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AN UNUSUAL REACTION PRODUCT FROM A 1,3-DIBOROLENE AND TETRACARBONYLNICKEL. STRUCTURE OF A BIS(ALLYL)NICKEL COMPLEX

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Summary

The bis(allyl)nickel complex (η^3-3-vinyl-2,4,5,6-tetraethyl-1-oxa-2,6-diboracyclohexenyl)(η^3-2,3,4,5,6-pentaethyl-1-oxa-2,6-diboracyclohexenyl)nickel(IV) is formed by initial insertion of CO from $Ni(CO)_4$ into the five-membered 1,3-diborolene I, to give a six-membered ring. Subsequent exchange of the CH—CH_3 group of I for the oxygen atom of the inserted CO and migration of a hydrogen atom from the $\geq C{=}CH{-}CH_3$ group of one ring to that of the other results in formation of the bis[1-oxa-2,6-diboracyclohexenyl]nickel, IV, having one vinyl and nine ethyl substituents. An X-ray structural analysis of IV shows the non-planarity of the C_3B_2O rings; the boron and oxygen atoms lie 0.4 and 0.7 Å, respectively, away from the best plane through the allyl carbon atoms. IV crystallizes in the space group $P2_1/n$ with a = 9.065(2), b = 16.264(3), c = 10.187(2) Å, β = 104.28(1)°, and Z = 2.

Introduction

The ligand properties of 2-methyl-1,3,4,5-tetraethyl-1,3-diborolene, I, obtained by thermolysis of hexaethyl-*cis*-diborylethene [1] have been recently examined. Following loss of hydrogen from the C(2) position, I can act as a three-electron ligand, forming the cyclopentadienyl-(1,3-diborolenyl)nickel sandwich II [2] and the 30-valence-electron triple-decker sandwich (cyclopentadienyliron)(μ-1,3-diborolenyl)(cyclopentadienylcobalt), (C_5H_5)Fe(μ-1,3-

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** X-ray analysis.

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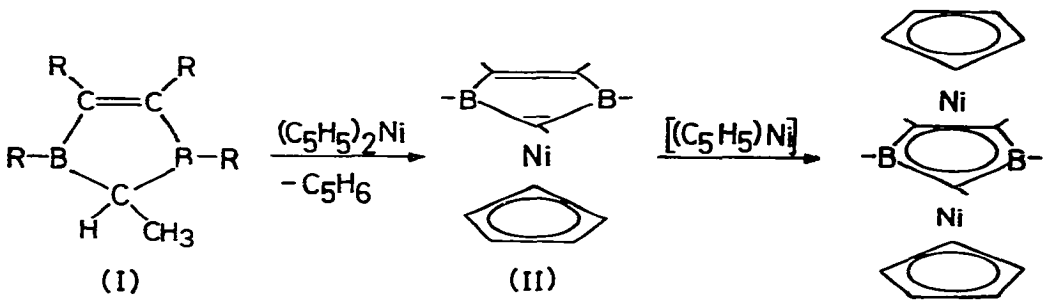
$C_2B_2C)Co(C_5H_5)$ [3]. In addition, paramagnetic triple-decker complexes with 31, 32 and 33 VE's (VE = valence electron) have been synthesized with the 1,3-diborolene ligand in the bridging position [4]. As predicted by EH-MO calculations for triple-decker complexes [5], the 33-VE species is reduced by potassium to give a diamagnetic anion. The 32- and 33-VE triple-decker complexes are obtained by stacking the sandwich II with the Lewis-base $(C_5H_5)M$ fragments (M = Co, Ni). This and the formation of the radical anion $[(C_5H_5)Ni(C_2B_2C)]^{-\cdot}$ demonstrate the good acceptor properties of the Lewis-acid sandwich.



