported [13] the synthesis of both the first linked cyclopentadienyl-tricarbadeboranyl and bis(tricarbadeboranyl) dianions and their use to form the first examples of *ansa*-ferratricarbadeboranyl complexes. The short length of the $-(\text{CH}_2)_2-$ linker used in the *ansa*-ferrabis(tricarbadeboranyl) complexes inhibited coordination of their two linked-cages in the most favorable interlocking

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configuration. In this paper, we report the synthesis of a new linked bis(tricarbadeboranyl) dianion with a longer, four-carbon tether that facilitates optimal metal-cage bonding interactions, as illustrated by the use of this dianion to form the first *ansa*-vanadabis(tricarbadeboranyl) complexes.

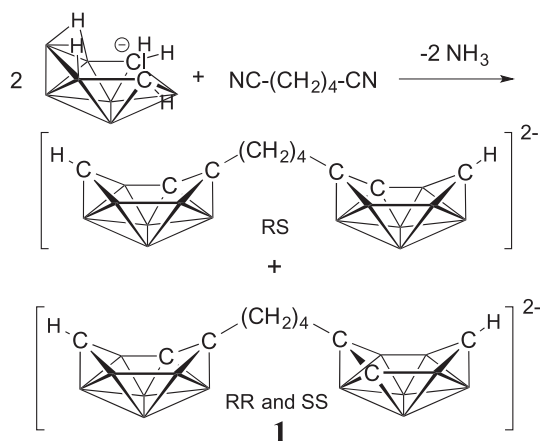
Results and discussion

We earlier demonstrated that the carbon insertion method originally developed by Kang [3,8], which employs the reaction of the *arachno*-4,6- $C_2B_7H_{12}$ anion with nitriles, could be used with succinonitrile to make the linked-cage [6,6-(CH_2)₂-*nido*-(5,6,9- $C_3B_7H_9$)₂]²⁻ dianion [13]. In a similar fashion, the reaction of two equivalents of *arachno*-4,6- $C_2B_7H_{12}$ with adiponitrile produced a solution of the Li_2^+ [6,6-(CH_2)₄-*nido*-(5,6,9- $C_3B_7H_9$)₂]²⁻ (**1**) salt containing the longer 4-carbon linkage. The ¹¹B NMR spectrum of the reaction solution at completion exhibited the seven resonance pattern that is highly characteristic of the 6-*R-nido*-5,6,9- $C_3B_7H_9$ anion and was similar to that observed for the previous [6,6-(CH_2)₂-*nido*-(5,6,9- $C_3B_7H_9$)₂]²⁻ dianion. Because the tricarbadeborane cage is enantiomeric, **1** is produced as a mixture of the two diastereomeric forms shown in Scheme 1 resulting from the R + S and R + R (or S + S) combinations of the 6-*R-nido*-5,6,9- $C_3B_7H_9$ enantiomers. **1** was not isolated at this point, but was instead stored as a stock solution under N₂ until its further reaction.

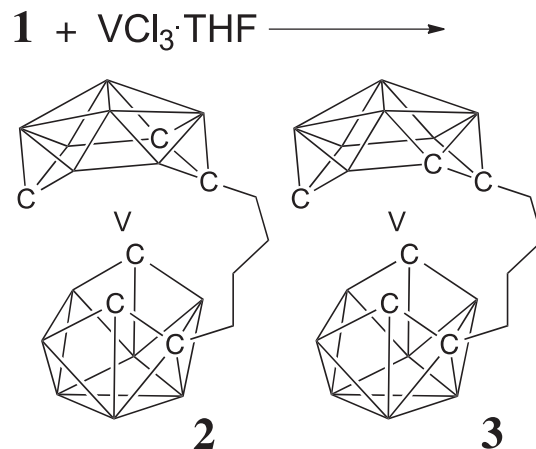
As depicted in Scheme 2, the 1:1 reaction of **1** with $VCl_3 \cdot THF$ in THF solution yielded, following purification by preparative TLC using a CH_2Cl_2 eluent, approximately equal amounts of two dark green crystalline solids.

