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Derivates of 1,2-diborabenzene

II *. (1,2-Dibora-3,5-cyclohexadiene)metal complexes. Crystal structure of $(C_5Me_5)Rh(C_4H_4B_2Cl_2)$ **

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Abstract

The 1,2-diboratabenzene derivative $Li_2[C_4H_4B_2(NMe_2)_2]$ (I) reacts with various transition metal compounds to form sandwich and triple-decked complexes such as $(C_6Me_6)RuL$ (III), $(C_5Me_5)RhL$ (IV), $(\mu\text{-}L)[Rh(COD)]_2$ (V), NiL_2 (VI), $Fe(CO)L_2$ (VII), and $Co_2(CO)_4L_2$ (VIII), where L is the 1,2-bis(dimethylamino)-1,2-dibora-3,5-cyclohexadiene ligand. Barriers to internal rotation around the B–N bond are 48(1), 56(1), and 38(1) kJ/mol for III, IV, and V, respectively, while VII and VIII are rigid on the NMR time scale. Nucleophilic substitution reactions at boron were examined for the rhodium complex IV. The Lewis acids $BF_3 \cdot OEt_2$ and BCl_3 bring about substitution to give $(C_5Me_5)Rh[C_4H_4B_2F(NMe_2 \cdot BF_3)]$ (XI) and $(C_5Me_5)Rh(C_4H_4B_2Cl_2)$ (XII), respectively. Attempted substitution with Al_2Me_6 and with AlH_3 in THF effected a novel ring contraction to produce the borole complexes $(C_5Me_5)Rh(C_4H_4BR)$ (XIII: R = Me; XIV: R = H); similarly, traces of air transform XII into $(C_5Me_5)Rh(C_4H_4BCl)$ (XV). The structure of XII determined by X-ray diffraction confirms the η^6-bonding mode of the diboracyclohexadiene ligand.

Introduction

Until recently 1,2-diborabenzene derivatives were unknown. In 1986 we described a straightforward route to the dilithium 1,2-diboratabenzene derivative I [1].

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* For part I, see ref. 1.

** Dedicated to Professor Ernst Otto Fischer on the occasion of his 70th birthday.

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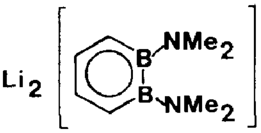
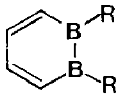
In this paper we develop the chemistry of transition metal complexes of 1,2-dibora-3,5-cyclohexadienes II using I as starting point.



(I)



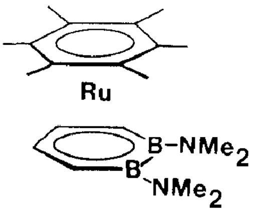
(II)

We note that the 1,2-dibora-3,5-cyclohexadiene ring is a 4π-electron system with a low-lying LUMO. In this respect it is similar to the borole ring, and some of the chemistry described here is closely related to our earlier work on boroles and (borole)metal complexes [2,3].

Results and discussion

Reactions of I with transition metal halides

Reactions of I with transition metal halides provide a wealth of [1,2-bis(dimethylamino)-1,2-dibora-3,5-cyclohexadiene]metal complexes whose types and composition are governed by the electron count. Organometallic halides like $[RuCl_2(C_6Me_6)]_2$ and $[RhCl_2(C_5Me_5)]_2$ which are sources of 14e-fragments afford the mononuclear products III [1] and IV, respectively, while use of $[RhCl(COD)]_2$ as source of the 13e-fragment Rh(COD) leads to the triple-decked complex V [1]. $NiCl_2 \cdot DME$ (DME = $MeOCH_2CH_2OMe$) gives the bis(ligand)nickel complex NiL_2 (VI) with L = $C_4H_4B_2(NMe_2)_2$ and elemental nickel, while $FeBr_2 \cdot DME$ and $CoBr_2 \cdot DME$ in the presence of CO as auxiliary ligand provide the mixed-ligand complexes $Fe(CO)L_2$ (VII) and $Co_2(CO)_4L_2$ (*Co–Co*) (VIII). The new complexes are rather sensitive to air and traces of water and other protic reagents. This sensitivity is obviously due to the presence of the B–B bond, and in many attempted syntheses it precluded the isolation of the products.



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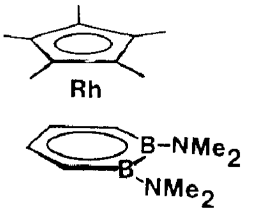

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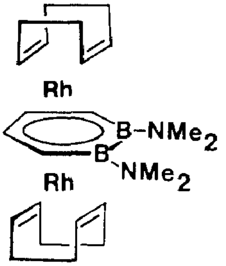
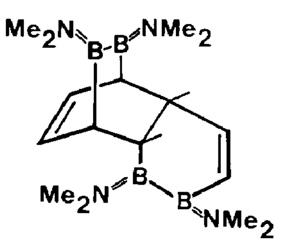


(V)

In all these reactions simple oxidation of the 1,2-diboratabenzene ion competes with complex formation. This oxidation becomes the sole reaction when I is treated with $SnCl_2$ in tetrahydrofuran. Instantaneous formation of elemental tin is observed at −78 °C, and the isolated product IX is probably the Diels–Alder dimer of 1,2-bis(dimethylamino)-1,2-dibora-3,5-cyclohexadiene (X).



