

Borole derivatives

XI *. 1-(Diisopropylamino)borole as ligand in transition metal complexes. Crystal and molecular structures of *cis*-Cr(CO)₂(C₄H₄BNPrⁱ₂)₂ and Mn(CO)(C₄H₄BNPrⁱ₂)₂

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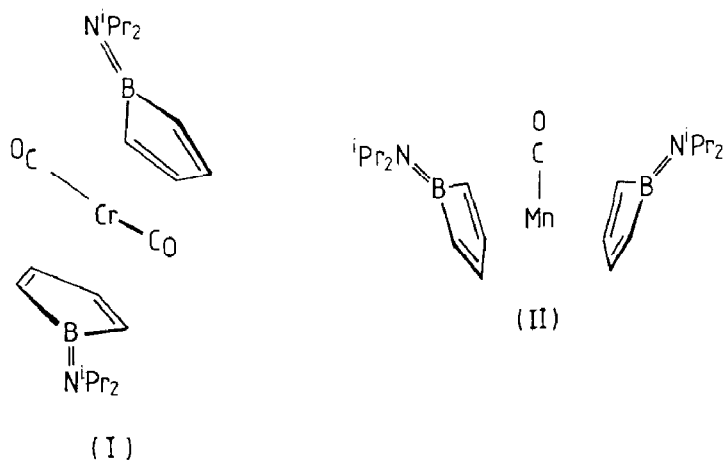
Abstract

X-ray diffraction studies on two 1-(diisopropylamino)borole complexes, *cis*-Cr(CO)₂(C₄H₄BNPrⁱ₂)₂ (I) and Mn(CO)(C₄H₄BNPrⁱ₂)₂ (II), are reported. The major changes caused by the presence of an amino substituent at the boron atom are the larger bending angles for the borole ligands (14.4° (av.) for I and 16.4° (av.) for II), increased slip distortions (19.5 pm for I and 13.6 pm for II), and lengthened metal-boron distances (Cr-B 258.7 pm (av.) and Mn-B 251.5 pm (av.)). These structural effects are largely caused by π-interactions between the boron and the amino group, and the aminoborole is essentially bonded as a diene ligand, with only weak direct metal-boron interaction. ESR data for II also show close similarity to corresponding diene complexes MnL(η⁴-C₄H₆)₂ (L = CO, PMe₃).

Introduction

Before the synthesis of the first (η⁵-borole)metal complexes [2,3], Grimes postulated that the planar borole ring system C₄BH₅ should be able to form metallocene-type π-complexes [4]. A large variety of (η⁵-borole)metal complexes has recently become accessible, mainly by reaction (with loss of hydrogen) of borolenes

* For part X see ref. 1.



with carbonylmetals [5,6] or complexes of Ru, Os and Rh [6,7], by reaction of borole dianions with suitable metal halides [8,9], by complex formation involving borole ammonia adducts [1], and by various other methods [8–11].

Exocyclic π -donor substituents at the boron influence the electron delocalization in cyclic conjugated boron heterocycles by π -interaction with the p_z -orbital of the boron atom. Structural studies have demonstrated this effect for substituents such as OMe in borabenzene complexes [12], NMe_2 in 1,2,5-thiadiborolene derivatives [13], and F in 1,4-dibora-2,5-cyclohexadiene compounds [14]. This effect has also been observed in carbaboranes. The nido structure of $\text{C}_4\text{B}_2\text{H}_6$ is destabilized by introduction of amino substituents at the boron atoms; with two amino substituents the 2,6-diborabicyclo[3.1.0]hex-3-ene isomer becomes energetically more favourable [15].

In this paper we discuss the electronic influence and the structural consequences of the presence of an amino substituent at the boron atom in $(\eta^5\text{-borole})\text{metal}$ complexes in the light of X-ray structure determinations on the selected 1-(diisopropylamino)borole complexes I and II and supporting spectroscopic data. The synthetic chemistry of 1-(diisopropylamino)borole complexes has been described in detail previously [8].

Results and discussion

The structure of the chromium complex I

Crystals of I and of II consist of discrete molecules, with one molecule in the asymmetric unit. Views of the molecules are given in Fig. 1 and 2, which also show the atom-numbering scheme. Details of the structure determinations of I and II are listed in Tables 1–5.

