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DIBORAETHENE COMPOUNDS AS LIGANDS IN METAL COMPLEXES

XIV *. SYNTHESIS AND CRYSTAL STRUCTURE OF BIS(η^5-3,4-DIETHYL-2,5-DIMETHYL-1,2,5-THIADIBOROLENE)MONOCARBONYLIRON

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Summary

Irradiation of a 2:1 mixture of 3,4-diethyl-2,5-dimethyl-1,2,5-thiadiborolene (I) and $Fe(CO)_5$ produces red-violet bis(1,2,5-thiadiborolene)monocarbonyliron (V). An X-ray diffraction study shows that the latter involves a tetragonal pyramidal arrangement of the sulfur atoms (Fe–S 2.328; 2.329 Å) and the $>C=C<$ groups (Fe–C 2.237, 2.241; 2.198, 2.176 Å) of the non-parallel thiadiborolene rings with CO in the vertex position; the structure resembles that of bis(η^4-1,3-cyclohexadiene)monocarbonyliron.

The ring atom distances are B–S 1.866(4), B–C 1.531(6), and C–C 1.419(3) Å. The complex crystallizes in the space group $P2_1/n$ with the cell parameters a 14.877(1), b 8.9209(8), c 16.739(1) Å, β 87.514(5)° and four molecules in the unit cell.

Reactions of V with carbonylmetal compounds did not lead to tetra-decker complexes but to 1,2,5-thiadiborolene-tricarbonyliron (II), sandwich and triple-decker complexes. Removal of CO from V with formation of the bis(1,2,5-thiadiborolene)iron (VII) was unsuccessful.

Introduction

The four-electron donor 3,4-diethyl-2,5-dimethyl-1,2,5-thiadiborolene (I) (denoted by C_2B_2S) reacts with carbonylmetal compounds to form sandwich complexes, e.g.

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* For Part XIII see Ref. 1.

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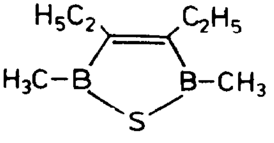
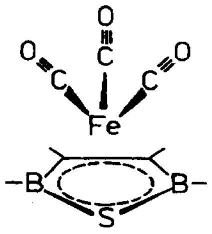


(I)



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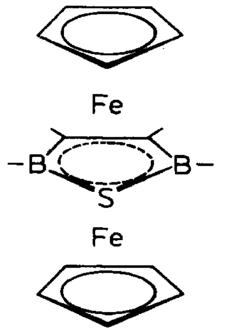

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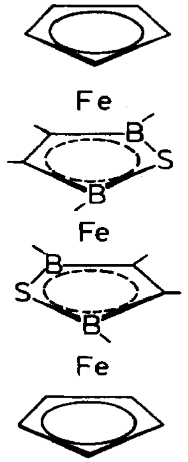
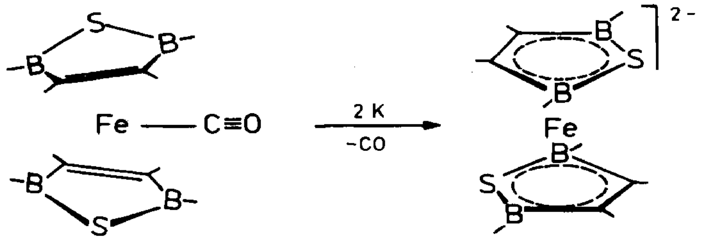


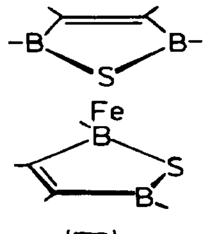
(IV)

$(C_2B_2S)_2Ni$ [2], $(C_5H_5)Co(C_2B_2S)$ [3] and III [4]. Spectroscopic and structural data of several mono-, as well as di- and tri-nuclear complexes indicate that the ligand can also act as a strong electron acceptor [5].