As observed in the reactions to form the $V(Me-C_3B_7H_9)_2$ complexes, during the reaction to form **2** and **3**, reduction to V(II) occurred with the lower oxidation state stabilized by the highly electron-withdrawing tricarbadeboranyl ligands [7,8,14]. Like the V(II) vanadocene complexes, Cp_2V [9] and Cp^*_2V [10], **2** and **3** are paramagnetic with a 15 electron count at the vanadium. However, unlike Cp_2V and Cp^*_2V , which are high spin complexes with three unpaired electrons, Evan's method measurements indicated, as was observed for the untethered $V(Me-C_3B_7H_9)_2$ complexes [8], that **2** ($\mu_{eff} = 1.77$) and **3** ($\mu_{eff} = 1.73$) had only one unpaired electron. This difference in magnetism is again consistent with both the lower symmetry and stronger bonding properties of the tricarbadeboranyl versus the Cp/Cp* ligands.

Owing to their paramagnetism, **2** and **3** could not be characterized with the aid of NMR; however, crystallographic determinations confirmed the *ansa*-structures shown in Figs. 1 and 2.



Scheme 1. Synthesis of Li_2^+ [6,6-(CH_2)₄-*nido*-(5,6,9- $C_3B_7H_9$)₂]²⁻ (**1**).



Scheme 2. Synthesis of *ansa*-complexes **2** and **3**.

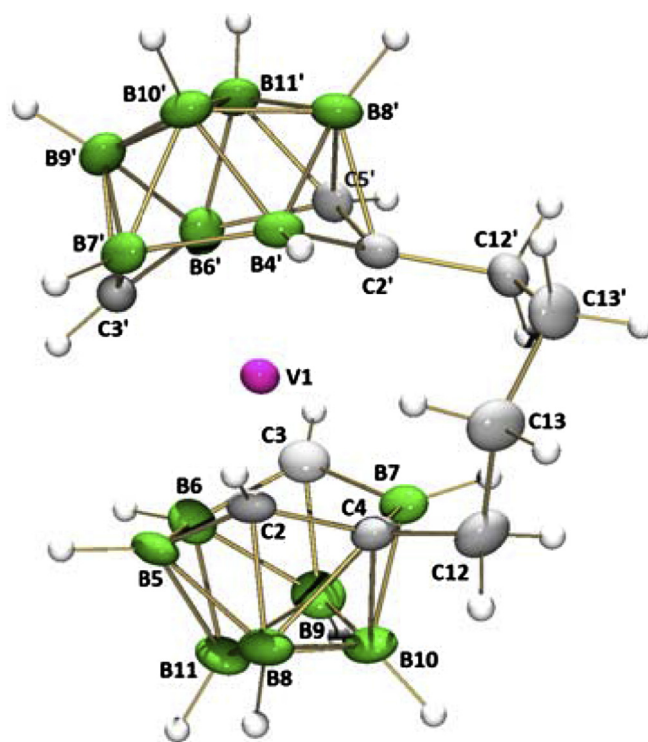


Fig. 1. Crystallographically determined structure of **2**. Selected distances (Å) and angles (deg): V1–C2, 2.002(4); V1–C3, 2.105(8); V1–C4, 2.381(4); V1–B5, 2.364(8); V1–B6, 2.424(5); V1–B7, 2.439(6); V1–(C4–B5–B6–B7)_{centroid}, 1.811(3); V1–(B4'–C5'–B6'–B7')_{centroid}, 1.755(3); C2–B5, 1.601(8); B5–B6, 1.832(8); C3–B6, 1.571(12); C3–B7, 1.586(11); C4–B7, 1.736(6); C2–C4, 1.515(6); C4–C12, 1.527(5); V1–C2', 2.058(4); V1–C3', 1.999(4); V1–C5', 2.363(4); V1–B4', 2.355(6); V1–B6', 2.339(9); V1–B7', 2.362(9); C2'–B4', 1.594(6); B4'–B7', 1.856(14); C3'–B6', 1.589(8); C3'–B7', 1.576(12); C5'–B6', 1.724(7); C2'–C5', 1.516(5); C12'–C2', 1.532(5); C3–V1–C2, 102.0(2); C3'–V1–C2', 105.31(15); V1–C4–C12, 129.0(2).

In both complexes, a formal V^{2+} ion is sandwiched between two tricarbadeboranyl ligands that are linked by the $-(CH_2)_4-$ chain. The **2** and **3** structures differ only in the handedness of the cages. Thus, as can be seen by comparing Figs. 1 and 2, in compound **2** the C4 and C5' cage-carbons are on opposite sides of the tether, whereas in **3** the C4 and C4' cage-carbons are on the same side. The vanadium in each complex is centered over the six-membered, puckered open faces of the two cages, with the C4–B5–B6–B7 and C4'(5')–B5'(4')–B6'–B7' planes being nearly parallel, but

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