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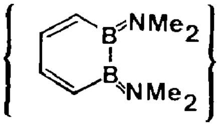
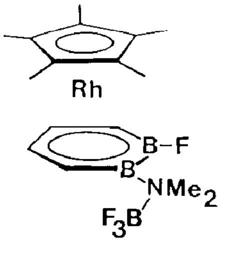


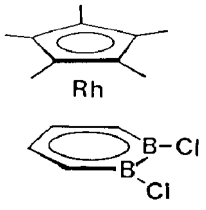
(X)

Substitution at the boron atom and an unexpected ring contraction

All products mentioned so far bear the dimethylamino group at boron. We chose the rhodium complex IV for the study of substitution reactions. Under Lewis-acidic conditions substitution at boron can be achieved. Thus, $BF_3 \cdot OEt_2$ effects replacement of one dimethylamino group to give the fluoro derivative XI, while the stronger electrophile BCl_3 affords the 1,2-dichloro derivative XII.

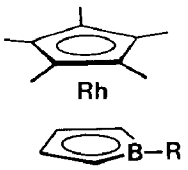


(XI)



(XII)

Attempted methylation with Al_2Me_6 resulted in a surprising ring contraction. One boranediyl fragment was lost and the product XIII contained a 1-methylborole ligand; the closely related complex $CpRh(C_4H_4BMe)$ had been previously obtained from μ-$(C_4H_4BMe)[Rh(C_4H_4BMe)]_2$/NaCp [4]. Similarly hydridation with soluble AlH_3 in THF produces the 1*H*-borole complex XIV. Ring contraction was also observed in NMR experiments with the 1,2-dichloro compound XII. With traces of air XII was converted into the 1-chloroborole complex XV, which was readily identified from its NMR spectra. These observations could well mean that 1,2-dibora-3,5-cyclohexadiene complexes with simple hydrocarbyl substituents at boron cannot exist.



(XIII , R = Me)
(XIV , R = H)
(XV , R = Cl)

X-Ray diffraction results

Compound XII crystallizes as discrete, orthorhombic, Van der Waals crystals. The molecule of XII shows crystallographic mirror symmetry. The molecular

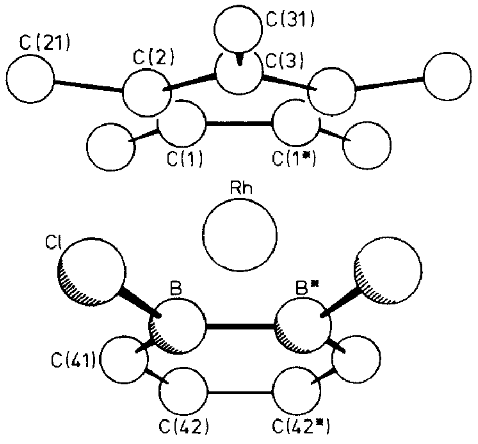


Fig. 1. The molecular structure of XII.

structure of XII is illustrated in Fig. 1 which also shows the atom-numbering scheme. Selected structural data are listed in Tables 1–3. We note that the thermal parameters are larger for the diboracyclohexadiene ring than for the cyclopentadienyl ligand, and the distances C(42)–C(42*) and B–B* are the least accurately determined bond lengths of the molecular skeleton.

The molecule XII shows a typical sandwich structure with the two rings nearly planar and coplanar (cf. Table 3). As expected, the 1,2-dibora-3,5-cyclohexadiene ring is slightly folded along the line C(41)–C(41*) so as to increase the Rh–B distance, the folding angle being 1.9°. The chlorine atoms show a second bent, this time of 9.5° towards the metal, thereby increasing the overlap between the p_z-orbital of the boron atom and the metal orbitals.

The bond distances within the diboracyclohexadiene ring of XII may be compared with those calculated for the hypothetical planar 1,2-dibora-3,5-cyclohexadiene molecule [5] (Fig. 2).

The C–C bond distances are similar to those of diene complexes of iron group metals, while the B–B bond and to a lesser extent the neighbouring B–C bonds are

Table 1

Non-hydrogen atom coordinates for XII

Atom	x	y	z	B_{eq} [a]
Rh	0.18924(3)	0.25	0.25592(6)	3.193(7)
C(41)	0.3087(3)	0.3558(4)	0.2252(8)	6.6(1)
C(42)	0.3173(3)	0.3015(5)	0.3658(8)	7.3(2)
B	0.3022(4)	0.3073(5)	0.0665(9)	5.7(1)
Cl	0.2775(2)	0.3845(2)	−0.1078(3)	10.44(5)
C(1)	0.0659(3)	0.3015(3)	0.3902(4)	3.32(7)
C(2)	0.0618(3)	0.3340(3)	0.2277(4)	3.34(7)
C(3)	0.0572(4)	0.25	0.1282(6)	3.3(1)
C(11)	0.0652(4)	0.3659(4)	0.5361(5)	5.3(1)
C(21)	0.0552(4)	0.4392(3)	0.1755(6)	5.1(1)
C(31)	0.0451(6)	0.25	−0.0508(8)	5.6(2)

[a] The anisotropic thermal parameters are given in the form of their isotropic equivalents; in 10^4 pm^2.

