$[{Br_2B(\eta^5-C_5H_4)}Mn(CO)_3] - A$ versatile Precursor for Boron-based Ligands

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Dedicated to Professor Dieter Fenske on the Occasion of his 65th Birthday

Abstract. A range of potential boron-based ligand precursors has been synthesized starting from $[{Br_2B(\eta^5-C_5H_4)}Mn(CO)_3]$ (1) *via* salt elimination reactions. These comprise ligand precursors suitable for the preparation of i) *ansa*-metallocenes such as $[CymB(\eta^1-C_5H_5)_2]$ (2), $[CymB(1-C_9H_7)_2]$ (3a), and $[CymB(3-C_9H_7)_2]$ (3b), ii) constrained geometry complexes such as [CymB(Br)N(H)tBu] (5) as well as iii) *ansa*-diamido complexes such as $[CymB{N(H)tBu}]$ (4) and $[CymB{N(H)tBu}_2]$ (6) (Cym = cymantrenyl, C_5H_5 = cyclopentadienyl, C_9H_7 = indenyl). Furthermore, we present the hydrolysis of 1, leading to the three-fold cymantrenyl-substituted boroxine [{OB(η^5 -C₅H₄)}Mn(CO)₃]₃ (7). All new compounds have been characterized by multinuclear NMR spectroscopic techniques and in the case of 1 and 7 by X-ray diffraction analyses.

Keywords: Boron; Boranes; Cymantrene; Ligand; ansa-Complexes

Introduction

Recently, we presented the molecular structure of $[{Br_2B(\eta^5-C_5H_3Me)}Mn(CO)_3]$ and emphasized the potential of its parent compound $[{Br_2B(\eta^5-C_5H_4)}Mn(CO)_3]$ for the synthesis of complexes of the type $[L_xM-B(Br)Cym]$ $(Cym = [(\eta^5 - C_5H_4)]Mn(CO)_3])$ [1]. Our interest in these both long-known half-sandwich complexes [2a] and their derivatives arose from recent investigations on the related boryl substituted metallocenes $[{R_2B(\eta^5-C_5H_4)}]Fe(\eta^5 C_5H_5$)], which established a correlation between the electronic stabilization of the boron atom provided by the iron atom and the structure of the molecule, i.e. bending of the exo-BR₂ group toward the iron atom [2]. This led to the question as to whether the metal atom in corresponding half-sandwich complexes, derived from $[{Br_2B(\eta^5 C_5H_4$ Mn(CO)₃] or [{Br₂B(η^5 -C₅H₃Me)}Mn(CO)₃], exhibits a similar stabilizing effect on Cp-bound BR₂ groups.

Apart from investigations concerning the nature of the metal-boron interactions, $[{Br_2B(\eta^5-C_5H_4)}Mn(CO)_3]$ should own potential as precursor for boron-bridged ligands, suitable for the synthesis of a range of *ansa*-complexes, as we have already shown for [FcBBr₂] (Fc = ferrocenyl) [3]. Such boron-bridged ligands have already attracted great attention as building blocks in strained (I) [4, 5] and unstrained (II, III) [6-8] metallocenophanes,

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Institut für Anorganische Chemie der Universität Am Hubland D-97074 Würzburg / Deutschland E-mail: h.braunschweig@mail.uni-wuerzburg.de constrained geometry complexes (CGCs, IV) [9, 10] as well as *ansa*-diamido complexes (V) [11].



Complexes derived from such boron-containing ligands play an important role in areas such as the synthesis of novel organometallic polymers and the homogeneous Ziegler-Natta type polymerization of olefins. The incorporation of a boron bridge has been associated with a number of beneficial characteristics, e.g. an improved catalytic activity of [n]bora-metallocenophanes (n = 1, 2) [6e]. Furthermore, the potential of a Lewis-acidic boron atom in *ansa*metallocenes to activate the pendant transition metal center without the need for added Lewis-acidic co-catalysts has been envisaged [10a]. However, the Lewis-acidity of the boron atom in currently known boron-bridged *ansa*-metallocenes of the types II and III is attenuated either by π -

2314

donation from an amino group or by the formation of base adducts.

