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Facile Syntheses of Trovacene, the Formation of [*n*]Boratrovacenophanes (*n* = 1, 2), and Their Reactivity toward [Pt(PEt$_3$)$_4$]

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*Summary: Trovacene (**1**) was prepared by two novel procedures, employing readily available vanadium precursors and after dimetalation converted into the [2]boratrovacenophane **2** and the [1]boratrovacenophane **4**. The reactivity of the boron−boron bond in **2** toward [Pt(PEt$_3$)$_4$] was studied and afforded the oxidative addition product **3**. X-ray crystallographic studies on **2**−**4** revealed mutual tiltings of the carbocyclic rings of 11.4, 4.98, and 28.23°, respectively.*

Cyclopentadienylcycloheptatrienylvanadium (**1**; trovacene) and its derivatives have attracted continuous interest over the past decade, mostly due to their potential to serve as facile probes for electrocommunication and magnetocommunication.[1] Trovacene (**1**) was first synthesized in 40% yield by King and Stone, by refluxing [(η^5-C$_5$H$_5$)V(CO)$_4$] in cycloheptatriene. An alternative route was reported by Müller and Goll based on the reaction of [(η^5-C$_5$H$_5$)VCl$_3$] with cycloheptatriene in the presence of an isopropyl Grignard reagent.[2] Since [(η^5-C$_5$H$_5$)VCl$_3$] has to be prepared by chlorination of [(η^5-C$_5$H$_5$)V(CO)$_4$], both procedures rely on the latter half-sandwich carbonyl complex as a starting material, which is solely accessible by reductive carbonylation of [(η^5-C$_5$H$_5$)$_2$V] or by reaction of [V(CO)$_6$]$^-$ with organomercurials.[3,4] These preparative drawbacks in the synthesis of trovacene (**1**) have prompted us to investigate further the possibility of utilizing cheap and easily accessible vanadium(III) trihalide compounds. In this paper we report on the results of our endeavors to give facile access to **1** and the reactivity studies of the derived [2]boratrovacenophane **2** with [Pt(PEt$_3$)$_3$], to yield **3**, the product of an oxidative addition of the boron−boron bond.

Stimulated by work reported by Teuben et al., we decided to utilize [(η^5-C$_5$H$_5$)VCl$_2$(PEt$_3$)$_2$] (**4**) for the preparation of trovacene, because this readily available compound has already proven its suitability to serve as a valuable precursor for the preparation of low-valent organometallics of vanadium.[5,6] To this end, **4** was reacted with cycloheptatriene in thf at room

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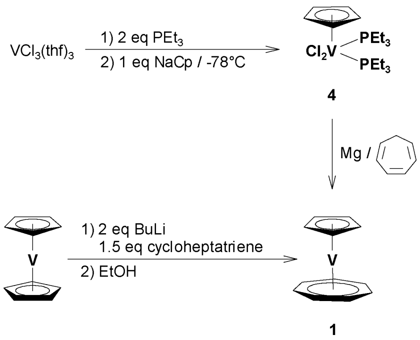
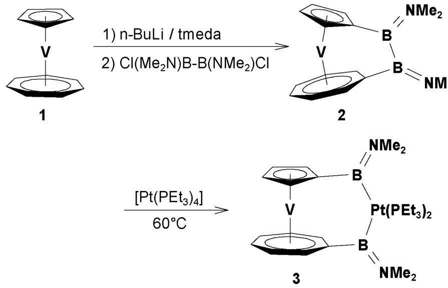
Scheme 1. Preparation of Trovacene (1)



Scheme 2. Synthesis of the [2]Boratrovacenophane 2 and Formation of 3, the Product of an Oxidative Boron−Boron Cleavage



temperature in the presence of magnesium turnings and afforded, after sublimation and recrystallization from hexanes, analytically pure purple crystals of **1** in 55% yield (Scheme 1). It is noteworthy that the entire amount of PEt_3 can be recovered in the form of its hydrochloride salt after addition of aqueous HCl.