The molecule of I consists of a *cis*-dicarbonylchromium fragment and two monofacially bound 1-(diisopropylamino)borole ligands, and possesses approximate C_2 symmetry. The geometry of the aminoborole ligand differs markedly from that previously established for 1-methyl- and 1-phenyl-borole ligands [1,5,6,11]. The borole rings are folded along the directions C(11)–C(14) and C(21)–C(24), respectively, thereby increasing the Cr–B distance. The mean bending angle of 14.4° is

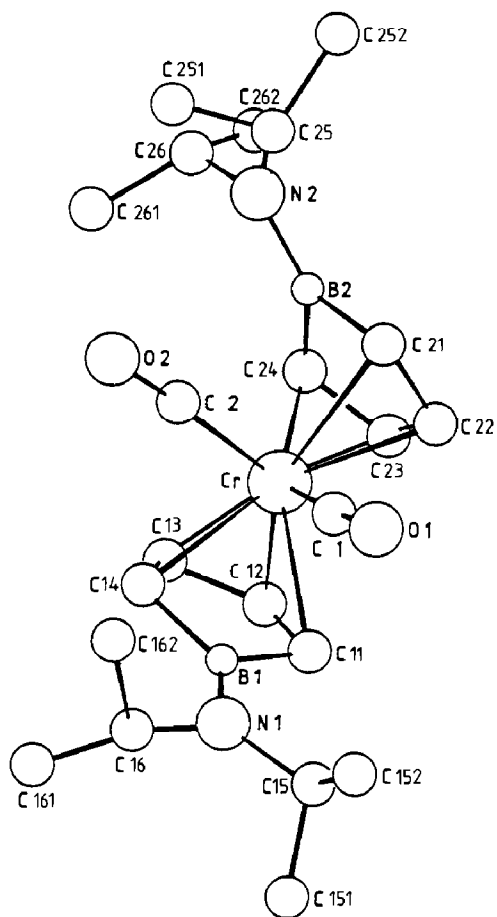


Fig. 1. Molecular structure of *cis*-Cr(CO)₂(C₄H₄BNPrⁱ₂)₂ (I).

comparatively large; typical values for 1-phenylborole ligands are e.g. 6.1° for (η⁵-C₄H₄BPh)Fe(CO)₃ [5] and 6.8° for (η⁵-C₄H₄BPh)Cr(CO)₄ [1]. The (diisopropylamino)boranediyl moiety shows the geometry typical of an aminoborane, with a trigonal planar arrangement at the boron atom (angle sum 359.9°) and, more importantly, also at the nitrogen atom (angle sum 359.9°), and with a B–N bond length of 142.3 pm (cf. ref. 17). The intraring C–C bond lengths (139.2/139.5/137.2 and 139.1/139.7/139.0 pm) indicate only moderate back bonding, as expected for a Cr(CO)₆ derivative [18]. The mean B–C bond lengths of 154.5 pm are similar to those in (η⁵-C₄H₄BPh)Fe(CO)₃ [5] (η⁵-C₄H₄BPh)Cr(CO)₄ [1]; they are slightly shorter than typical single bonds (e.g. 157.8 pm for BMe₃ [19] and 157.7 pm (mean) for BPh₃ [20]).

The structural relationship between the metal and the aminoborole ring is depicted in Fig. 3. The Cr–B distance of 258.7 pm (mean) is much larger than those in (η⁵-C₄H₄BPh)Cr(CO)₄ (240.3(2) pm) [1], the 1,2-diaza-3,6-dibora-4-cyclohexene complex [η⁶-(EtC)₂(BMe)₂(NH)₂]Cr(CO)₃ (236(1) pm) [21], the 1,3-diaza-2,4-diboretidine complex [η⁴-(BuBNBu^t)₂]Cr(CO)₄ (236.0(4) pm) [22], and the dihydroazaborolyl complex [η⁵-{C₃H₃(BMe)-(NBu^t)}]Cr(CO)₃SnMe₃ (235.6(11) pm) [23]. This large Cr–B separation is achieved by an exceptionally large slip distortion (cf.

Table 5) of 19.5 pm, compared to 6.9 pm for $(\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{Fe}(\text{CO})_3$ [5] and 9.6 pm for $(\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{Cr}(\text{CO})_4$ [1].

Taking account of the observations on the large bending angle, the exceptionally large slip distortion, and the large Cr–B separation, we conclude that the aminoborole is essentially bonded as a diene ligand, with the direct Cr–B interaction very weak. Thus, complex I can be viewed as a close analogue of the well known *cis*-dicarbonylbis(η^4 -1,3-diene)metal complexes of the chromium group metals [24].