Table 2

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

Rh-B	237.9(5)	B-C(41)	148.3(8)	B-B*	156.4(11)
Rh-C(41)	223.6(4)	C(41)-C(42)	139.3(7)	B-Cl	183.0(6)
Rh-C(42)	214.7(4)	C(42)-C(42*)	140.5(12)		
Rh-C(1)	218.8(3)	C(1)-C(2)	142.7(4)	C(1)-C(11)	150.1(5)
Rh-C(2)	214.7(3)	C(2)—C(3)	141.7(4)	C(2)-C(21)	150.2(5)
Rh-C(3)	214.9(5)	C(1)-C(1*)	140.6(7)	C(3)-C(31)	150.3(7)
B*-B-C(41)	116.5(3)	C(1*)-C(1)-C(11)	125.8(2)		
B*-B-Cl	125.1(2)	C(1*)-C(1)-C(2)	108.1(2)		
C(41)-B-Cl	117.7(4)	C(11)-C(1)-C(2)	126.1(3)		
B-C(41)-C(42)	121.3(5)	C(1)-C(2)-C(3)	107.9(3)		
C(41)-C(42)-C(42*)	122.1(3)	C(1)-C(2)-C(21)	125.1(3)		
		C(21)-C(2)-C(3)	126.8(3)		
		C(2)-C(3)-C(2*)	108.0(4)		
		C(2)-C(3)-C(31)	126.0(2)		

Table 3

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

Plane A ≡ [C(1)...C(3)] [a,b]		
Plane B ≡ [B, C(41), C(42)] [a,c]	angle (A,B)	1.8
Plane C ≡ [C(41), C(42)] [a]	angle (A,C)	2.9
Plane D ≡ [B, C(41)] [a]	angle (C,D)	1.9
Plane E ≡ [B, Cl] [a]	angle (D,E)	9.5

[a] Including symmetry related atoms. [b] Maximum vertical deviation of 1.2 pm for C(3). [c] Maximum vertical deviation of 1.3 pm for C(41).

shortened. These changes indicate considerable back-bonding of the metal to the ligand LUMO.

The B-C bond lengths observed are close to those found in complex borabenzene derivatives (150.0–152.5 pm) [6] and in the 1,4-dibora-2,5-cyclohexadiene complex $CpCo[MeB(CHCH)_2BMe]$ (151.4 pm (mean)) [7].

The B-B distance demands more detailed consideration. The hypothetical planar B_2H_4 molecule which may be taken as a standard for a $B(sp^2)$-$B(sp^2)$ single bond has a calculated B-B distance of 176 pm [8]. Systems with additional π-interactions have shorter B-B bond lengths. Examples are $CH_2[B(NMe_2)B(NMe_2)]_2CH_2$ (171.1 pm) and related molecules [9]. A similar distance is found in the 1,2-diboratabenzene ion in $[Li(TMEDA)]_2[1,2\text{-}C_4H_4B_2(NMe_2)_2]$ (170.6 pm) [1]; here the effect of

Fig. 2. (a) Bond lengths (pm) observed for the diboracyclohexadiene ligand of XII. (b) Calculated bond lengths for planar 1,2-dibora-3,5-cyclohexadiene.

much stronger π-interactions is counter-balanced by the repulsive effect of the negative charge, and thus does not induce further shortening of the B–B bond. In contrast, this repulsive effect is not operative in XII, and all (!) distances within the ring are shorter than those in the 1,2-diboratabenzene ion. On the basis of these considerations it seems reasonable to expect an exceptionally small value for the B–B bond length of XII. However, we cannot exclude that librational motions of the diboracyclohexadiene ring have contributed some apparent shortening to the B–B distance observed, and more structural work is required.

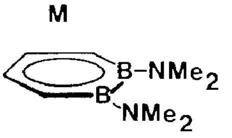
The metal–ligand interaction is characterized by a slip distortion of 13.5 pm, the metal being shifted towards the ring carbon atoms to improve the overlap between metal and ligand orbitals. The Rh–B distance of 237.9(5) pm may be compared with a value of 240.0(5) pm for $RhCl(PPh_3)_2(C_4H_4BPh)$ [10].

Finally we note a peculiarity of the crystal packing. All ring ligands are roughly oriented parallel to the *yz*-plane. The molecules of XII form stacks parallel to the *x*-axis, with all rhodium atoms very close to the stack axis (*x*, 0.25, ≈ 0.25). This arrangement seems to permit some intermolecular charge transfer within the stack.