Reminiscent of the synthesis of $[(\eta^5\text{-}C_5H_5)V(\eta^6\text{-}C_6H_6)]$ from $[(\eta^5\text{-}C_5H_5)_2V]$, *n*-BuLi, and 1,3-cyclohexadiene described by O'Hare et al., **1** can also be obtained in 42% yield by a modified procedure employing cycloheptatriene rather than 1,3-cyclohexadiene (Scheme 1).[7] The relative merits of these procedures are the avoidance of any vanadium carbonyl species and, particularly in the case of the latter synthesis, the use of readily available standard reagents.

In addition to its aforementioned importance for the elucidation of intermetal communication, trovacene displays a rich and interesting organometallic chemistry. In particular, the dilithiated species $[(\eta^5\text{-}C_5H_4Li)V(\eta^7\text{-}C_7H_6Li)]\cdot$tmeda has proven to be a versatile precursor for the preparation of silicon-derived ansa compounds of trovacene.[1b,8] In continuation of our current efforts to prepare [*n*]bora ansa sandwich compounds ($n = 1$, 2) that are potentially useful for the generation of metallopolymers[9] or as catalysts,[10] $[(\eta^5\text{-}C_5H_4Li)V(\eta^7\text{-}C_7H_6Li)]\cdot$tmeda was reacted with stoichiometric amounts of $Cl(NMe_2)B-B(NMe_2)Cl$. According to Scheme 2 the [2]boratrovacenophane **2**, which represents the first example of a diboron-bridged *ansa*-vanadium complex, was isolated in 45% yield as purple crystals extremely sensitive to air and moisture.

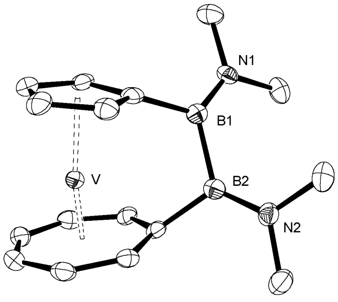


Figure 1. Molecular structure of [2]boratrovacenophane **2**. The hydrogen atoms are omitted for clarity.

The solid-state structure of **2** closely resembles that of the previously reported isomorphous [2]boratrochrocenophane $[(\eta^5\text{-}C_5H_5)(NMe_2)B-B(NMe_2)(\eta^7\text{-}C_7H_7)Cr]$ (**2a**).[9d] In particular, the boron−boron distance of 1.725(5) Å is, within experimental error, identical (Figure 1). The ring separations in the parent metallocenes are markedly different (3.38 Å for **1** versus 3.26 Å for $[(\eta^5\text{-}C_5H_5)Cr(\eta^7\text{-}C_7H_7)]$), and hence, **2** is expected to exhibit a greater molecular strain than **2a**. Interestingly, this is not reflected by significantly different tilt angles α (11.4° for **2** versus 8.9° for **2a**) but by elongated interatomic metal−carbon distances to the five-membered (2.225(4)−2.276(3) Å) and seven-membered rings (2.158(3)−2.190(4) Å), compared to the metal−carbon distances found in **2a** for the five-membered ring (2.1616(20)−2.2056(18) Å) and seven-membered ring (2.1370(18)−2.1683(20) Å).

Boron−boron bonds are prone to undergo facile oxidative addition reactions toward a variety of low-valent transition-metal species with concomitant formation of bis(boryl)−metal complexes $[L_xM(BR_2)_2]$,[11] thus effectively enabling the transition-metal-catalyzed diboration of alkenes,[12] alkynes,[13] and 1,3-dienes.[14] Treatment of **2** with stoichiometric amounts of $[Pt(PEt_3)_4]$ in benzene at elevated temperature afforded the oxidative addition product **3** as purple crystals in 84% yield. To establish unequivocally the structure of **3** in the solid state, a single-crystal X-ray diffraction study was carried out (Figure 2).