The two carbonyl ligands of the $\text{Cr}(\text{CO})_2$ fragment from a right angle $\text{C}(1)\text{--Cr--C}(2)$ ($91.3(1)^\circ$). The rotational orientation of the borole ligands is such that each of the carbonyl groups eclipses the boron atom of one of the borole rings. This conformation is completely analogous to that in the *cis*-dicarbonylbis(η^4 -1,3-diene)metal complexes of the chromium group [24].

Complex I exists as pairs of enantiomers. If the coordination sphere of the chromium is considered as quasioctahedral (with the borole regarded as equivalent to a bidentate chelating ligand), it is possible to define the configuration of the enantiomers [25]. The enantiomer illustrated in Fig. 3 then possesses the Δ -configuration.

The structure of the manganese complex II

The molecule of II (Fig. 2) possesses approximate C_{2v} symmetry. The borole

Table 1

Crystallographic data, data collection parameters, and refinement parameters

	I	II
Formula	$\text{C}_{22}\text{H}_{36}\text{B}_2\text{CrN}_2\text{O}_2$	$\text{C}_{21}\text{H}_{36}\text{B}_2\text{MnN}_2\text{O}$
Formula weight	434.16	409.09
Space group	<i>Pbca</i> (no. 61)	<i>P2</i> ₁ / <i>c</i> (no. 14)
<i>a</i> (pm)	774.0(2)	1422.1(2)
<i>b</i> (pm)	1160.8(2)	849.8(2)
<i>c</i> (pm)	5344.8(9)	2017.2(3)
β ($^\circ$)		110.98(1)
<i>V</i> (nm ³)	4.802	2.276
<i>Z</i>	8	4
<i>d</i> _c (g cm ⁻³)	1.20	1.19
Crystal size (mm ³)	0.25 × 0.2 × 0.2	0.5 × 0.5 × 0.2
μ (Mo- <i>K</i> α) (cm ⁻¹) ^a	4.82	5.70
Radiation, λ (pm)	Mo- <i>K</i> α (71.073)	Mo- <i>K</i> α (71.073)
Monochromator	graphite	graphite
Temperature ($^\circ\text{C}$)	20	20
Scan model (θ range ($^\circ$))	$\omega - 2\theta$ (1–30)	$\omega - 2\theta$ (1–40)
No. of unique reflcns obsd ^b	2880	5509
No. of unique reflcns ^c	2020	4720
No. of params refined	262	244
<i>R</i> ^d	0.050	0.041
<i>R</i> _w ^e	0.028	0.052
<i>w</i> ⁻¹	$\sigma^2(F_0)$	$\sigma^2(I)/4F_0^2 + 0.0004F_0^2$

^a No absorption correction was applied. ^b $I > \sigma(I)$. ^c $I > 3\sigma(I)$. ^d $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^e $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