(I) (II)

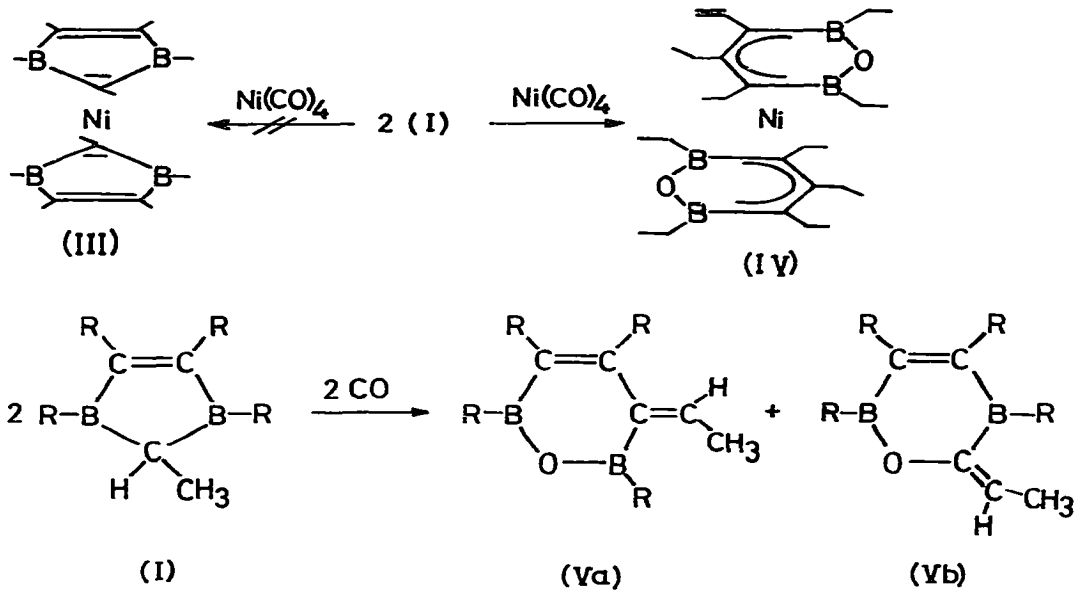
Replacing both C_5H_5ligands in nickelocene by 1,3-diborolene should yield the electron-poor 16-VE complex III, which is expected to show stronger acceptor character than II. It should be possible to stack III on both sides to give tetra-decker complexes. In addition III could act as a building block for multiple-decked stacked compounds having columnar structures. This article describes the reaction between I and $Ni(CO)_4$ in an attempt to synthesize the electron-poor sandwich III.

Results and discussion

Heating I and $Ni(CO)_4$ in benzene produced an orange-red solution, from which the bis(allyl)nickel complex was isolated in 15% yield. The orange-red, air-sensitive IV sublimes at 130—140°C/0.01 Torr and melts at 225°C (from pentane); in solution, IV slowly decomposes [6]. From spectroscopic and analytical data it was difficult to elucidate the constitution of IV, and so an X-ray structure analysis was carried out, and this showed IV to be a cyclic (π-allyl)-nickel complex. Its formation results from an insertion of one CO molecule into the 1,3-diborolene, followed by an exchange of the $CH—CH_3$ group between the two boron atoms for the oxygen atom of the inserted CO molecule. Subsequently, one $C{=}CH—CH_3$ group is dehydrogenated, and the other is hydrogenated. Probably a nickel hydride species is involved in the formation of the nickel d^8 complex with the 1-oxa-2,6-dibora-cyclohexenyl ligands, one having five ethyl substituents and the other four ethyl substituents and one vinyl substituent.

Since CO inserts into I at 20°C yielding Va and Vb (~1 : 3), IV could be formed from Va and $Ni(CO)_4$. However, the mixture of Va and Vb and $Ni(CO)_4$ yields only minor amounts of IV.

The molecular structure of IV is shown in Fig. 1. The X-ray analysis (Tables



1—3) reveals a *trans* arrangement of the two cyclic allyl ligands, with corresponding Ni—C bond lengths almost identical (2.058—2.077 Å). The 1-oxa-