Consequently, we attempted to synthesize corresponding complexes with more pronounced Lewis-acidic boron bridges, i.e. less electronic stabilization of the electron deficient boron atoms. Ligands based on substituted ferrocenyl or cymantrenylboranes appeared to be a suitable starting point since both transition-metal fragments are known to provide only a moderate stabilization of the boron atom [1, 12]. Based on the versatile chemistry of ferrocenyldibromoborane, [FcBBr₂], we now focused on the related cymantrenyl system.

In the present paper, we describe the structural characterization of the precursor $[{Br_2B(\eta^5-C_5H_4)}Mn(CO)_3]$ and present a series of substitution reactions as well as its behaviour towards hydrolysis, leading to an unusual three-fold cymantrenyl-substituted boroxine, which could also be structurally characterized. The cymantrenylboranediylbridged ligand precursors thus obtained may find application in the preparation of new *ansa*-metallocenes, CGCs and *ansa*-diamido complexes.

Results and Discussion

Synthesis and structure of cymantrenyl(dibromo)borane

According to equation (1), cymantrenyl(dibromo)borane (1) was obtained similarly to procedures already described 30 years ago by *Siebert* and co-workers and isolated as a low-melting product of oily appearance [2a]. Due to the toxicity of CS₂, we replaced this solvent by hexane, leading to 1 in 66 % yield, which is just slightly lower than the yield obtained from CS₂ (76 %). From such an oily sample, extremely air- and moisture-sensitive single crystals – suitable for diffraction analysis – were obtained after storage at -30 °C over the period of months.



 $[{Br_2B(\eta^5-C_5H_4)}Mn(CO)_3]$ (1) crystallizes in the orthorhombic space group *Pbca* and is presented in figure 1. Selected bond distances and angles are listed below and crystal data and refinement parameters in table 2 in the experimental section. For a better comparison, some selected data are listed in table 1 together with those of $[{Br_2B(\eta^5-C_5H_4)}FeCp]$ and $[{Br_2B(\eta^5-C_5H_3Me)}-Mn(CO)_3]$.



Fig. 1 Molecular structure of $[{Br_2B(\eta^5-C_5H_4)}Mn(CO)_3]$ (1) in the solid state with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level and the hydrogen atoms have been omitted for clarity.

Selected bond lengths /Å, bond and torsion angles /°: Br1-B1 1.928(4), B1-C11 1.520(5), B1-Br2 1.901(4), C11-B1-Br2 121.7(2), C11-B1-Br1 120.5(3), Br2-B1-Br1 117.79(19), C15-C11-B1 126.2(3), C12-C11-B1 126.2(3), B1-C11-Mn1 111.7(2).

The molecular structure of 1 is very similar to that of the methyl derivative [{ $Br_2B(\eta^5-C_5H_3Me)$ }Mn(CO)₃], and likewise displays the characteristic bending of the *exo*-boryl group toward the manganese atom which can be regarded as the most important structural feature of both compounds. With a dip angle of 11.71°, the deviation from planarity is less pronounced than that in $[{Br_2B(\eta^5 C_5H_3Me$) $Mn(CO)_3$ or [FcBBr₂] (12.3° and 17.7, 18.9°, respectively) but still significant. The greater value of α^* for $[{Br_2B(\eta^5-C_5H_3Me)}Mn(CO)_3]$ in comparison to 1 is supposed to be due to the presence of the cyclopentadienylbound methyl group in the latter, which slightly increases the electron density at the manganese atom, thus leading to a more pronounced Mn...B interaction. As a consequence, the Mn···B distance in $[{Br_2B(\eta^5-C_5H_3Me)}Mn(CO)_3]$ (2.992 Å) is slightly shorter than that in 1 (3.028 Å).