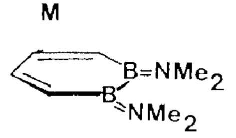
Structure and spectra

The new complexes III–VIII and XI–XV were characterized by elemental analyses, mass spectra, and ^1H, ^{11}B, and (in part) ^{13}C NMR spectra.

The complexes III–VIII with dimethylamino substituents at boron show π-interactions between the metallacarbaborane core and the dimethylamino substituents. The structural consequences of this type of π-interactions have recently been discussed in detail for complexes of the 1-(diisopropylamino)borole ligand [11]. The bonding situation in III–VIII can be described in terms of two resonance formulae XVIa and XVIb. Here, formula XVIa emphasizes the metal-boron bonding while formula XVIb is that of a diene complex attached to a bis(amino)diborane(4) moiety.



(XVIa)



(XVIe)

Experimentally, the complexes III and IV with electron-rich metal centres show low rotational barriers around the B–N bond, and magnetically more shielded boron nuclei ($\delta(^{11}B)$ ca. 30 ppm), that is predominant metal–boron bonding. There is also less double bond character between C(3) and C(4) of the diboracyclohexadiene ring as evidenced by the smaller vicinal coupling constants $^3J_{34}$ ($N = {}^3J_{34} + {}^4J_{35}$ ca. 9 Hz).

In contrast, the complexes VI–VIII show less metal-to-ligand back bonding. Internal rotation of the dimethylamino substituents is slow at ambient temperature, the shielding of the boron is reduced ($\delta(^{11}B)$ ca. 38 ppm) and more close to that of an aminoborane ($\delta(^{11}B)$ ca. 45 ppm [12]). The diene character of the diboracyclohexadiene ring is more pronounced and the vicinal coupling constants $^3J_{34}$ ($N = {}^3J_{34} + {}^4J_{35}$ ca. 10.8 Hz) are significantly larger.

The nickel complex VI shows an ABCD type ^1H NMR spectrum up to 80 °C for the four ring protons and four ring carbon atoms are seen in the ^{13}C NMR spectrum over the entire temperature range from −70 to 105 °C. Thus, we have a C_2 ground state conformation. The same situation is found in other NiL_2 type complexes such as $Ni[\eta^5\text{-}\{(EtC)_2(BMe)_2S\}]_2$ [13] and $Ni[\eta^5\text{-}\{Me_2Si(CHCH)_2BPh\}]_2$ [14] where the two rings are rotated by about 90° with respect to each other. The temperature-dependent NMR signals of the dimethylamino groups were not analysed because it was not possible to observe fully resolved spectra at the low temperature limit. We note, however, that the ^{13}C spectrum shows only one signal for the four methyl groups above 98 °C; this indicates fast ligand–ligand rotation as expected for the high temperature limiting spectrum.

The cobalt complex VIII belongs to the well-known type $Co_2(\mu\text{-}CO)_2(CO)_2L_2$ (*Co–Co*). The IR spectrum of VIII in hexane solution shows two $\nu(CO)$ bands for terminal and three for bridging CO ligands. The band number and intensities indicate that VIII exists as the doubly bridged *trans* isomer with an admixture of the doubly bridged *cis* isomer; a similar situation is known for the corresponding 1,3-cyclohexadiene complex [15].

The spectra of the borole complexes XIII–XV agree well with those of established borole complexes [3,4]. However, the ^{11}B signal of the B-unsubstituted complex XIV, a prominent doublet at $\delta(^{11}B)$ 8.3 ppm ($^1J(^{11}B\text{-}^1H) \approx 130$ Hz), appears at the highest chemical shift known for a monofacially bound borole ligand. In known series of thiadiborolene complexes ($[\eta^5\text{-}\{(EtC)_2(BX)_2S\}]Fe(CO)_3$) [16] and 1,4-dibora-2,5-cyclohexadiene complexes $[CpCo[\eta^6\text{-}\{XB(CHCH)_2BX\}]$ and $(C_5Me_5)Rh[\eta^6\text{-}\{XB(CHCH)_2BX\}])$ [17], the hydrido compounds (X = H) also show ^{11}B signals with unusually high chemical shift values.

Experimental

Experiments were carried out by standard Schlenk techniques under nitrogen. All solvents were thoroughly dried and deoxygenated. All products are air-sensitive; traces of water or other protic agents induce decomposition.

NMR spectra were recorded on a Bruker WP 80 PFT-spectrometer (^1H, 80 MHz), a Bruker WH 270 PFT-spectrometer (^{13}C, 67.88 MHz), and a JEOL NM-PS-100 spectrometer (^{11}B, 32.08 MHz). Electron-impact (70 eV) mass spectra were run on a Varian MAT CH5-DF spectrometer. Infrared spectra were recorded on a Perkin–Elmer 580 spectrometer and calibrated against the 1601 cm^{-1} band of polystyrene.