Table 2
Atom coordinates for the non-hydrogen atoms in I^a

Atom	I (M = Cr)				II (M = Mn)				z	B _{eq} ^b
	x	y	z	B _{eq} ^b	x	y	z	B _{eq} ^b		
M	0.0394(1)	0.18856(6)	0.12524(1)	3.70(2)	0.24025(2)	0.01703(3)	0.12235(1)	3.100(5)		
C(1)	0.0206(6)	0.1108(4)	0.10792(8)	4.7(1)	0.2196(1)	-0.1901(3)	0.0981(1)	4.18(4)		
C(2)	-0.0452(7)	0.0539(4)	0.13827(8)	4.5(1)						
O(1)	0.3248(4)	0.0660(3)	0.09854(6)	6.8(1)	0.2042(1)	-0.3185(2)	0.08053(9)	6.73(4)		
O(2)	-0.1026(4)	-0.0344(3)	0.14446(6)	6.5(1)						
C(11)	0.0182(6)	0.2875(4)	0.08864(8)	4.7(1)	0.4038(2)	0.0056(2)	0.1467(1)	3.78(4)		
C(12)	-0.1016(6)	0.3223(4)	0.10655(8)	5.8(1)	0.3673(2)	0.1614(2)	0.1402(1)	4.52(5)		
C(13)	-0.2139(7)	0.2326(4)	0.11266(8)	5.5(1)	0.2962(2)	0.1868(2)	0.0712(1)	4.51(5)		
C(14)	-0.1751(6)	0.1370(4)	0.09865(8)	4.1(1)	0.2849(2)	0.0497(2)	0.0299(1)	3.77(4)		
B(1)	-0.0414(7)	0.1688(5)	0.07834(9)	3.8(1)	0.3699(2)	-0.0681(3)	0.0713(1)	3.06(4)		
N(1)	0.0129(5)	0.1115(3)	0.05651(6)	4.4(1)	0.4043(1)	-0.2021(2)	0.04575(8)	3.08(3)		
C(15)	0.1430(6)	0.1613(5)	0.03974(8)	6.1(2)	0.4883(2)	-0.3017(2)	0.0906(1)	3.94(4)		
C(151)	0.0615(8)	0.2129(5)	0.01640(9)	8.5(2)	0.4642(2)	-0.3835(3)	0.1488(1)	5.76(7)		
C(152)	0.2926(7)	0.0837(6)	0.03405(10)	9.9(2)	0.5875(2)	-0.2123(3)	0.1193(1)	5.90(7)		
C(16)	-0.0656(7)	0.0042(5)	0.04772(9)	6.7(2)	0.3620(1)	-0.2476(3)	-0.02884(9)	3.57(4)		
C(161)	-0.2586(8)	0.0134(5)	0.04276(9)	8.0(2)	0.3136(2)	-0.4088(3)	-0.0406(1)	4.82(5)		
C(162)	-0.0213(8)	-0.0985(4)	0.06396(12)	9.5(2)	0.4388(2)	-0.2338(3)	-0.0656(1)	4.99(5)		
C(21)	0.2420(6)	0.1617(4)	0.15548(7)	4.0(1)	0.2074(2)	-0.0077(2)	0.22020(9)	3.58(4)		
C(22)	0.2564(7)	0.2690(4)	0.14194(8)	5.3(1)	0.2103(2)	0.1502(2)	0.2000(1)	4.17(4)		
C(23)	0.1125(7)	0.3382(3)	0.14671(9)	5.4(1)	0.1355(2)	0.1786(2)	0.1333(1)	4.13(4)		
C(24)	-0.0055(6)	0.2831(4)	0.16224(7)	4.5(1)	0.0799(1)	0.0403(3)	0.1069(1)	3.75(4)		
B(2)	0.0844(7)	0.1756(5)	0.17302(9)	4.1(2)	0.1092(2)	-0.0843(3)	0.1682(1)	3.19(4)		
N(2)	0.0400(5)	0.1048(3)	0.19376(6)	4.1(1)	0.0587(1)	-0.2242(2)	0.17232(8)	3.54(3)		
C(25)	0.1534(6)	0.0078(4)	0.20151(8)	4.6(1)	-0.0374(2)	-0.2662(3)	0.1156(1)	4.25(5)		
C(251)	0.0587(8)	-0.1073(4)	0.20257(9)	6.6(2)	-0.0314(2)	-0.4156(3)	0.0770(1)	5.69(6)		
C(252)	0.2481(8)	0.0309(4)	0.22584(9)	6.9(2)	-0.1247(2)	-0.2675(3)	0.1419(1)	5.21(6)		
C(26)	-0.1083(6)	0.1270(4)	0.20984(9)	5.2(1)	0.0937(2)	-0.3336(3)	0.2325(1)	4.37(5)		
C(261)	-0.2790(8)	0.1129(5)	0.19676(10)	7.7(2)	0.0885(2)	-0.2623(4)	0.2998(1)	5.95(7)		
C(262)	-0.0961(7)	0.2444(4)	0.22299(9)	7.2(2)	0.1963(2)	-0.4030(3)	0.2432(2)	5.85(7)		

^a The anisotropic thermal parameters are given in the form of their isotropic equivalents defined as $\frac{1}{3}[\alpha^2\beta_{11} + \dots + ab(\cos \gamma)\beta_{12} + \dots]$. ^b In 10^4 pm^2 .

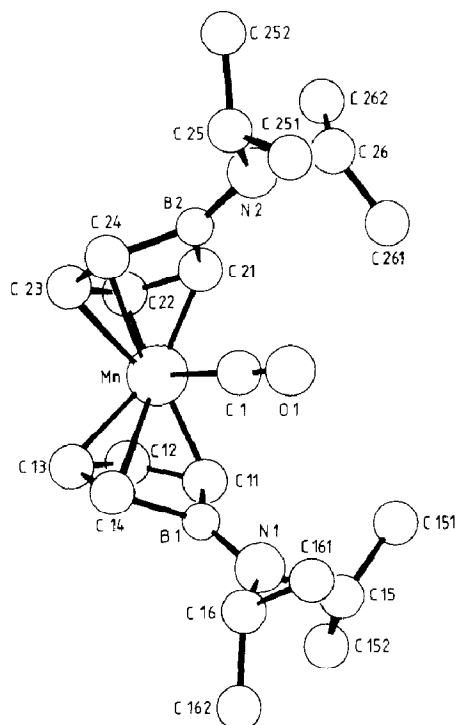


Fig. 2. Molecular structure of $\text{Mn}(\text{CO})(\text{C}_4\text{H}_4\text{BNPr}^i_2)_2$ (II).