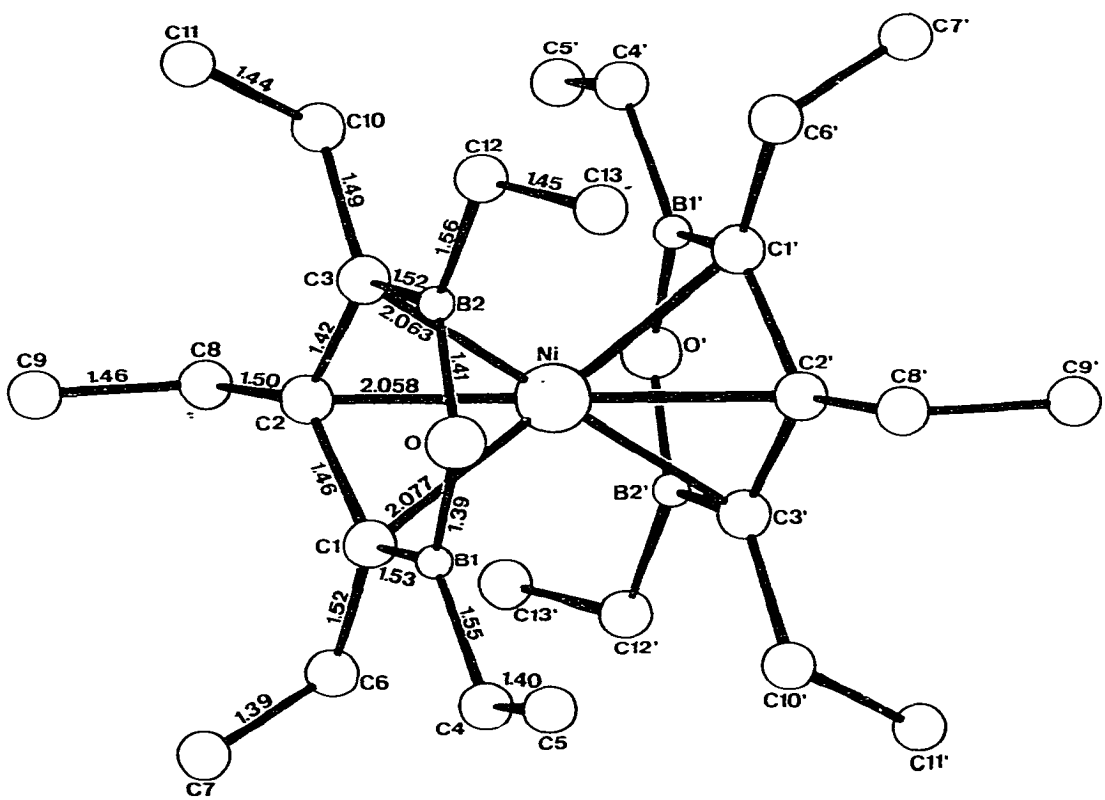


Fig. 1. Molecular structure of IV.

TABLE 1

EXPERIMENTAL DETAILS OF THE X-RAY STRUCTURAL ANALYSIS

Crystal data	
a = 9.065(2) Å	Space group: $P2_1/n$
b = 16.264(3) Å	Nonius CAD-4 Diffractometer
c = 10.187(2) Å	λ(Mo-K_α) 0.71069 Å
β = 104.28(1)°	Graphite monochromator
V = 1455.526 Å^3	Data collected hkl, $\bar{h}kl$
Z = 2	3263 reflections, of which
d_c = 1.133 gcm^{-3}	1506 were considered unobserved
R = 0.062	$(I/\sigma(I) \leq 2.0)$
R_w = 0.072	

TABLE 2

FINAL ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS (×10^4)

Atom	X	Y	Z
Ni	0	0	0
B(1)	—2681(7)	448(4)	51(9)
B(2)	—2310(7)	—766(4)	—1253(7)
O	—3100(3)	—38(3)	—1101(3)
C(1)	—1474(5)	114(4)	1259(5)
C(2)	—915(5)	—724(3)	1254(6)
C(3)	—1143(5)	—1099(3)	—36(6)
C(4)	—3527(7)	1281(4)	—65(8)
C(5)	—4574(10)	1514(4)	—1267(10)
C(6)	—1148(7)	625(5)	2545(7)
C(7)	—2241(11)	625(7)	3294(9)
C(8)	—34(6)	—1124(4)	2535(6)
C(9)	—963(8)	—1608(5)	3238(7)
C(10)	—492(6)	—1930(4)	—157(7)
C(11)	—1502(9)	—2622(4)	—235(9)
C(12)	—2838(7)	—1173(4)	—2679(7)
C(13)	—3483(7)	—672(5)	—3855(7)
H(4A)	—2758	1743	166
H(4B)	—4146	1302	639
H(5A)	—4014	1513	—2051
H(5B)	—5375	1072	—1578
H(5C)	—5064	2032	—1301
H(6A)	—999	1218	2248
H(6B)	—132	468	3128
H(7A)	—3178	843	2766
H(7B)	—2311	93	3646
H(7C)	—1861	1020	4103
H(8A)	510	—669	3181
H(8B)	794	—1472	2370
H(9A)	—1786	—1250	3484
H(9B)	—1501	—2054	2673
H(9C)	—387	—1847	4116
H(10A)	435	—1990	583
H(10B)	—175	—1930	—1027
H(11A)	—1821	—2634	716
H(11B)	—2431	—2574	—895
H(11C)	—1000	—3145	—243
H(12A)	—3597	—1613	—2665
H(12B)	—1952	—1432	—2914
H(13A)	—4490	—414	—3744
H(13B)	—2845	—233	—3993
H(13C)	—3814	—1005	—4709