[1,2-Bis(dimethylamino)-1,2-dibora-3,5-cyclohexadiene](hexamethylbenzene)ruthenium (III)

Preparative and spectral data see ref. 1. Anal. Found: C, 56.36; H, 8.05. $C_{20}H_{34}B_2N_2Ru$ calc.: C, 56.50; H, 8.06%. MS: m/e ($I_{rel.}$) 426 (41; M^+), 371 (100; $M-BNMe_2$), 328 (80; 371 − $MeNCH_2$). ^1H DNMR (80 MHz, CD_2Cl_2): T_c 225 K, $\Delta\nu(Me)$ 17.2 Hz, $\Delta G^{\neq}$ 48(1) kJ/mol.

[1,2-Bis(dimethylamino)-1,2-dibora-3,5-cyclohexadiene](pentamethylcyclopentadienyl)rhodium (IV)

$[RhCl_2(C_5Me_5)]_2$ (2.04 g, 3.30 mmol) is added with stirring to a suspension of I (1.16 g, 6.60 mmol) in THF (40 ml) at −70 °C. Warming up to ambient temperature affords a dark red solution. Evaporation to dryness, repeated extraction with hexane, filtration through sea sand, reduction of the volume in vacuo, and cooling to −78 °C gives IV (1.25 g, 3.13 mmol; 47%) as brownish red crystals, m.p. 104–108 °C, dec. > 120 °C, soluble in aprotic solvents. Anal. Found: C, 53.90; H, 7.70. $C_{18}H_{31}B_2N_2Rh$ calc.: C, 54.05; H, 7.81%.

MS: m/e ($I_{rel.}$) 400 (100; M^+), 356 (28; $M-NMe_2$), 345 (22; $M-BNMe_2$), 342 (20; $M-Me$, $-MeNCH_2$), 313 (20; $356-MeNCH_2$), 302 (24; $345-MeNCH_2=(C_5Me_5)Rh(C_4H_4BH)^+$). ^1H NMR ($\delta(^1H)$ (ppm), 80 MHz, measured vs. $CHDCl_2$, ref. TMS, CD_2Cl_2): 4.92 m (H(4)/H(5), $N={}^3J_{34}+{}^4J_{35}=9.1$, $^2J(^{103}Rh-^1H)$ 0.9 Hz), 3.26 m (H(3)/H(6), N 9.1 Hz), 2.82 s ($2NMe_2$), 1.91 d (C_5Me_5, $^3J(^{103}Rh-^1H)$ 0.5 Hz). ^{13}C NMR ($\delta(^{13}C)$(ppm) (J(Hz)), 67.88 MHz, measured vs. $CHDCl_2$, ref. TMS, CD_2Cl_2, 203 K): 94.8 d ($^1J(^{103}Rh-^{13}C)$ 7.3) (C_5Me_5), 88.1 dd (^1J 161.3, $^1J(^{103}Rh-^{13}C)$ 8.7) (C(4)/C(5)), 71.7 dd (^1J 133.7, $^1J(^{103}Rh-^{13}C)$ 7.3) (C(4)/C(5)), 44.3 q (^1J 133.7) (2 NMe), 38.1 q (^1J 132.2) (2 NMe), 10.6 q (^1J 126.9) ($C_5\mathit{Me}_5$). ^{11}B NMR ($\delta(^{11}B)$, CD_2Cl_2, 300 K): 31 ppm (half-width 310 Hz), vs. ext. $BF_3 \cdot OEt_2$. ^{13}C DNMR (67.88 MHz, CD_2Cl_2): T_c 298 K, $\Delta\nu$(Me) 423.2 Hz, $\Delta G^{\neq}$ 56(1) kJ/mol.

μ-[1,2-Bis(dimethylamino)-1,2-dibora-3,5-cyclohexadiene]bis[(η⁴-1,5-cyclooctadiene)-rhodium] (V)

Preparative and spectral data see ref. 1. Anal. Found: C, 49.28; H, 6.91. $C_{20}H_{40}B_2N_2Rh_2$ calc.: C, 49.36; H, 6.90%. MS: m/e ($I_{rel.}$) 584 (100; M^+), 472 (42; $M-C_8H_{12}$, $-2H_2$), 470 (82; $472-H_2$). ^{13}C DNMR (67.88 MHz, CD_2Cl_2): T_c 198 K, $\Delta\nu$(Me) 152.6 Hz, $\Delta G^{\neq}$ 38(1) kJ/mol.

Bis[1,2-bis(dimethylamino)-1,2-dibora-3,5-cyclohexadiene]nickel (VI)

$NiCl_2 \cdot DME$ (0.80 g, 3.64 mmol) [18] is treated with I (0.64 g, 3.64 mmol) in THF (20 ml) as above. Warming up to ambient temperature affords a dark red solution and suspended elemental nickel. Work-up as above gives VI (0.28 g, 0.73 mmol; 40%) as dark red, almost black crystals; m.p. 123–124 °C (dec.), soluble in aprotic solvents. Anal. Found: C, 50.40; H, 8.43. $C_{16}H_{32}B_4N_4Ni$ calc.: C, 50.26; H, 8.43%.

