Journal of Organometallic Chemistry, 375 (1989) 161–166
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20088

The crystal structure of [1,3-bis(diisopropylamino)-1,3-dibora-5-cyclohexene-2,4-diyl]dicarbonyl(trimethylphosphine)iron: the first structurally characterized 1,3-diborabenzene derivative

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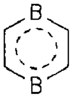
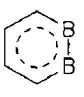
(Received April 27th, 1989)

Abstract

The structure of [1,3-bis(diisopropylamino)-1,3-dibora-5-cyclohexene-2,4-diyl]dicarbonyl(trimethylphosphine)iron as determined by an X-ray diffraction study is described. The 1,3-diborabenzene ring shows a chair conformation with large deviations from planarity and long Fe–B separations (245.7(3) pm).

Transition metal complexes of isomeric $C_4B_2H_6$ ring ligands continue to present a challenge to the synthetic chemist. While complexes of 1,4-diborabenzene ligands (I) have been known since 1975 [1], systematic synthetic routes to the 1,2-isomeric system (II) [2] and to complexes of 1,3-dihydro-1,3-diborapentafulvene ligands (III) [3] have been developed only recently. By contrast, very little is known about the 1,3-diborabenzene system (IV) [4].


(I)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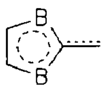
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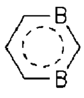
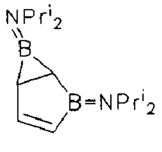

(IV)

We have previously shown that metal-assisted ring opening of the bicyclic $C_4B_2H_6$-isomer V [5] provides the first route to complex 1,3-diborabenzene derivatives [4]. Thus, complexes VI (yellow-orange oil) and VII (yellow crystals) were made [4], but as we shall see below, these are probably structurally atypical for 1,3-diborabenzene complexes.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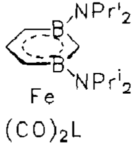
(VI: L = CO;
VII: L = PMe_3)

Attempts to generalize our synthesis of VI have so far failed. We now present the result of an X-ray structure determination of the crystalline complex VII. This work confirms the constitution of VI and VII as originally derived from spectral data and, in addition, provides insight into the perturbing effects of the amino substituents on the structure of the 1,3-C_4B_2 ring.

X-Ray diffraction results and discussion

The molecular structure of complex VII is shown in Fig. 1, which also gives the crystallographic atom-numbering scheme. The structural data are listed in Tables 1-3.

Complex VII crystallizes in an orthorhombic space group with one half of the molecule in the asymmetric unit; the molecule possesses crystallographic mirror symmetry. The molecule of VII (which resembles a lobster with the diisopropylamino groups as the claws and the trimethylphosphine ligand as the tail) consists of a 1,3-diborabenzene ring attached to a $Fe(CO)_2(PMe_3)$ fragment. Important structural features are summarized in Fig. 2.

The two boranediyl groups of the 1,3-diborabenzene ring are bent away from the metal. This results in a chair conformation with a slight folding (7.3°) along the line C(2)-C(2′) (crystallographic numbering) and a marked folding (31.8°) along the line B-B′ which brings C(3) within bonding distance of the Fe centre (cf. Table 3 and Fig. 2). The B-C bond distances (C(2)-B 155.8(4) and C(3)-B 153.3(3) pm) are slightly shorter than typical single bonds (e.g. 157.8 pm for BMe_3 [6] and 157.7 pm (av.) for BPh_3 [7]), while the exocyclic B-N bond (142.7(3) pm) is not significantly longer than typical B-N bonds in aminoboranes (cf. ref. 8).

The Fe-C distances in the C(2)-C(1)-C(2′) part of the ring (215.1(2)/209.9(3)/215.1(2) pm) are typical for (η^3-allyl)iron compounds [9,10] while the Fe-C(3) (219.4(3) pm) distance is comparatively long [10]. The bending away from the metal of the boranediyl groups results in long Fe-B separations (245.7(3) pm) which can be compared to the Fe-B bond lengths in e.g. the borabenzene derivative

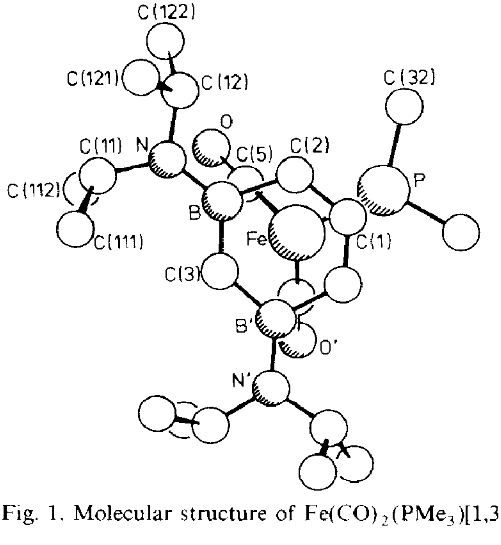

Fig. 1. Molecular structure of $Fe(CO)_2(PMe_3)[1,3\text{-}C_4H_4B_2(NPr^i_2)_2]$ (VII).