TABLE 3

BOND DISTANCES (Å) AND BOND ANGLES (°) WITH THEIR STANDARD DEVIATIONS

Bond distances		Bond angles	
C(1)—Ni	2.077(5)	B(1)—O—B(2)	122.0(5)
C(2)—Ni	2.058(6)	O—B(2)—C(3)	118.7(6)
C(3)—Ni	2.063(5)	O—B(1)—C(1)	118.0(6)
B(1)—Ni	2.551(7)	B(1)—C(1)—C(2)	120.7(6)
B(2)—Ni	2.501(7)	B(2)—C(3)—C(2)	121.2(5)
O—Ni	2.759(4)	C(1)—C(2)—C(3)	115.8(5)
B(1)—C(4)	1.55(1)	O—B(1)—C(4)	114.0(7)
B(2)—C(12)	1.56(1)	O—B(2)—C(12)	114.2(6)
B(1)—C(1)	1.53(1)	B(2)—C(3)—C(10)	117.7(6)
B(2)—C(3)	1.52(2)	B(1)—C(1)—C(6)	116.6(6)
B(1)—O	1.39(1)	C(6)—C(1)—C(2)	121.5(6)
B(2)—O	1.41(1)	C(10)—C(3)—C(2)	119.7(6)
C(2)—C(1)	1.46(1)	C(3)—C(2)—C(8)	123.1(5)
C(2)—C(3)	1.42(1)	C(1)—C(2)—C(8)	120.9(5)
C(1)—C(6)	1.52(1)	C(12)—B(2)—C(3)	127.0(6)
C(3)—C(10)	1.49(1)	C(4)—B(1)—C(1)	128.0(7)
C(2)—C(8)	1.50(1)		
C(4)—C(5)	1.40(1)		
C(6)—C(7)	1.39(1)		
C(8)—C(9)	1.46(1)		
C(10)—C(11)	1.44(1)		
C(12)—C(13)	1.45(1)		

2,6-diboracyclohexenyl ring is non-planar, with the boron atoms (0.4 Å) and the oxygen atom (0.7 Å) bent away from the Ni atom. This inclination of the diboryloxide plane of the ligand suggests a reduced interaction between the p_z-orbitals of the boron atoms and the *d*-orbitals of the nickel atom.

The mass spectrum of IV shows the parent peaks (m/e = 494 with 100% rel. int.); observed intensities are in good agreement with the calculated intensities based on the natural isotopic distribution of one nickel atom, four boron and 26 carbon atoms. The high-resolution mass spectrum of IV provides further evidence for its composition. The ^{1}H NMR spectrum of IV (Fig. 2) falls into four distinct groups. The exocyclic vinyl group exhibits 12 signals characteristic for an ABX-spin system. The chemical shifts of the individual protons were ascertained with the help of a simulated spectrum: $\delta(H_a)$ = 5.30, $\delta(H_b)$ = 5.34, $\delta(H_x)$ = 6.25 ppm; J_{bx} = 17.5, J_{ax} = 11.4 and J_{ab} = 1.5 Hz. The second group of signals consists of two quartets at 2.67 and 2.55 ppm, and these quartets are assigned to the CH_2 protons of the C(2) and C(2') ethyl groups. The quartet appearing downfield is assigned to the CH_2 protons of the ring which carries the vinyl group. The third group of signals arises from the CH_2 protons of the allyl C—ethyl groups. These methylene protons are not magnetically equivalent and exhibit a multiplet (ABX_3) at about 2 ppm in an intensity ratio 3 : 2 to the quartets. The remaining signals appear as a multiplet around 1 ppm; the signals of the B-ethyl groups are coincident with the triplets of the C—ethyl groups.