Table 3

Selected bond lengths (pm) for I, II, and $\text{Mn}[\text{P}(\text{OMe})_3](\eta^4\text{-C}_4\text{H}_6)_2$ (III)

Bond	I	II	III [16]
M–C(1)	183.1(3)	182.3(2)	
M–C(2)	182.8(3)		
C(1)–O(1)	116.9(3)	114.3(2)	
C(2)–O(2)	116.5(3)		
M–C(11)	228.2(3)	220.1(2)	214.1(3)
M–C(12)	214.8(3)	210.5(2)	207.3(2)
M–C(13)	213.7(3)	208.9(2)	206.8(3)
M–C(14)	227.2(3)	219.2(2)	213.7(3)
M–B(1)	260.3(3)	251.8(2)	
M–C(21)	225.9(3)	219.5(2)	212.9(2)
M–C(22)	211.5(3)	209.6(2)	206.5(2)
M–C(23)	215.2(3)	209.5(2)	207.3(2)
M–C(24)	228.0(3)	219.7(2)	214.1(2)
M–B(2)	257.2(3)	251.1(2)	
B(1)–C(11)	155.4(4)	155.4(3)	
C(11)–C(12)	139.2(4)	141.1(3)	140.7(4)
C(12)–C(13)	139.5(4)	141.4(3)	140.5(4)
C(13)–C(14)	137.2(4)	140.8(3)	140.4(4)
C(14)–B(1)	154.4(4)	156.1(3)	
B(1)–N(1)	142.3(4)	140.7(2)	
B(2)–C(21)	154.1(4)	155.9(3)	
C(21)–C(22)	139.1(4)	140.7(2)	140.9(4)
C(22)–C(23)	139.7(4)	140.6(3)	140.8(3)
C(23)–C(24)	139.0(4)	141.1(3)	141.4(3)
C(24)–B(2)	154.1(4)	156.6(3)	
B(2)–N(2)	142.3(4)	140.6(2)	

Table 4

Selected bond angles for I and II (°)

Angle	I	II
C(1)–M–C(2)	91.3(1)	
M–C(1)–O(1)	172.8(3)	177.5(2)
M–C(2)–O(2)	174.4(3)	
B(1)–C(11)–C(12)	107.6(3)	108.2(2)
C(11)–C(12)–C(13)	111.1(3)	110.2(2)
C(12)–C(13)–C(14)	109.8(3)	110.2(2)
C(13)–C(14)–B(1)	109.7(3)	108.2(2)
C(14)–B(1)–C(11)	99.3(3)	100.1(2)
C(11)–B(1)–N(1)	128.4(3)	131.1(2)
C(14)–B(1)–N(1)	132.2(3)	128.8(2)
B(1)–N(1)–C(15)	121.4(3)	123.3(2)
B(1)–N(1)–C(16)	122.2(3)	121.5(1)
C(15)–N(1)–C(16)	116.2(3)	115.0(1)
B(2)–C(21)–C(22)	109.0(3)	108.4(2)
C(21)–C(22)–C(23)	109.3(3)	110.5(2)
C(22)–C(23)–C(24)	111.6(3)	110.3(2)
C(23)–C(24)–B(2)	107.4(3)	108.1(2)
C(24)–B(2)–C(21)	100.5(3)	99.8(2)
C(21)–B(2)–N(2)	128.9(3)	131.8(2)
C(24)–B(2)–N(2)	130.5(3)	128.4(2)
B(2)–N(2)–C(25)	120.8(3)	120.5(2)
B(2)–N(2)–C(26)	123.2(3)	123.8(2)
C(25)–N(2)–C(26)	115.8(3)	115.7(2)

rings are folded as in I, with a bending angle of 16.4° (av.). The (diisopropylamino)boranediyl moiety again has a planar arrangement at both the boron atom (angle sum 360.0°) and the nitrogen atom (angle sum 359.9°); the distance B–N is 140.7 pm. The intraring C–C bond lengths of 141.0 pm (av.) are somewhat longer than those of I, and the same is true for the B–C bond lengths of 156.0 pm (av.). These features indicate that the diene part of the borole ring interacts more strongly with the metal than it does in I, while the resonance with the aminoboranediyl moiety seems to be even weaker than in I.