Table 1 Comparison of selected structural parameters, bond lengths /Å, and bond angles /°

	[CymBBr ₂]	[Cym'BBr ₂] [1]	[FcBBr ₂] [2]
X1 - [M]	1.767	1.764	1.642, 1.644
B - [M]	3.028	2.992	2.840, 2.856
$C_{ipso} - B$	1.520(5)	1.504(5)	1.474, 1.484
Br1 - B	1.928(4)	1.920(4)	1.945, 1.947
Br2 – B	1.901(4)	1.915(4)	1.921, 1.916
$\alpha = X1 - C_{ipso} - B$	168.29	167.7	162.3, 161.1
$\alpha^* = 180 - \alpha$	11.71	12.3	17.7 , 18.9
$C_{ipso} - B - Br2$	121.7(2)	120.9(3)	121.8, 123.25
$C_{ipso} - B - Br1$	120.5(3)	122.3(2)	121.8, 120.77
Br2 - B - Br1	117.8(2)	116.8(2)	116.3, 115.96

 $Cym' = [(\eta^5 - C_5 H_3 Me) Mn(CO)_3]$

X1 = centroid of corresponding compound.

ansa-Metallocene ligand precursor

The reaction of $[{Br_2B(\eta^5-C_5H_4)}Mn(CO)_3]$ (1) and two equivalents of Na[C₅H₅] (C₅H₅ = cyclopentadienyl) or

 $Li[C_9H_7]$ (C₉H₇ = indenvl) in toluene leads to the formation of the cymantrenylboranes 2 and 3, according to equation (2). Both compounds were obtained in almost quantitative yields as orange oils, and identified by mass spectrometry and multinuclear NMR spectroscopy. The latter reveals the formation of one symmetrical major isomer (i.e. va/va or vh/vh [13]) but the question remains open whether the va/va or vh/vh isomer was generated. This finding differs from the analogous ferrocenyl compound, which consists of two isomers [3]. In the ¹H and ¹³C NMR spectra. this symmetric isomer exhibits only one resonance corresponding to the methylene groups of the cyclopentadienyl rings at $\delta = 3.19$ and 47.53, respectively. The ¹³C NMR resonance corresponding to the boron bound carbon atom could not be detected due to quadrupolar ¹³C-¹¹B coupling [14]. In the ¹¹B NMR spectrum of **2**, a single resonance at $\delta = 52.2$ is observed, which is shifted to low field by 4 ppm compared to the corresponding signal of 1.

The cymantrenyl(diindenyl)borane **3a** is obtained as the kinetically favoured product, in which the boron atom is linked to the *sp*³ hybridized carbon atoms of the indenyl substituents, i.e. in 1-position, thus resulting in two chiralities in the molecule [13]. Hence, **3a** is consisting of a mixture of two diastereomers with the possible *RR*, *SS* and *RS* configurations and the interpretation of the ¹H and ¹³C NMR spectroscopic data proved difficult. The ¹¹B NMR spectrum reveals a singlet at $\delta = 68.2$, i.e. low field shifted by about 20 ppm relative to that of **1**.



As recently reported for the analogous ferrocenyl(diindenyl)borane [3], **3a** can be isomerized in the presence of catalytic amounts of NEt₃ to the thermodynamically more stable 3-indenyl isomer **3b**, i.e. the isomer in that the boron atom is bound to an sp^2 hybridized carbon atom (Eq. (3)). The isomerization was carried out in toluene and finished after 6 hours at ambient temperature, leading to a single isomer without any chirality in 60 % yield. The ¹H and ¹³C NMR spectra are significantly simplified when compared to the corresponding spectra of the starting compound, and all observed signals can be assigned. The isomerization results in a shielding of the boron atom that is reflected by an ¹¹B NMR signal at $\delta = 60.2$, which is shifted by about 8 ppm with respect to that of **3a**.