Table 1

Non-hydrogen atom coordinates for VII

Atom	x	y	z	B_{eq}^{a}
Fe	0.08698(4)	0.250	0.48458(4)	2.925(8)
C(1)	0.0906(3)	0.250	0.3067(3)	2.99(6)
C(2)	0.1349(2)	0.3131(1)	0.3424(2)	3.06(5)
C(3)	0.2763(3)	0.250	0.4675(3)	2.81(6)
B	0.2488(3)	0.3194(2)	0.4125(2)	2.83(5)
N	0.3061(2)	0.3836(1)	0.4283(2)	3.47(5)
C(11)	0.4013(2)	0.3950(1)	0.5094(3)	3.98(5)
C(111)	0.5108(3)	0.3580(2)	0.4769(3)	5.89(8)
C(112)	0.3676(3)	0.3848(2)	0.6314(3)	5.47(8)
C(12)	0.2707(3)	0.4456(2)	0.3653(3)	5.23(8)
C(121)	0.3692(4)	0.4795(2)	0.3006(3)	7.6(1)
C(122)	0.2060(4)	0.4955(2)	0.4372(4)	8.7(1)
C(5)	0.0812(3)	0.3176(2)	0.5822(3)	5.84(8)
O	0.0741(3)	0.3619(2)	0.6454(2)	11.46(8)
P	−0.10490(8)	0.250	0.47091(9)	3.62(2)
C(31)	−0.1802(4)	0.250	0.6064(5)	6.7(1)
C(32)	−0.1681(3)	0.1773(2)	0.3983(3)	5.57(8)

[a] The anisotropic thermal parameters are given in the form of their isotropic equivalents defined as $\frac{4}{3}[a^2\beta_{11}+\ldots+ab(\cos\gamma)\beta_{12}+\ldots]$; in 10^4 pm^2.

Table 2

Selected bond distances (pm) and bond angles (°) for VII

Fe–C(1)	209.9(3)	C(1)–C(2)	139.5(3)	N–C(11)	147.4(3)
Fe–C(2)	215.1(2)	C(2)–B	155.8(4)	C(11)–C(111)	150.4(4)
Fe–B	245.7(3)	C(3)–B	153.3(3)	C(11)–C(112)	150.4(4)
Fe–C(3)	219.4(3)	B–N	142.7(3)	N–C(12)	147.4(4)
Fe–P	222.0(1)	P–C(31)	181.9(5)	C(12)–C(121)	151.9(5)
Fe–C(5)	175.0(3)	P–C(32)	180.9(3)	C(12)–C(122)	149.1(5)
		C(5)–O	114.4(4)		
C(5)–Fe–C(5′)	97.6(3)	C(2)–B–N	122.0(2)		
C(5)–Fe–P	90.6(1)	C(3)–B–N	128.4(2)		
C(2)–C(1)–C(2′)	123.4(3)	B–N–C(11)	124.2(2)		
C(1)–C(2)–B	122.6(2)	B–N–C(12)	121.5(2)		
C(2)–B–C(3)	109.2(2)	C(11)–N–C(12)	114.3(2)		
B–C(3)–B′	123.8(3)				

Table 3

Definition of best planes and interplanar angles (°) for VII

Plane A ≡ [C(1), C(2), C(2′)]	∢(A,B)	7.3
Plane B ≡ [C(2), B, C(2′), B′]	∢(B,C)	31.8
Plane C ≡ [B, C(3), B′]		
Plane D ≡ [C(2), B, C(3)]	∢(D,E)	9.7
Plane E ≡ [C(11), N, C(12)]		

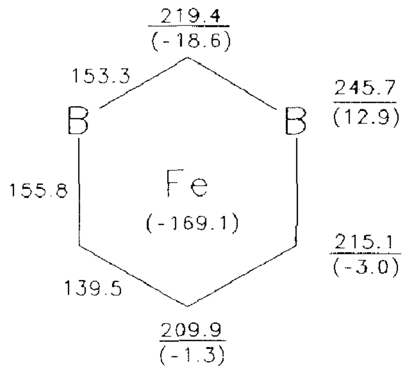

Fig. 2. The geometry of metal–ligand bonding in VII. Underlined numbers are distances from Fe atom, numbers in parentheses are distances from the best plane through all six ring atoms, the remaining numbers give intra-ring bond lengths (pm).