MS: m/e ($I_{rel.}$) 382 (100; M^+), 339 (38; $M-MeNCH_2$). ^1H NMR ($\delta(^1H)$(ppm), 80 MHz, measured vs. $CHDCl_2$, ref. TMS, CD_2Cl_2, 30 °C: 5.63 m and 5.50 m (H(4)/H(5)), 4.51 m and 4.45 m (H(3)/H(6)), $^3J_{34}$ 9.1, $^4J_{35}$ 1.5, $^3J_{45}$ 4.9, $^5J_{36}$ 0 Hz, 2.83 s (6 NMe), 2.62 s (2NMe); at 30 °C in toluene-d_8: 4.49 dd (2H(3)/H(6), accidentally isochronous); at 70 °C in toluene-d_8; 2.73 s (4 NMe), 2.59 s (4 NMe). ^{13}C NMR ($\delta(^{13}C)$(ppm) (J(Hz)), 67.88 MHz, int. TMS, CD_2Cl_2, 203 K): 100.7 d (^1J 160.0) and 97.0 d (^1J 162.8) (2C(4) and 2(C(5)), 92.0 d (^1J 138.4) and 80.1 d (^1J 135.6) (2C(3) and 2(C(6)), 45.3 q (^1J 134.3) (4NMe), 38.8 q (^1J 132.9) (4NMe); in toluene-d_8 coalescence of the NMe signals at 371 K. ^{11}B NMR ($\delta(^{11}B)$, CD_2Cl_2, 300 K): 37 ppm (half-width 550 Hz), vs. ext. $BF_3 \cdot OEt_2$.

Bis[1,2-bis(dimethylamino)-1,2-dibora-3,5-cyclohexadiene]carbonyliron (VII)

Carbon monoxide is bubbled through a suspension of I (0.85 g, 4.84 mmol) in THF (25 ml) and $FeBr_2 \cdot DME$ (1.48 g, 4.84 mmol) [18] is added at −70 °C. As the mixture warms up to ambient temperature a brownish red colour develops. Work-up as usual and two crystallizations from hexane afford VII (0.23 g, 0.56 mmol; 23%)

as brick-red crystals; m.p. 138–142°C (dec.), soluble in aprotic solvents. Anal. Found: C, 50.25; H, 7.91. $C_{17}H_{32}B_4FeN_4O$ calc.: C, 50.10; H, 7.91%.

MS: m/e ($I_{rel.}$) 408 (13; M^+), 380 (100; $M-CO$), 335 (54; 380 − $NHMe_2$). ^1H NMR ($\delta(^1H)$(ppm), 80 MHz, int. TMS, CD_2Cl_2, 30°C): 5.61 m (2H(4)/H(5) and 2.28 m (2H(3)/H(6) with $N = {}^3J_{34} + {}^4J_{35} = 10.2$ Hz), 2.88 s (4 NMe), 2.63 s (4 NMe). ^{11}B NMR ($\delta(^{11}B)$, CD_2Cl_2, 300 K): 39 ppm (half-width 400 Hz), vs. ext. $BF_3 \cdot OEt_2$. IR (hexane): ν(CO) 1953 s cm^{-1}.

Bis[1,2-bis(dimethylamino)-1,2-dibora-3,5-cyclohexadiene]tetracarbonyldicobalt (Co–Co) (VIII)

Treatment of I (0.82 g, 4.67 mmol) with CO and $CoBr_2 \cdot DME$ (1.86 g, 6.0 mmol) [19,20] as described above for VII affords VIII (0.22 g, 0.40 mmol; 17%) as orange red crystals; dec. > 128°C, soluble in aprotic solvents. Anal. Found: C, 50.25; H, 7.91. $C_{20}H_{32}B_4Co_2N_4O_4$ calc.: C, 43.39; H, 5.83%.

MS: m/e ($I_{rel.}$) 470 (33; $M-3CO$), 442 (21; $M-4CO$), 387 (100; 442 − $BNMe_2$), 332 (40; 387 − $BNMe_2$), 273 (26; 332 − Co). ^1H NMR ($\delta(^1H)$ (ppm), 80 MHz, int. TMS, CD_2Cl_2, 30°C): 5.56 m (2H(4)/H(5) and 3.78 m (2H(3)/H(6) with $N = {}^3J_{34} + {}^4J_{35} = 10.7$ Hz), 2.84 s (4NMe), 2.79 s (4 NMe). ^{11}B NMR ($\delta(^{11}B)$, CD_2Cl_2, 300 K): 38 ppm (half-width 400 Hz), vs. ext. $BF_3 \cdot OEt_2$. IR (hexane) with tentative assignment: ν(CO) 2027 vs, 1822 s cm^{-1} (*trans* isomer) and 2037 m, 2004 m, 1825 m cm^{-1} (*cis* isomer) (cf. ref. 15).

Oxidation of I with $SnCl_2$

Anhydrous tin dichloride (1.16 g, 6.12 mmol) is added to a suspension of I (1.08 g, 6.15 mmol) in THF (30 ml) at −78°C. The mixture turns black instantaneously. After the mixture has warmed up to ambient temperature elemental mercury (5 ml) is added, and stirring is continued for 24 h. The solution is then decanted and evaporated to dryness. Repeated extraction with hexane, filtration through sea sand, and cooling to −78°C affords IX (0.42 g, 1.30 mmol; 42%) as sand-coloured crystals; m.p. 78–80°C. The product is soluble in aprotic solvents, in which there is a slow decomposition as evidenced by ^1H NMR spectrum (signals of olefinic proton disappear). Anal. Found: C, 59.25; H, 9.89; $C_{16}H_{32}B_4N_4$ calc.: C, 59.37; H, 9.96%.