Table 5

Definition of best planes, interplanar angles (°), and slip distortions (pm) for I and II

	Angle	I	II
Plane A1 ≡ [C(11)...C(14)]	(A1,B1)	14.8	16.9
Plane B1 ≡ [C(11), B(1), C(14)]	(B1,C1)	5.6	2.7
Plane C1 ≡ [C(15), N(1), C(16)]			
Plane A2 ≡ [C(21)...C(24)]	(A2,B2)	14.0	16.0
Plane B2 ≡ [C(21), B(2), C(24)]	(B2,C2)	4.4	2.4
Plane C2 ≡ [C(25), N(2), C(26)]	(A1,A2)	43.8	33.2
Slip distortion ^a		19.5	13.6

^a Defined in plane A; distance between projection of metal atom and projection of geometrical centre of C₄B ring; cf. ref. 5.

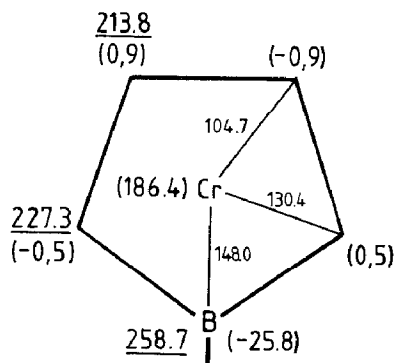


Fig. 3. The geometry of the metal–ligand bonding in I. Underlined numbers are averaged distances from Cr atom and the numbers in parentheses are average distances from the best plane through ring carbon atoms (plane A1 and A2, cf. Table 5). The remaining numbers refer to the projections of bond lengths onto plane A (A).

The metal–ligand bonding is depicted in Fig. 4. The Mn–B distance of 251.5 pm (mean) is much larger than in the triple-decked compound $\mu\text{-}[\eta^5\text{-}(2\text{-EtC}_4\text{H}_3\text{BPh})][\text{Mn}(\text{CO})_3]_2$ (224 pm) [2] and in $(\eta^5\text{-C}_5\text{H}_5\text{BPh})\text{Mn}(\text{CO})_3$ (238.5 pm) [26]. This large Mn–B separation is accompanied by a large slip distortion (cf. Table 5) of 13.6 pm (mean) and the large bending angle already mentioned. As in the case of the chromium complex I, we conclude that the aminoborole is essentially bonded as a diene ligand, and that the direct Mn–B interaction is very weak. Hence complex II may be regarded as a close of the well known bis(butadiene) complex $\text{Mn}(\text{CO})(\eta^4\text{-C}_4\text{H}_6)_2$ (IV) [16,27,28] and its derivatives $\text{MnL}(\eta^4\text{-C}_4\text{H}_6)_2$ with L = e.g. $\text{P}(\text{OMe})_3$ (III) [16] or PMe_3 (V) [16,29].

The rotational orientation of the borole ligands is such that the boron atoms again eclipse the carbonyl group. The two planes defined by the four diene carbon atoms (cf. Table 5, planes A1 and A2) form an interplanar angle of 33.2° which is much larger than the 11.8° for $\text{Mn}(\text{CO})(\eta^4\text{-C}_4\text{H}_6)_2$ [27], presumably owing to the steric requirements of the bulky diisopropylamino substituents.

ESR spectroscopy of II

The crystallographic study has revealed a close similarity between II and

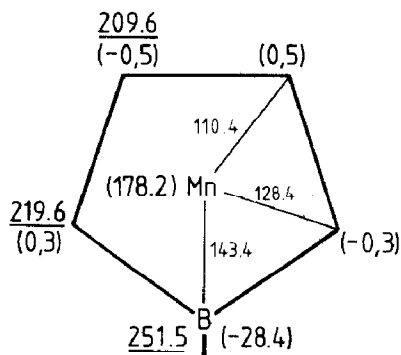


Fig. 4. The geometry of metal–ligand bonding in II. For details see the legend to Fig. 3.

complexes like $\text{Mn}(\text{CO})(\eta^4\text{-C}_4\text{H}_6)_2$ [27,28]. For further comparison an ESR study was undertaken. As a 17e complex, II is paramagnetic with a single unpaired electron [8]. Dilute solutions of II in pentane give intense ESR spectra with a characteristic six-line splitting as the result of a hyperfine interaction with a single ^{55}Mn ($I 5/2$) nucleus; the ESR parameters are listed in Table 6. As a consequence of the large value of the Mn isotropic coupling constant the six hyperfine structure components are not equidistant. The g -value of 2.030 ± 0.001 was thus determined from the position of the signal centre and the isotropic coupling constant was taken from the mean separation of the hyperfine structure components.