Synthesis of phenylamino-substituted cymantrenylboranes

The alkali salt elimination reaction of 1 and one equivalent of Li[NHPh] in toluene leads to the formation of the diphenylamino-substituted cymantrenylborane 4 (Eq. (4)). 4 was obtained as an orange powder in 60 % yield. The ¹¹B NMR spectrum displays a singular resonance at $\delta = 28.1$ which is significantly high-field shifted relative to the corresponding signal for 1. This value resembles that of the analogous ferrocene compound (31.5 ppm) [3], and the significant high-field shift of about 20 ppm with respect to 1 and $[FcBBr_2]$ is the result of π donation from the nitrogen lone pair into the empty p orbital on the Lewis-acidic boron atom. Ambient temperature ¹H and ¹³C NMR spectra of 4 exhibit only one set of signals corresponding to the target compound, consistent with facile rotation about the B-N bonds, whose bond orders are expected to be 1.5 at most [3].



Synthesis of tert-butylamino-substituted cymantrenylboranes

Precursor 1 was reacted with one and two equivalents of Li[NH*t*Bu] in toluene to give the *tert*-butylamino- and di*tert*-butylamino substituted cymantrenylboranes 5 and 6 via salt elimination (Eq. (5)). Both compounds are obtained after work up as orange solids in moderate yields of 30 (5) and 45 % (6). As already found for the phenylaminosubstituted cymantrenyl derivative, the ¹H and ¹³C NMR spectra of 5 and 6 display each only one set of signals corresponding to the target compounds. In the proton NMR spectrum, the signals for the *tert*-butyl groups are detected at $\delta = 1.21$ (5) and 1.13 (6). The ¹¹B NMR resonances are found at $\delta = 32.6$ (5) and 27.0 (6), which are very similar to the value of the phenylamino derivative **4**. The observed values are significantly high-field shifted (mean: 17 ppm) relative to the corresponding signal for **1**.



Synthesis and structure of tricymantrenylboroxine

In the past we reported on the synthesis and structure of the first half-sandwich-substituted borazine compound showing two η^1 -coordinated [CpFe(CO)₃] fragments [15]. Borazines with such boron-transition metal bond substitution patterns are believed to play an important role in the Rh-catalyzed hydroboration of acetylenes with (HBNH)₃. In addition, polynuclear aggregates of transition metals are of great current interest [17]. In this context, following investigations were undertaken.

When a toluene solution of 1 is treated with water, the exclusive formation of the tri-cymantrenyl-substituted boroxine [$\{OB(\eta^5-C_5H_4)\}Mn(CO)_3$]₃ (7) can be observed (Eq. (6)). 7 was obtained as an almost white solid in quantitative yield.



Suitable single crystals have been obtained from slow evaporation of a saturated CDCl₃ solution of **7**. The result of the X-ray diffraction analysis is depicted in figure 2. $[{OB(\eta^5-C_5H_4)}Mn(CO)_3]_3$ (**7**) crystallizes in the triclinic space group $P\overline{1}$. Selected bond distances and angles are listed below, and crystal data and refinement parameters in table 2 in the experimental section.

The boroxine framework is planar and interestingly the aromatic cyclopentadienyl rings lie in the same plane. This arrangement and the fact that all angles around boron and oxygen atoms lie very close to 120° (from 117.6 to 122.4°) confirm the expected sp^2 hybridization of the respective atoms. The boron– C_{Cp} distances ranges from 1.540 (B3–C51) to 1.547 Å (C11–B1) and the boron–oxygen bond lengths from 1.371 (O1–B3) up to 1.383 Å (O3–B3), with an average of 1.378 Å. All these values agree very well with the data of the analogue triferrocenylboroxine [16]. The most characteristic feature of the structure is the orientation of the three cymantrenyl fragments, which occupy all the same side of the central six-membered boroxine ring. The cymantrenyl fragment with Mn3 is slightly bent out of the planarity of the whole system [6.7(5)°] which is reflected by the torsion angle O3–B3–C51–C55 and is supposedly due to sterical reasons or packing effects.