MS: m/e ($I_{rel.}$) 324 (50; M^+), 279 (19; $M-NHMe_2$), 204 (100; $M-2NHMe_2$, −2Me). ^{11}B NMR ($\delta(^{11}B)$, $CDCl_3$, 300 K): 48 ppm (half-width 650 Hz).

[1-(Dimethylamino)-2-fluoro-1,2-dibora-3,5-cyclohexadiene](pentamethylcyclopentadienyl)rhodium-boron trifluoride (XI)

A solution of $BF_3 \cdot OEt_2$ (1 ml, 9 mmol) is added dropwise to IV (0.15 g, 0.38 mmol) in ether (5 ml). The yellow precipitate formed is recrystallized from CH_2Cl_2/Et_2O to give XI (80 mg, 0.18 mmol; 48%) as yellow crystals; dec. > 174°C, soluble in CH_2Cl_2, insoluble in ether and pentane. Anal. Found: C, 43.35; H, 5.80. $C_{16}H_{25}B_3F_4NRh$ calc.: C, 43.41; H, 5.69%.

MS: m/e ($I_{rel.}$) 375 (100; $M-BF_3$), 360 (76; 375 − Me), 345 (28; 375 − BF), 331 (89; 375 − NMe_2), 302 (22; $(C_5Me_5)Rh(C_4H_4BH)^+$), 238 (32; $Rh(C_5Me_5)^+$), 235 (34; ?). ^1H NMR ($\delta(^1H)$(ppm), 80 MHz, int. TMS, CD_2Cl_2, 30°C): 5.44 m (H(4)/H(5)), 4.99 m and 4.32 m (H(3)/H(6)), 2.69 s (NMe_2), 2.01 d (C_5Me_5, $^3J(^{103}Rh-^1H)$ 0.3 Hz). ^{11}B NMR ($\delta(^{11}B)$, CD_2Cl_2, 300 K): 32 ppm (half-width 420 Hz), 1.7 ppm (half-width 64 Hz), vs. ext. $BF_3 \cdot OEt_2$.

[1,2-Dichloro-1,2-dibora-3,5-cyclohexadiene](pentamethylcyclopentadienyl)rhodium (XII)

Boron trichloride (0.5 ml, 6 mmol) is added dropwise to a solution of IV (0.34 g, 0.85 mmol) in hexane (30 ml) at −78 °C. A yellow solid separates. Crystallization from CH_2Cl_2/pentane yields XII (0.21 g, 0.55 mmol; 65%) as yellow crystals; m.p. 238 °C (dec.), soluble in CH_2Cl_2 and benzene, insoluble in ether or pentane. Anal. Found: C, 43.69; H, 4.87. $C_{14}H_{19}B_2Cl_2Rh$ calc.: C, 43.93; H, 5.00%.

MS: m/e ($I_{rel.}$) 382 (100; M^+), 346 (34: $M-$ HCl), 336 (93; $M-$ BCl), 321 (25; 336 − Me), 238 (62; $Rh(C_5Me_5)^+$). ^1H NMR ($\delta(^1H)$ (ppm), 80 MHz, int. TMS, CD_2Cl_2, 30 °C): 5.59 m (H(4)/H(5), $N = {}^3J_{34} + {}^4J_{35} = 9.2$ Hz), 4.74 m (H(3)/H(6), N 9.2 Hz), 1.92 d (C_5Me_5, $^3J(^{103}Rh-^1H)$ 0.3 Hz). ^{11}B NMR ($\delta(^{11}B)$, CD_2Cl_2, 300 K): 28.6 ppm (half-width 220 Hz), vs. ext. $BF_3 \cdot OEt_2$.

(1-Methylborole)(pentamethylcyclopentadienyl)rhodium (XIII)

A solution of Al_2Me_6 in pentane (2.5 mol/l, 1.5 ml, 7.5 mmol $AlMe_3$) is added with stirring to IV (0.50 g, 1.25 mmol) in pentane (15 ml) at −78 °C. The colour changes from dark red to pale yellow and a yellow solid separates upon warming to room temperature. Excess Al_2Me_6 is hydrolyzed by addition of alumina (7% H_2O, 3 g) at −78 °C. Filtration of the mixture through alumina, reduction of the volume in vacuo (to ca. 3 ml), and cooling to −78 °C affords XIII (0.23 g, 0.73 mmol; 58%) as yellow needles; m.p. 64–65 °C (no dec. < 220 °C), slightly air-sensitive. Anal. Found: C, 57.07; H, 6.91. $C_{15}H_{22}BRh$ calc.: C, 57.00; H, 7.02%.