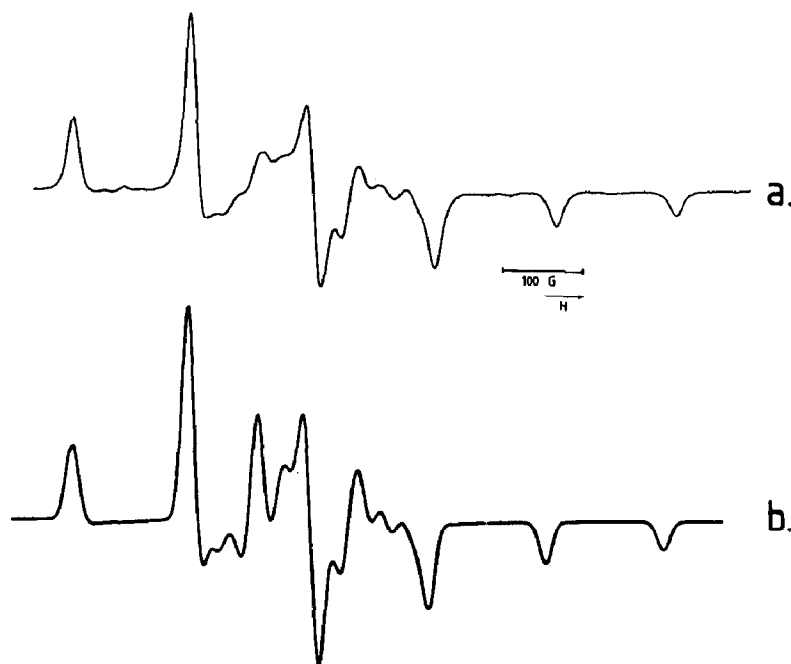


Fig. 5. ESR spectrum (X-band) of $\text{Mn}(\text{CO})(\text{C}_4\text{H}_4\text{BNPr}_2)_2$ (II). (a) Measured spectrum; (b) simulated spectrum.

Table 6

ESR data for selected manganese complexes

	$\text{Mn}(\text{CO})_3(\text{PBu}_3)_2$ [30]	IV [16]	V [29]	II
g_{\parallel}	2.040	01.992	1.986	1.999
$g_{\perp 1}$	2.040	2.048	2.046	2.080
$g_{\perp 2}$	2.040	2.023	2.030	2.012
a_{\parallel} (Mn) (G)	54.1	163.5	164.0	154.0
$a_{\perp 1}$ (Mn) (G)	-35.7	< 5	41.7	29.5
$a_{\perp 2}$ (Mn) (G)	-35.7	73	57.4	28.5
g_{iso}	2.030	2.014	2.018	2.030
a_{iso} (Mn) (G)	7	83.5	82.5	68.2

Anisotropic ESR parameters for II were obtained by recording powder spectra at room temperature of samples of $\text{Fe}(\text{CO})(\text{C}_4\text{H}_4\text{BNPr}^i_2)_2$ [8] doped with 5% of the manganese analogue II. Spectral parameters were evaluated by application of first-order theory on the assumption that the iron complex used as host material is isostructural with II. The parameters thus obtained are listed in Table 6, together with data for comparison. Observed and simulated spectra are shown in Fig. 5. In view of the fact that only first-order contributions were taken into account, the calculated spectrum shows good agreement with the observed spectrum. A set of six lines is immediately apparent with $g_{\parallel} = 1.999$ and a remarkably large $a_{\parallel} = 154$ G. This reveals once more an analogy with the corresponding butadiene complexes (compare the values in Table 6) [16,29] and underlines the structural and electronic similarity of these complexes.

Two additional ^{55}Mn hyperfine splittings can be observed as in IV and V, thus confirming the rhombic symmetry of the SOMO. Finally it should be noted that the isotropic coupling constant calculated from anisotropic parameters, $a_{\text{iso}} = 1/3(a_1 + a_2 + a_3) = 70.7$ G, is in good agreement with the observed value (68 ± 1 G).

Infrared spectral data

Qualitative MO considerations show that a borole ligand should be a better electron acceptor than a diene ligand because of an additional empty low-lying orbital in the borole system. However, when π -interactions with exocyclic substituents are present, the energy of the borole LUMO will be increased, and thus the borole ligand will become more similar to a diene ligand. This effect should be particularly pronounced for amino substituents, such as in the case of the 1-(diisopropylamino)borole complexes considered here.