Fig. 2 Molecular structure of $[{OB(\eta^5-C_5H_4)}Mn(CO)_3]_3$ (7) in the solid state with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level and the hydrogen atoms have been omitted for clarity.

Conclusions

We presented the X-ray structure of $[{Br_2B(\eta^5-C_5H_4)}Mn(CO)_3]$ (1) and demonstrated that this compound is a very versatile precursor for boron-based ligands, which can be readily modified with respect to the aromatic groups being attached to boron as well as the organo groups of the amines.

Thus, the work reported in this paper opens the door to a range of new *ansa*-metallocenes, CGCs and *ansa*-diamido complexes, which are currently under investigation.

Experimental Section

General considerations

All manipulations were carried out under a dry argon atmosphere with common Schlenk techniques. Solvents were dried with a solvent purification system (SPS) from M. Braun and stored under argon over molecular sieves; reagents were dried and purified by standard procedures. [CymBBr₂](1) [2a] and Na[C₅H₅] [18] were obtained according to literature procedures. Lithium indenide and lithium amides were prepared by deprotonation of indene and corresponding amines, respectively, utilising butyl lithium. NMR spectra were recorded on either a Bruker 200 Avance spectrometer at 200.1 (¹H, internal standard TMS) and 64.2 MHz (¹¹B, BF₃·OEt₂ in C₆D₆ as external standard), a Bruker 400 Avance spectrometer at 400.13 (¹H, internal standard TMS) and 100.61 MHz ($^{13}C{^{1}H}$, APT, internal standard TMS) or a Bruker Avance 500 at 500.13 MHz (¹H, internal standard TMS), 125.77 MHz (¹³C{¹H}, APT, internal standard TMS) and 160.46 MHz (¹¹B, BF₃·OEt₂ as external standard).

Elemental analyses (C, H, N) were obtained from a Vario Micro (Elementar Analysensysteme).

$[CymB(\eta^1-C_5H_5)_2]$ (2)

A solution of 1.00 g (2.68 mmol) [CymBBr₂] (1) in 20 mL toluene was added at 0 °C to a suspension of 0.50 g (5.68 mmol) Na[C₅H₅] in 20 mL toluene. After stirring the mixture for 16 h, insoluble material was removed by centrifugation and all volatiles were removed in vacuo to yield 2 0.90 g (98 %) as an orange oil. ¹H an ¹³C NMR spectra showed to sets of signals corresponding to an isomeric mixture, the data refer to the main isomer.

¹H NMR (C₆D₆, 500 MHz): δ = 3.19 (4H, CH_{2Cp}); 4.26 (m, 2H, CH, Cp_{Cym}); 4.75-4.93 (kB, 2H, CH, Cp_{Cym}); 6.65-7.20 (kB, 6H, CH, Cp_{Cp}). – ¹¹B NMR (C₆D₆, 160 MHz): δ = 52.2. – ¹³C NMR (C₆D₆, 125 MHz): δ = 47.53 (CH₂, Cp); 86.79, 94.33 (CH, Cp_{Cy}); 134.17, 141.96, 149.90 (CH, Cp); 225.20 (CO). – MS *m*/*z* (%): 344 (2) [M⁺]; 260 (14) [M⁺ – 3 CO]; 55 (20) [Mn⁺].

$[CymB(\eta^1-C_9H_6)_2]$ (3a,b)

In analogy to the synthesis of **2**, 1.00 g (2.68 mmol) [CymBBr₂] (**1**) was dissolved in 20 mL tolueneand added at 0 °C to a suspension of 0.70 g (5.73 mmol) Li[C₉H₆] in 20 mL toluene. After stirring the mixture for 16 h, a catalytic amount of NEt₃ was added to the suspension to form only one isomer. After another 16 h all insoluble material was removed by centrifugation and all volatiles were removed in vacuo to yield **3a** 0.71 g (60 %) as a yellow solid.