Several aspects of the title compound V aroused our interest. First, the monocarbonyliron complex should have synthetic potential for the construction of the 42-valence electron tetra-decker sandwich IV by stacking the sandwich-type V with two $(C_5H_5)Fe$ moieties with the elimination of carbon monoxide. Secondly, V poses an interesting conformational question, namely is the compound a trigonal bipyramid with the sulfur atoms in a *trans*-arrangement or a tetragonal pyramid with CO in the apical position (as it is observed for bis(1,3-diene)monocarbonyliron complexes [6])? Thirdly, reductive elimination of CO from V should lead to the sandwich dianion VI, which in turn could serve as building unit for polydecker compounds. VI is isoelectronic with the bis(thiadiborolene)cobalt anion $[(C_2B_2S)Co(C_2B_2S)]^-$, for which a *trans*-arrangement of the C_2B_2S ligands has been proposed [7].



(V) (VI)



(VII)

Results and discussion

Synthesis and reactions

Thermal reaction of I and $Fe(CO)_5$ produces only the tricarbonyliron complex II [8], but irradiation of a 2:1 mixture of the ligand and $Fe(CO)_5$ in hexane for 2 h leads to the monocarbonyliron compound V and II in 68 and 25% yields, respectively. The two products can be separated by recrystallization from hexane. Irradiation of the ligand and the tricarbonyliron complex II for 1 h also yields V in 58% yield; 21% of II is recovered. The crystals of bis(thiadiborolene)monocarbonyliron (V) are dark-violet, are air-sensitive but stable under nitrogen. The compound decomposes at 154°C with evolution of carbon monoxide. Formation of the sandwich VII might be expected when CO is released from V, but under these conditions VII is unstable. Recently this electron-deficient 16-valence electron sandwich was obtained in low yield obtained from I, $FeCl_2$ and $Na[Et_3BH]$ in THF at $-30°C$ [9].

At room temperature carbon monoxide replaces one thiadiborolene ring in V to yield the tricarbonyliron complex II and the free ligand I. Similar substitutions occur with the carbonylmetal complexes $[(C_5H_5)Fe(CO)_2]_2$ and $[Mn_2(CO)_{10}]$, which can provide the one-electron donor fragments $(C_5H_5)Fe$ and $(CO)_3Mn$ when they are treated with V in boiling mesitylene. In both cases the replacement of the C_2B_2S ligand by CO is favored over a stacking of V to tetra-decker complexes, e.g. IV.

$$\mathrm{V} + [(C_5H_5)Fe(CO)_2]_2 \rightarrow \mathrm{II} + \mathrm{III} + 2CO$$

$$\mathrm{V} + [Mn_2(CO)_{10}] \rightarrow \mathrm{II} + (CO)_3Mn(C_2B_2S)Mn(CO)_3$$

Besides II the triple-decker complexes III and $(CO)_3Mn(C_2B_2S)Mn(CO)_3$ [10] are formed in 18 and 51% yield, respectively. With cyclopentadienylcobalt and -nickel compounds the following known products [3,11] are obtained [12]:

$$\mathrm{V} + [(C_5H_5)Co(CO)_2] \rightarrow \mathrm{II} + (C_5H_5)Co(C_2B_2S) + 2CO$$

$$\mathrm{V} + [(C_5H_5)Ni(CO)]_2 \rightarrow \mathrm{II} + (C_5H_5)_2Ni + (C_5H_5)Ni(C_2B_2S) + (C_2B_2S)_2Ni$$

Attempts to obtain the anionic sandwich VI from V by reductive elimination of CO have so far been unsuccessful.

Spectra

The mass spectrum of V (70 eV) shows the molecular ion at $m/e = 416$ (3.4% rel. int.), and a sharp cut-off at $m/e = 388$ (100% rel. int.), corresponding to the loss of CO. The intensity profile of the parent peak is in good agreement with that of VII [9].