The ^{11}B NMR spectrum of IV exhibits a broad signal at 41.4 ppm in C_6D_6 solution. Compared with results for the mixture Va and Vb ($\delta(^{11}B)$ = 50.3, 79.9 ppm) and for alkoxyboranes and diboryloxides ($\delta(^{11}B)$ = 49 to 54 ppm [7]), the shift (~9 ppm) of the ^{11}B signal reflects a shielding effect on the

TABLE 4

HIGH RESOLUTION MASS SPECTRUM AND ISOTOPIC PATTERN OF THE PARENT PEAKS OF IV

Combinations	Calcd.	Found	Δ (10^{-3} u)
$^{12}C_{26}H_{48}O_2{}^{10}B_2{}^{11}B_2{}^{58}Ni$	492.3451	492.3442	−0.9
$^{12}C_{26}H_{48}O_2{}^{10}B{}^{11}B_3{}^{58}Ni$	493.3415	493.3415	0
$^{12}C_{26}H_{48}O_2{}^{11}B_4{}^{58}Ni$	494.3379	494.3400	2.1
$^{12}C_{25}{}^{13}CH_{48}O_2{}^{11}B_4{}^{58}Ni$	495.3412	495.3391	−2.1
$^{12}C_{26}H_{48}O_2{}^{11}B_4{}^{60}Ni$	496.3334	495.3352	1.8

m/e	Calcd.	Found	*m/e*	Calcd.	Found
491	3.50	3.59	496	40.97	44.03
492	23.53	23.06	497	15.15	14.77
493	73.12	69.70	498	7.04	7.96
494	100.00	100.00	499	2.70	2.58
495	52.28	53.06	500	1.75	1.29

boron atoms through complexation. This $\delta(^{11}B)$ value is comparable with those found for borazine- [8] and 1,2-diaza-3,6-diborin-tricarbonylchromium complexes [9] (8—10 ppm).

There is no indication of a *cis/trans* isomer mixture of IV in solution, such as is known to exist for bis(π-allyl)nickel complexes of the type $(CH_2CHCH_2)Ni$ and $(CH_3CHCHCH_2)Ni$ [10]. This is also supported by the ^{13}C NMR spectrum of IV which shows 15 of the expected 18 signals associated with the asymmetry of the molecule arising from the vinyl group. The observation of the

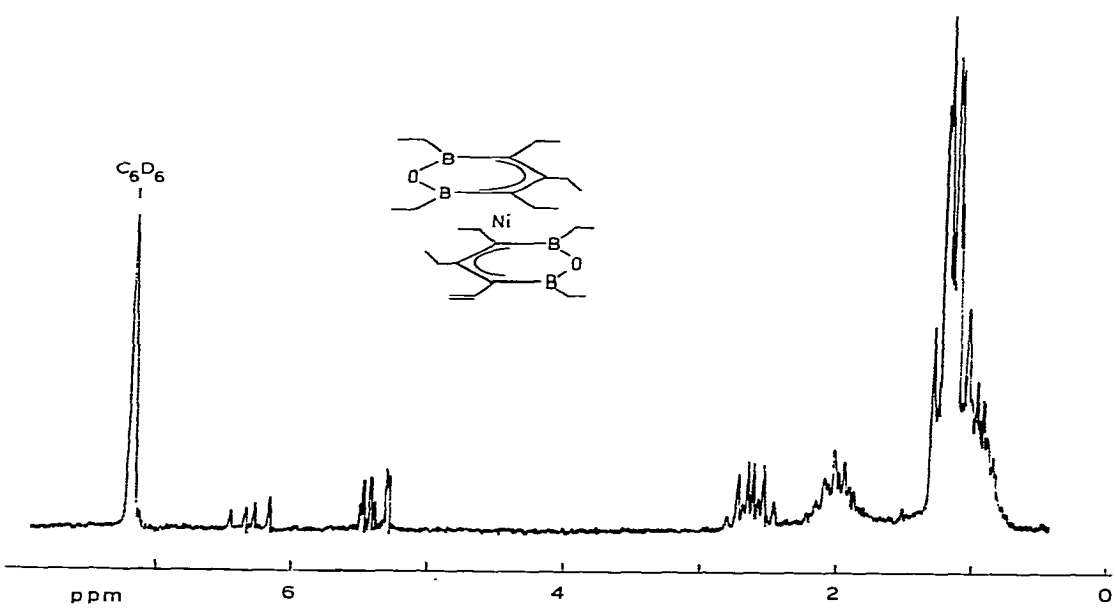


Fig. 2. ^1H NMR of IV.

carbon atoms directly bonded to boron is diffibult because of its nuclear quadrupole moment.