(Borole)carbonylmetal complexes are expected to have their $\nu(\text{CO})$ bands at higher frequencies than the corresponding diene complexes. Ample experimental evidence (ref. 5 and Table 7) shows this to be the case for complexes with 1-methyl- and 1-phenyl-borole ligands. For 1-(diisopropylamino)borole complexes the shift of the $\nu(\text{CO})$ bands to higher frequencies will be lower. For complex II and its iron analogue $\text{Fe}(\text{CO})(\text{C}_4\text{H}_4\text{BNPr}^i_2)_2$ [8] the trend is even reversed. This exceptional and unexpected trend reversal should be connected with the sterically enforced

Table 7

$\nu(\text{CO})$ frequencies for selected ν complexes

Complex	$\nu(\text{CO})$ (cm^{-1})	solvent	lit.
$\text{Mn}(\text{CO})(\text{C}_4\text{H}_4\text{BNPr}^i_2)_2$	1952	hexane	8
$\text{Mn}(\text{CO})(\text{C}_4\text{H}_6)_2$	1968	pentane	28
$\text{Fe}(\text{CO})(\text{C}_4\text{H}_4\text{BNPr}^i_2)_2$	1968	hexane	8
$\text{Fe}(\text{CO})(\text{C}_4\text{H}_6)_2$	1985	hexane	32
$\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_4\text{BPh})$	2064, 2007, 1998	pentane	5
$\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_4\text{BNPr}^i_2)$	2060, 1994, 1990	hexane	8
$\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_6)$	2056, 1990, 1980	hexane	31
<i>cis</i> - $\text{Co}_2(\text{CO})_4(\text{C}_4\text{H}_4\text{BMe})_2$	2057, 2028, 1955	hexane	5
<i>cis</i> - $\text{Co}_2(\text{CO})_4(\text{C}_4\text{H}_4\text{BNPr}^i_2)_2$	2038, 2010, 1832	hexane	8
<i>cis</i> - $\text{Co}_2(\text{CO})_4(\text{C}_4\text{H}_6)_2$	2038, 2016, 1824	cyclohexane	33

increase of the interplanar angle between the two borole ligands that was noted above in the discussion of the structure of II.

Conclusions

The boracarbocyclic ligand 1*H*-borole is a pentahapto bonding 4e-ligand. This has been demonstrated by a number of single crystal X-ray diffraction studies on 1-methyl- [11], 1-phenyl- [1,5,6,10b], and 2-ethyl-1-phenyl-borole complexes [2b]. The structures of the 1-(diisopropylamino)borole complexes I and II show larger bending angles for the aminoborole ligand, exceptionally large slip distortions, and unusually large metal–boron separations. Thus, the two structures provide clear evidence that the aminoborole is essentially bonded as a diene ligand, while the direct metal–boron interaction is weak. This conclusion is corroborated by the close similarity between the ESR spectrum of II and that of its butadiene analogue IV.

The structural peculiarities of the 1-(diisopropylamino)borole complexes are caused by π -interactions between the B-amino group and the p_z -orbital at the boron atom and, to some extent, by the steric requirements of the bulky diisopropylamino groups. It should be clear that the extent of these effects will greatly depend on the nature of the metal centre and of the substituent at the boron. Thus, we should not expect a dichotomy between η^5 - and η^4 -borole complexes, but rather a continuum of intermediate situations.

Experimental

Samples were handled by standard Schlenk techniques under nitrogen. All solvents were thoroughly dried and deoxygenated.

Crystal structure analyses of $Cr(CO)_2(C_4H_4BNPr^i_2)_2$ (I) and of $Mn(CO)(C_4H_4BNPr^i_2)_2$ (II)

Yellow-orange crystals of I [8] and dark green crystals of II [8] were grown from hexane solutions at -20°C . Diffraction data were collected on a CAD4 autodiffractometer. No significant decay was observed during irradiation. The structures were solved and refined by means of standard heavy-atom methods, alternating least-squares refinements, and difference Fourier calculations [37]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at calculated positions ($d(\text{C-H})$ 95 pm, $B_{\text{eq}} 5.0 \times 10^4 \text{ pm}^2$) and were not refined. All calculations were performed with a PDP 11/45 computer for I and a VAX11/730 computer (Digital Equipment Corporation) for II using the SDP program system [34].

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-52924, the names of the authors, and the journal citation.

ESR Measurements

ESR spectra were recorded on a Bruker spectrometer ER 420 (X-band). Solutions of II in hexane and powders of $Fe(CO)(C_4H_4BNPr^i_2)_2$ doped with II (19/1) were studied at ambient temperature. The spectra were analyzed on the basis of first-order theory.

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