In contrast to the situation in the solid, V does not exhibit any conformational preference in solution. The methylene protons of the C-ethyl groups show two multiplets in the ^1H NMR spectrum for the two different kinds of protons expected for an ABX_3-spin system. However, the separation of the two multiplets by 1.1 ppm is unusually large and reflects the difference in the electronic environment of the two methylene protons. It is likely that the protons directed towards the metal center are subjected to the anisotropic effect of the carbonyl group. Accordingly, the absorption of these protons is observed at higher fields ($\delta(^1H)$ 1.2) than that of the protons directed away from the iron atom ($\delta(^1H)$ 2.3). The latter value is comparable with the observed chemical shifts of the CH_2 protons in the thiadiborolene tricarbonyliron complexes, in which this anisotropic effect is less marked.

In addition to the multiplets, the spectrum exhibits a triplet for the CH_3 protons of the ethyl groups and a singlet for BCH_3 groups, showing that the CCH_3 and

TABLE 1

CRYSTAL STRUCTURE DATA FOR V

Formula: $C_{17}H_{32}B_4FeOS_2$	Mol. wt. 415.66
a 14.877(1) Å	Crystal system: monoclinic
b 8.9209(8) Å	Space group: $P2_1/n$
c 16.739(1) Å	λ(Mo-K_α) 0.71069 Å
β 87.514(5)°	4523 reflections measured
$Z = 4$	($\pm h$, $+k$, $+l$; $0.5° \leqslant \theta \leqslant 26.44°$)
D_c 1.24 g cm^{-3}	3482 reflections observed ($I > 2.0\sigma(I)$)
μ 8.62 cm^{-1}	$\Omega/2\theta$ scan technique
Parameters refined: 354	
$R = 0.0341$	
$R_w = 0.0429$ ($w = 1/\sigma^2(F_0)$)	
Standard heavy atom method; hydrogen atoms located, but not refined	

BCH_3 groups in V are identical in solution. The ^{13}C off-resonance spectrum of V also supports the view that the ligands in V do not adopt a fixed position with respect to the carbonyl group and vice versa. A quartet at 16.6 and a triplet at 22.7 ppm are found for the ethyl carbon atoms. The carbon atoms attached to boron appear as broad signals because of the quadrupole moment of boron.

The ^{11}B NMR spectrum of V shows a broad signal (δ 32.8) which corresponds to a $\Delta\delta(^{11}B)$ value of 33.2 ($\Delta\delta(^{11}B)$ 38.2 for II). The substitution of two CO groups in II by the ligand I results in a downfield shift of 5 ppm. The reduced *d*-electron density about the iron atom of V in comparison to that of II is also evident from Mössbauer spectra, which show a larger isomer shift of the Fe atom in V (δ_{IS} 0.712 mm s^{-1} for V, δ_{IS} 0.411 mm s^{-1} for II) [13].

Structure

Experimental details of the structural determination on V are summarized in Table 1*. Atomic coordinates are listed in Table 2, bond lengths in Table 3 and angles in Table 4. In contrast to a recent structural study of an isoelectronic nickel compound [2], which was hampered by the disorder of the ethyl groups of the ligand, no disorder was observed in the present case. The molecular structure of V is shown in Fig. 1. Both five-membered rings are almost planar (±0.08 Å). The interplanar angle is 28.6°. The arrangement of both rings is such that the sulfur atoms occupy *trans*-positions (S(1)–Fe–S(2) 152.7°) with respect to each other. The coordination of the iron atom resembles that in bis(η^4-1,3-cyclohexadiene)monocarbonyliron [6]. Thus, the four-electron ligands occupy the basal positions of a tetragonal pyramid, whereas the carbonyl group (Fe–C–O 178.8°) is located at the vertex. The bonding of both ligands towards the iron appears to be similar. However, different B–Fe distances are observed within each entity. The B–Fe bonds adjacent to the carbonyl group (Fe–B(2) 2.304, Fe–B(3) 2.302 Å) are markedly shorter than the other pair (Fe–B(1) 2.391, Fe–B(4) 2.390 Å). This effect can be attributed to a steric repulsion

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* Supplementary data may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, by specifying registry number CSD 50980, author, and source.