Conclusion

Although the insertion of CO into trialkylboranes is known, the formation of IV and V appears to represent the first examples of ring expansions caused by insertion of CO into a cyclic boron compound. The fact that one of the C_3B_2O rings in IV carries a vinyl group indicates that the reaction is accompanied by the transfer of a hydrogen atom from the CH—CH_3 group of one ring to a corresponding group at the other ring. Probably this "hydride-transfer" is caused by the nickel atom, since migration of hydrogen atoms is common in the catalytic chemistry of nickel.

Experimental

Manipulations were performed under dried nitrogen. Solvents were purified by standard techniques. 100 MHz ^1H NMR spectra were recorded on a Varian XL-100, 63.15 MHz ^{11}B and 20 MHz ^{13}C NMR spectra on a CFT-20, and mass spectra on a CH 7 MAT. instrument.

(η^3-3-Vinyl-2,4,5,6-tetraethyl-1-oxa-2,6-diboracyclohexenyl)(η^3-2,3,4,5,6-pentaethyl-1-oxa-2,6-diboracyclohexenyl)nickel(IV)

A solution of I (1.1 g, 5.8 mmol) in benzene (10 ml) was treated with 5.0 g $Ni(CO)_4$ (29.3 mmol) at 60—70°C for 5 h. After removal of the solvent, distillation at 60—65°C/0.1 Torr gave 0.6 g of a colorless product (Va and Vb, 47%). When the residue was heated to 130—140°C/0.01 Torr 0.22 g red IV (15%) sublimed, m.p. 225°C. ^{11}B: 41.4 ppm (in C_6D_6, $BF_3 \cdot OEt_2$ ext. ref.); ^{13}C: 143.5, 142.5, 137.7, 117.6, 23.7, 23.5, 23.3, 23.0, 21.9, 16.5, 16.4, 16.2, 15.0, 8.4, 8.3 ppm (in C_6D_6, TNS as ref.); IR: 2970m, 2936m, 2875s, 1616w, 1475m, 1454m, 1420(sh), 1406s, 1385(sh), 1372m, 1365m, 1310w, 1270s, 1246s, 1235(sh), 1218(sh), 1185w, 1113s, 1094(sh), 1060w, 1012s, 994(sh), 973w, 960(sh), 910s, 825s, 815(sh), 756w (KBr, cm^{-1}). Found: C, 63.03; H, 9.74. $C_{26}H_{48}B_4O_2Ni$ calcd.: C, 63.14; H, 9.78%.

Insertion of CO into I

0.77 g I (4.1 mol) was stirred in 10 ml C_6H_6 in an atmosphere of dry CO at 20°C for 2 h. Removal of the solvent followed by distillation of the residue at 65—70°C/0.2 Torr gave a colorless liquid, 0.57 g (64%), which according to spectroscopic data consist of a mixture of Va and Vb (~1 : 3). Mass spec.: *m/e* 218 (33, M^+), 189 (9, $\{M - C_2H_5\}^+$), 161 (29, $\{M - C_2H_4 - C_2H_5\}^+$), 132 (13, $\{M - C_2H_4 - 2\,C_2H_5\}^+$). ^1H NMR: δ 6.80 (q, 1), 6.18 (q, 1), 2.3 (m, 8), 1.98 (d, 3), 1.84 (d, 3), 1.04 (s), 0.99 (t) ppm in C_6D_6, TMS as ref.; ^{11}B NMR: δ 50.3 and 79.9 ppm in C_6D_6, $BF_3 \cdot OEt_2$ ext. ref.. The signal δ 79.9 ppm is assigned to the boron atom having three carbons attached to it, the signal δ 50.3 to the other boron in Vb and both of Va.

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