The incorporation of the $Pt(PEt_3)_2$ moiety leads to a drastic release of the molecular strain, and hence, the carbocyclic ligands in **3** adopt an almost parallel arrangement, which is reflected by a decreased tilt angle α of 4.98°. Notable pertinent

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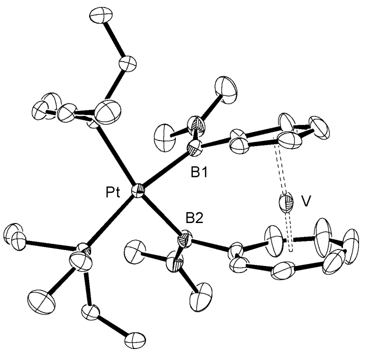
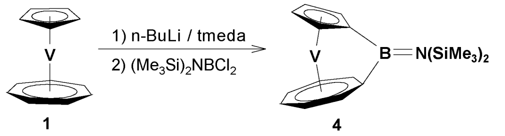


Figure 2. Molecular structure of [3]boraplatinatrovacenophane **3**. The hydrogen atoms are omitted for clarity.

Scheme 3. Synthesis of the [1]Boratrovacenophane 4



metric parameters around the platinum center include the Pt−B bond lengths (Pt1−B1 = 2.101(3) Å, Pt1−B2 = 2.108(3) Å), the Pt−P distances (Pt1−P1 = 2.3411(6) Å, Pt1−P2 = 2.3502(7) Å), the B−Pt−B angle (77.17(12)°), and the P−Pt−P bond angle (99.22(2)°), all of which lie within previously reported ranges.[9d,11d,13b,c,e]

Analogously to the preparation of **2**, $[(\eta^5\text{-}C_5H_4Li)V(\eta^7\text{-}C_7H_6Li)]\cdot$tmeda was reacted with $(Me_3Si)_2NBCl_2$ to give the [1]boratrovacenophane **4** in 37% yield (Scheme 3). Interestingly, the formation of **4** was accomplished by addition of either a stoichiometric amount or an excess of $(Me_3Si)_2NBCl_2$ (2.5 equiv).

Owing to the small atomic radius of the bridging boron atom, a significantly greater intrinsic strain in **4** and, thus, a greater tilt angle α compared to that in the corresponding [1]silatrovacenophanes might be anticipated in the solid state.[1b] In fact, as it can be deduced from the crystallographic data (Figure 3), **4** displays a tilt angle α of 28.23°, which is significantly greater than those reported for the corresponding [1]silatrovacenophanes ($\alpha = 17.26°$) and [1]silatroticenophanes ($\alpha = 24.1°$).[1b,15]

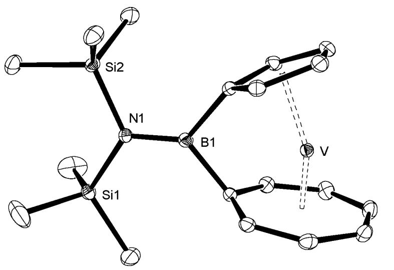


Figure 3. Molecular structure of [1]boratrovacenophane **4**. The hydrogen atoms are omitted for clarity.

Table 1. Comparison of Relevant EPR Parameters for Compounds 2−4

	4	**2**	**3**
α (deg)	28.23	11.40	4.98
g_{iso}	2.00380	1.99101	1.99068
$a_0(^{51}V)$ (G)	65.52	69.55	70.96

In addition, the paramagnetic compounds **2**−**4** were the subject of EPR spectroscopic investigations. Inspection of the parameters extracted for the species **2**−**4** from their solution X-band EPR spectra reveals that the observed values of g_{iso} and $a(^{51}V)$ are in agreement with values previously reported for related [1]sila-, [2]sila-, and [2]platinasilatrovacenophanes.[1b,8] In particular, the previously observed trend that an increasing tilt angle α goes along with an increase of g_{iso} and a decrease in $a(^{51}V)$ was confirmed (Table 1).[1b,8]

In conclusion, two improved syntheses of trovacene (**1**) are reported, utilizing readily available vanadium precursors. The first [*n*]boratrovacenophanes (*n* = 1, 2) thus obtained, **2** and **4**, have the potential for further interesting transformations that may be achieved via metal-mediated activation of the B−B bond in the case of **2** to afford **3** or by ROP processes releasing the intrinsic high strain of **4**. Corresponding studies are currently ongoing in our laboratories.

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Supporting Information Available: Text and figures giving full details of the syntheses and EPR studies and CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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