TABLE 2

FINAL ATOMIC COORDINATES FOR V WITH STANDARD DEVIATIONS ($\times 10^4$)

Atom	*x*	*y*	*z*
Fe	5136(1)	305(1)	2499(1)
S(1)	4147(1)	497(1)	3610(1)
S(2)	5882(1)	1275(1)	1361(1)
B(1)	4736(2)	2311(3)	3392(2)
B(2)	5215(2)	−500(3)	3802(1)
B(3)	5285(2)	−535(3)	1200(2)
B(4)	4807(2)	2283(3)	1595(2)
O(1)	5807(2)	−2791(2)	2497(1)
C(1)	3536(2)	−1588(3)	2497(1)
C(2)	5747(1)	1984(2)	3307(1)
C(3)	6004(1)	511(2)	3523(1)
C(4)	4240(2)	3852(3)	3466(2)
C(5)	5196(2)	−2050(3)	4242(2)
C(6)	6975(2)	−16(3)	3535(2)
C(7)	7335(2)	96(4)	4370(2)
C(8)	6419(2)	3191(3)	3069(2)
C(9)	6636(2)	4153(4)	3827(2)
C(10)	4310(1)	−365(3)	1520(1)
C(11)	4060(1)	1128(3)	1713(1)
C(12)	4741(2)	4041(3)	1511(2)
C(13)	5759(2)	−1869(3)	738(2)
C(14)	3672(2)	−1687(3)	1574(1)
C(15)	3273(2)	−2076(4)	785(2)
C(16)	3092(2)	1550(4)	1988(2)
C(17)	2567(2)	2043(4)	1253(2)

of the ring ligands at the basal side of the coordination pyramid (B(1)–B(4) 3.007 Å). The effect of this repulsion is also reflected in slightly different Fe–C distances (see Tab. 3).

TABLE 3

BOND DISTANCES (Å) FOR V WITH STANDARD DEVIATIONS

Fe–C(1)	1.791(2)	C(1)–O(1)	1.147(3)
Fe–S(1)	2.328(1)	Fe–S(2)	2.329(1)
Fe–B(1)	2.391(3)	Fe–B(3)	2.302(3)
Fe–B(2)	2.304(3)	Fe–B(4)	2.390(3)
Fe–C(2)	2.237(2)	Fe–C(10)	2.176(2)
Fe–C(3)	2.198(2)	Fe–C(11)	2.241(2)
S(1)–B(1)	1.869(3)	S(2)–B(3)	1.868(3)
S(1)–B(2)	1.863(3)	S(2)–B(4)	1.862(3)
C(2)–C(3)	1.421(3)	C(10)–C(11)	1.417(3)
B(1)–C(2)	1.533(4)	B(3)–C(10)	1.532(3)
B(2)–C(3)	1.536(3)	B(4)–C(11)	1.523(4)
B(1)–C(4)	1.564(4)	B(3)–C(13)	1.570(4)
B(2)–C(5)	1.566(4)	B(4)–C(12)	1.579(4)
C(2)–C(8)	1.511(3)	C(10)–C(14)	1.515(3)
C(3)–C(6)	1.520(3)	C(11)–C(16)	1.540(4)
C(8)–C(9)	1.578(4)	C(14)–C(15)	1.511(4)
C(6)–C(7)	1.523(4)	C(16)–C(17)	1.551(4)