MS: m/e ($I_{rel.}$) 316 (100; M^+), 301 (73; $M-$ Me), 181 (28; $Rh(C_4H_4BMe)^+$). ^1H NMR ($\delta(^1H)$(ppm), 80 MHz, measured vs. $CDCl_3$, ref. TMS, $CDCl_3$): 4.70 m (H(3)/H(4)), 3.38 m (H(2)/H(5)), 1.96 d (C_5Me_5, $^3J(^{103}Rh-^1H)$ 0.4 Hz), 0.25 s (Me). ^{11}B NMR ($\delta(^{11}B)$, $CDCl_3$, 300 K): 17 ppm (half-width 190 Hz), vs. ext. $BF_3 \cdot OEt_2$.

(1H-Borole)(pentamethylcyclopentadienyl)rhodium (XIV)

A solution of AlH_3 (4 mmol, freshly prepared from 114 mg $LiAlH_4$ and 133 mg $AlCl_3$) in ether (10 ml) is added with stirring to IV (0.32 g, 0.80 mmol) in ether (8 ml) at −78 °C. Work-up as for XIII affords XIV (0.14 g, 0.46 mmol; 58%) as yellow crystals, m.p. 127–128 °C (no dec. < 220 °C), moderately sensitive to air and traces of water, soluble in aprotic solvents. Anal. Found: C, 55.61; H, 6.63. $C_{14}H_{20}BRh$ calc.: C, 55.67; H, 6.67%.

MS: m/e ($I_{rel.}$) 302 (100; M^+), 287 (24; $M-$ Me). ^1H NMR ($\delta(^1H)$ (ppm), 80 MHz, int. TMS, CD_2Cl_2, 30 °C): 4.77 m (H(3)/H(4)), 3.63 m (H(2)/H(5)), 2.03 d (C_5Me_5, $^3J(^{103}Rh-^1H)$ 0.5 Hz). ^{11}B NMR ($\delta(^{11}B)$, CD_2Cl_2, 300 K): 8.3 ppm (half-width 190 Hz), vs. ext. $BF_3 \cdot OEt_2$, d, ($^1J(^{11}B-^1H)$ 130 Hz).

(1-Chloroborole)(pentamethylcyclopentadienyl)rhodium (XV)

Crystals of XII (383 mg, 1.00 mmol) are exposed to air for 5 min and then dissolved in hexane. Removal of the solvent and repeated sublimation at 40 °C/10^{-6} bar gives XV (0.2 g, 0.6 mmol; 60%, not optimized) as pale yellow solid. Anal. Found: C, 50.01; H, 5.58; $C_{14}H_{19}BClRh$ calc.: C, 49.98; H, 5.69%.

MS: m/e ($I_{rel.}$) 336 (100; M^+), 321 (74; $M-$ Me), 236 (37; $Rh(C_5Me_5)^+$). ^1H NMR ($\delta(^1H)$(ppm), 80 MHz, int. TMS, $CDCl_3$): 4.68 m (H(3)/H(4)), 3.51 m

(H(2)/H(5), $N = {}^3J_{23} + {}^4J_{24} = 5.1$ Hz), 1.98 d (C_5Me_5, ${}^3J({}^{103}Rh-{}^1H)$ 0.4 Hz). ${}^{11}B$ NMR ($\delta({}^{11}B)$, $CDCl_3$, 300 K): 18.3 ppm (half-width 90 Hz), vs. ext. $BF_3 \cdot OEt_2$.

Determination of the structure of XII

$C_{14}H_{19}B_2Cl_2Rh$ (XII); *M* 382.74 g/mol, orthorhombic, space group: *Pnma* (no. 62), *a* 1413.2(2), *b* 1364.1(5), *c* 834.5(2) pm, $Z = 4$ (8/2), V 1.609(1) nm^3, d_c 1.58 g/cm^3, $\mu(Mo\text{-}K_\alpha)$ 13.6 cm^{-1}.

Single crystals were grown from CH_2Cl_2/pentane solutions of XII. The crystal selected for X-ray analysis was a parallelepiped ($0.4 \times 0.5 \times 0.55$ mm^3). The intensity data were collected on a CAD 4 automatic four-circle diffractometer (Enraf–Nonius, Delft, The Netherlands) using Mo-K_α radiation with a graphite crystal monochromator (λ 71.069 pm). Intensity data for reflections with $0.1° < \theta < 35°$ were collected at room temperature using the ω–2θ scan mode. Three standard reflections were measured periodically to check crystal and electronic stability. No decay was observed.

The structure was solved by standard heavy atom methods using 2667 independent reflections with $I > \sigma(I)$ [21]. An absorption correction was applied by means of the program DIFABS [21,22]. The least squares full matrix refinement (91 parameters) [21] was carried out using 2257 reflections with $I > 3\sigma(I)$. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions (*d*(C–H) 95.0 pm, B_{eq} 5.0×10^4 pm^2). Convergence resulted in an *R* value of 0.048 (R_w 0.048, unit weights, GOF 1.5) [23*].

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-53166, the names of the authors, and the journal reference.

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