$[Fe(CO)_2(C_5H_5BMe)]_2$ (230.9(12) pm [11]), the 1,2,5-thiadiborolene complex $Fe(CO)_3[C_6H_4(BMe)_2S]$ (227.7(< 4), 228.2(< 4) [12]), and borole compound $Fe(CO)_3(C_4H_4BPh)$ (228.6(2) pm [13]). We conclude that the Fe–B distance in VII indicates only weak metal-to-boron bonding.

The interpretation of these structural observations relies heavily on a recent paper on the structures of two (1-diisopropylamino)borole complexes *cis*-$Cr(CO)_2(C_4H_4BNPr^i{}_2)_2$ and $Mn(CO)(C_4H_4B\text{-}NPr^i{}_2)_2$ [14]. Complexes of 1-methyl- and 1-phenyl-borole ligands show small deviations from ring ligand planarity, normal metal-to-boron bond distances, and moderate slip distortions which shift the metal away from the boron towards the C(3)/C(4) part of the borole ring. By contrast, the two 1-(diisopropylamino)borole complexes mentioned above show unusually large ring ligand folding angles, long metal–boron separations, and large slip distortions. These structural peculiarities are caused by π-interactions between the exocyclic B-amino group and the p_z-orbital at the boron atom. The boron-nitrogen π-interactions are antibonding with respect to the metal-to-boron bonding; the steric requirements of the bulky diisopropylamino groups also contribute to some extent to the observed structural effects.

The situation in VII is likely to be completely analogous. Thus, the structure of VII is atypical, and the large deviations from planarity of the 1,3-diborabenzene ring and the large Fe–B separation are caused by the presence of the amino groups. To avoid structural perturbations by the substituents at boron it will be necessary to synthesize complexes with, for instance, 1,3-dimethyl-1,3-diborabenzene ligands.

Experimental

Complex VII was obtained as described previously [4]. A suitable crystal was sealed under dry dinitrogen in a thin glass capillary. Diffraction data were collected on a CAD 4 autodiffractometer. Details of the structure determination are given in Table 4. The data were corrected for Lorentz and polarization effects. No signs of crystal decay during irradiation were observed. An attempted empirical absorption correction by the method of differential absorption [15] did not give improved *R* values.

The structure was solved and refined by standard heavy-atom methods, alternating least-squares refinements, and difference Fourier calculations. The non-hydro-

Table 4

Crystallographic data, data collection parameters, and refinement parameters for VII

Formula	$C_{21}H_{11}B_2FeN_2O_2P$
Formula weight	462.02 g/mol
Space group	*Pnma* (no. 62)
a (pm)	1153.8(2)
b (pm)	1947.7(5)
c (pm)	1179.7(2)
V (nm^3)	2.6510(16)
Z	4
d_c (g/cm^3)	1.158
Crystal size (mm^3)	0.3×0.4×0.5
μ(Mo-K_α) (cm^{-1})	6.435
Diffractometer	CAD4 (Enraf–Nonius)
Radiation, λ (pm)	Mo-K_α, 71.073
Monochromator	graphite
Temperature	ambient
Scan mode (θ range (°))	$\omega-2\theta$ ($0.1 < \theta < 35$)
No. of unique reflcns	3357 ($I > \sigma(I)$)
N_o, No. of reflcns used	2420 ($I > 3\sigma(I)$)
N_p, No. of params refined	144
R [a]	0.040
R_w [b], unit weights	0.040
GOF [c]	1.144

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$. [c] $[\Sigma w(|F_o| - |F_c|)^2 / (N_o - N_p]^{1/2}$.

gen atoms were refined anisotropically. All hydrogen atoms were placed at calculated positions (d(C–H) 95 pm, B_{eq} 5.0×10^4 pm^2) using a riding model. 9 of the 22 independent hydrogen atoms could also be found by difference Fourier synthesis. Isotropic temperature factors for 5 hydrogen atoms (those of the ring CH groups and those of the isopropyl CH groups) were included in the refinement. The calculations were performed with a VAX 11/730 computer (Digital Equipment Corporation) using the SHELX 76 [16] and SDP program system [17] including the programs DIFABS and PLUTO.

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD-53889, the names of the authors, and the journal citation.

Acknowledgement

This work was supported by Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie.

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