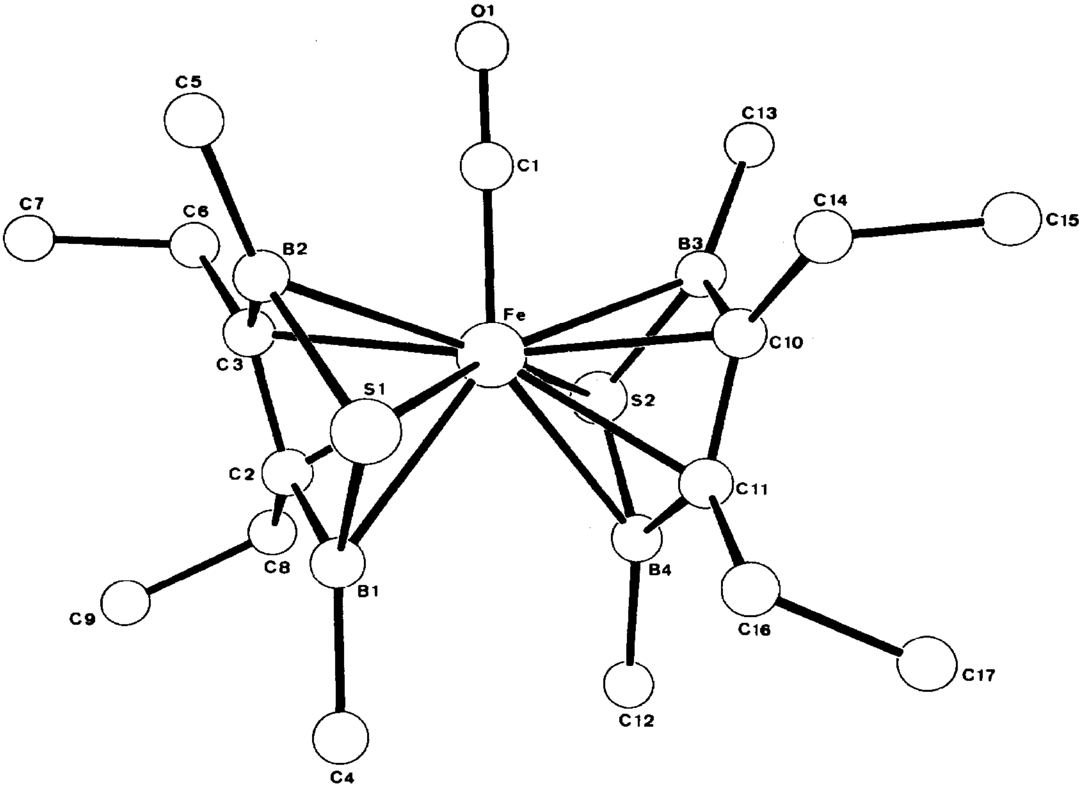

Fig. 1. The molecular structure of V.

All the boron–sulfur bonds are essentially identical, and the average is 1.866 ± 0.004 Å. The average C–C distances within both rings (1.419 Å) are typical for π-bonded systems. All of the ethyl groups attached to the ring carbon atoms point

TABLE 4

SELECTED BOND ANGLES (°) FOR V WITH STANDARD DEVIATIONS

S(1)–Fe–S(2)	152.7(1)	B(2)–Fe–B(4)	148.2(1)
S(1)–Fe–B(3)	144.1(1)	B(2)–Fe–C(11)	136.5(1)
S(1)–Fe–C(10)	105.3(1)	B(2)–Fe–C(10)	132.9(1)
S(1)–Fe–C(11)	90.1(1)	B(2)–Fe–B(3)	141.8(1)
S(1)–Fe–B(4)	108.2(1)	B(3)–Fe–C(2)	139.8(1)
S(2)–Fe–B(2)	148.0(1)	B(3)–Fe–C(3)	136.8(1)
S(2)–Fe–C(3)	109.4(1)	B(4)–Fe–C(3)	125.2(1)
S(2)–Fe–C(2)	93.1(1)	B(4)–Fe–C(2)	89.3(1)
S(2)–Fe–B(1)	109.3(1)	C(2)–Fe–C(10)	153.8(1)
B(1)–Fe–B(3)	147.7(1)	C(2)–Fe–C(11)	117.1(1)
B(1)–Fe–C(10)	122.9(1)	C(3)–Fe–C(10)	168.8(1)
B(1)–Fe–C(11)	87.5(1)	C(3)–Fe–C(11)	152.9(1)
B(1)–Fe–B(4)	77.9(1)	Fe–C(1)–O(1)	178.8(2)
C–B–$\text{S}_{\text{av.}}$	108.2(2)		
B–S–$\text{B}_{\text{av.}}$	92.6(5)		
C–C–$\text{B}_{\text{av.}}$	114.7(6)		

away from the center of the molecule. There are no especially short intermolecular contacts.