¹H NMR (C₆D₆, 500 MHz): δ = 3.26 (d, ³J = 1.89 Hz, 4H, CH_{2 Ind}); 4.21, 4.85 (m, 4H, Cp_{Cym}); 6.97 (t, ³J = 1.89 Hz, 2H, CH_{αInd}); 6.98 – 7.15 (kB, 8H, CH_{Ind}); 7.32 (m, 2H, CH_{Ind}); 7.42 (m, 2H, CH_{Ind}). – ¹¹B NMR (C₆D₆, 64 MHz): δ = 60.2. – ¹³C NMR (C₆D₆, 100 MHz): δ = 41.53 (CH_{2 Ind}); 87.70, 95.43 (CH, Cp_{Cym}); 123.70, 124.50, 125.50, 127.02 (CH_{Ind}); 144.88 (C_{Ind}); 145.27 (CH_{Ind}); 148.30 (C_{Ind}) ppm. – MS *m*/z (%): 148 (8) [MnCpCO⁺]; 120 (44) [MnCp⁺]; 115 (100) [Ind⁺]; 55 (56) [Mn⁺].

$[CymB(NHC_6H_5)_2]$ (4)

Following essentially the same procedure as for the synthesis of 2, 1.00 g (2.68 mmol) [CymBBr₂] (1) was reacted with 0.53 g (5.35 mmol) Li[NHC₆H₅]. After work-up, 4 0.64 g (60 %) was obtained as an orange solid.

¹H NMR (C₆D₆, 500 MHz): δ = 4.01, 4.30 (m, 4H, Cp_{Cym}); 5.09 (m, 2H, NH); 6.77-7.01 (kB, 10H, CH_{Ph}). – ¹¹B NMR (C₆D₆, 160 MHz): δ = 28.1. – ¹³C NMR (C₆D₆, 125 MHz): δ = 84.70, 91.04 (CH, Cp); 123.01, 123.20, 129.84 (CH_{Ph}); 143.75 (C_{ipso}, Ph); 225.93 (CO). – MS *m*/*z* (%): 204 (26) [Cym⁺]; 148 (24) [MnCpCO⁺]; 120 (100) [MnCp⁺]; 93 (19) [NH₂C₆H₅⁺].

$[CymBBr(NHt-C_4H_9)] (5)$

1.00 g (2.68 mmol) [CymBBr₂] (1) was dissolved in 15 mL toluene, cooled to -80 °C and a suspension of 0.21 g (2.68 mmol) Li[NH*t*-C₄H₉] in 15 mL toluene was added. After stirring the mixture for a few minutes, it was allowed to warm up to ambient temperature and stirred for further 16 h. The pale yellow precipitate was removed by centrifugation. All volatiles were then removed in vacuo to yield after recrystallization from hexane at -30 °C 5 0.29 g (30 %) as a yellow solid. C₁₂H₁₄BBrMnNO₃ (365.90): C 39.57 (calc. 39.39); H 4.46 (calc. 3.86); N 2.88 (calc. 3.83) %.

¹H NMR (C₆D₆, 400 MHz): δ = 1.21 (9H, CH₃); 4.09 (2H, Cp_{Cym}); 4.45 (1H, NH); 4.48 (2H, Cp_{Cym}). $^{-11}$ B NMR (C₆D₆, 64 MHz): δ = 32.6. $^{-13}$ C NMR (C₆D₆, 100 MHz): δ = 31.89 (CH₃, *t*-Bu); 52.37 (C, *t*-Bu); 85.47, 91.10 (CH, Cp); 225.28 (CO). $^{-}$ MS *m*/*z* (%): 204 (12) [Cym⁺]; 120 (34) [MnCp⁺]; 71 (1) [NC₄H₉⁺]; 58 (100) [C₄H₁₀⁺].