Conclusion

Replacement of two CO groups in II by I is easily achieved in a photochemical reaction, which apparently increases the Lewis acidity of the Fe atom in V. This is evident from the ^{11}B chemical shift and the isomer shift of the Fe atom. The transfer of CO onto the Fe atom of V in its reaction with CO as well as with carbonylmetal compounds illustrates the high reactivity of V.

Experimental section

The reactions were carried out using standard techniques under dry and purified nitrogen; the solvents were dried and degassed. A mercury vapour lamp (25 W) was used for photolysis. 100 MHz ^1H, 63.15 MHz ^{11}B, 20 MHz ^{13}C NMR and mass spectra were recorded on Varian XL 100 and CH 7 MAT spectrometers.

Bis(2,5-dimethyl-3,4-diethyl-1,2,5-thiadiborolene)monocarbonyliron (V)

A solution of 0.78 g (4.70 mmol) I and 0.46 g (2.35 mmol) $Fe(CO)_5$ in 80 ml hexane was irradiated at room temperature. Evolution of CO took place immediately and the originally yellow solution gradually became deep red. After 2 h the solution was concentrated to about 5 ml and cooled to 0°C to give V as dark violet crystals. The latter were obtained analytically pure by washing several times with small portions of hexane at 0°C.

When a solution of 1.10 g (3.60 mmol) of II and 0.66 g (4.00 mmol) of I in 80 ml of hexane was irradiated for 1 h, 0.86 g (58%) of V was isolated and 0.23 g of II (21%) was recovered.

Complex V has m.p. 154°C (decomp.), $m/e = 416$ (3.4%) M^+; 388 (100%) $[M - CO]^+$ $\delta(^1H)$ 2.3(m); 1.2(m); 1.18(s); 1.02(t) (in C_6D_6, TMS). $\delta(^{11}B)$ 33.2 (in C_6D_6, $F_3B \cdot OEt_2$). $\delta(^{13}C)$ BCH_3, 1.7(br); CCH_3, 16.6; CCH_2C, 22.7(t); BCCB, 124.5(br); CO, 224.5(s) (in C_6D_6, TMS). ν(CC) 1950 cm^{-1} (KBr). Found: C, 48.97; H, 7.86. $C_{17}H_{32}OB_4FeS_2$ calcd.: C, 49.12; H, 7.76%.

Reactions of V with dimanganese decacarbonyl

A mixture of 0.52 g (1.25 mmol) of V and 0.51 g (1.31 mmol) of $Mn_2(CO)_{10}$ in 10 ml of mesitylene was kept at 160°C for 2 h. After removal of the solvent 0.32 g (84%) of II (b.p. 35–38°C/0.01 Torr) and 0.28 g (51%) of V (subl. 80–90°C/0.01 Torr) were obtained.

Reaction of V with cyclopentadienyl(dicarbonyl)iron

A solution of 0.23 g (0.55 mmol) of V and 0.43 g (1.21 mmol) of $[(C_5H_5)Fe(CO)_2]_2$ in 8 ml of mesitylene was kept at 160°C for 4 h. Mesitylene was evaporated off using high vacuum. Distillation from the residue gave at 50°C/0.01 Torr II, along with ferrocene. At 120°C/0.01 Torr 80 mg (18%) of III sublimed out.

Reaction of V with cyclopentadienyl(dicarbonyl)cobalt

A solution of 0.66 g (1.6 mmol) of V and 0.58 g (3.2 mmol) of $(C_5H_5)Co(CO)_2$ in 10 ml mesitylene was kept at 160°C for 5 h. Working up the reaction products as above yielded 0.26 g (54%) of II and 0.31 g (67%) of $(C_5H_5)Co(C_2B_2S)$.

Acknowledgements

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