[CymB(NHt-Bu)₂] (6)

Following essentially the same procedure as for the synthesis of 5, 1.00 g (2.68 mmol) [CymBBr₂] (1) was reacted with 0.43 g (5.44 mmol) Li[NH*t*-C₄H₉]. After work-up, **6** 0.85 g (89 %) was obtained as an orange solid. $C_{16}H_{24}BMnN_2O_3$ (358.12): C 53.57 (calc. 53.90); H 6.23 (calc. 6.19); N 6.67 (calc. 6.84) %.

¹H NMR (C₆D₆, 400 MHz): δ = 1.13 (18H, CH_{3 *t*-Bu}); 3.09 (2H, NH) 3.99, 4.58 (4H, Cp_{Cym}). – ¹¹B NMR (C₆D₆, 64 MHz): δ = 26.99. – ¹³C NMR (C₆D₆, 100 MHz): δ = 33.39 (CH₃, *t*-Bu); 49.41 (C, *t*-Bu); 82.05, 92.61 (CH, Cp); 226.48 (CO). – MS *m*/*z* (%): 204 (14) [M⁺ – BN₂C₈H₂₀]; 148 (14) [M⁺ – BN₂C₈H₂₀ – 2CO]; 120 (58) [MnCp⁺]; 58 (100) [C₄H₁₀⁺].

[CymBO]₃ (7)

3.00 g (8.04 mmol) [CymBBr₂] (1) was dissolved in 20 mL toluene and treated with an excess of water at 0 °C, immediately a light grey solid appeared. After stirring the mixture for a few more minutes, the solid was filtered and washed twice with 10 mL of toluene. Yielding 7 3.7 g (67 %) as a white Powder.

 ^{1}H NMR (CDCl₃, 200 MHz): δ = 5.29; (2H, Cp_{Cym}) 4.95 (2H, Cp_{Cym}). $-^{11}B$ NMR (CDCl₃, 64 MHz): δ = 28.05. $-^{13}C$ NMR (D₈-THF, 500 MHz): δ = 88.58 (CH, Cp); 94.36 (CH, Cp); 227.28 (CO). - MS m/z (%): 690 (21) [M⁺]; 606 (91) [M⁺ - 3 CO]; 438 (100) [M⁺ - 9 CO].

Crystal structure determination

The crystal data of 1 and 7 were collected with a Bruker APEX2 diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structures were solved using direct methods, refined with the Shelx software package (G. M. Sheldrick, University of Göttingen 1997) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized position and were included in structure factor calculations.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC nos 642883 (1) and 642884 (7). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

Compound	1	7
Empirical formula	C ₈ H ₄ BBr ₂ MnO ₃	C ₁₆ H ₂₀ B ₂ Br ₄ Mn ₂ O ₆
Formula weight /g·mol ⁻¹	373.68	759.46
Temperature /K	100(2)	100(2)
Radiation, $\lambda / \text{Å}$	Μο _{κα} 0.71073	Мока 0.71073
Crystal system	orthorhombic	triclinic
Space group	Pbca	ΡĪ
Unit cell dimensions		
a /Å	13.5414(13)	7.2244(10)
b /Å	11.9003(12)	12.4316(18)
c /Å	13.7776(13)	15.719(2)
$\alpha /^{\circ}$		107.670(7)
β /°		92.889(7)
γ /°		99.896(7)
Volume /Å ³	2220.2(4)	1317.2(3)
Ζ	8	2
Calculated density /Mg·m ⁻³	2.236	1.915
Absorbtion coefficient /mm ⁻¹	8.366	7.052
<i>F</i> (000)	1408	728
Theta range for collection	2.72 to 28.45°	1.75 to 29.36°
Reflections collected	104645	61027
Independent reflections	2789	6825
Minimum/maximum transmision	0.2029/0.5366	0.3328/0.5694
Refinement method	Full-matrix	Full-matrix
	last-squares on F^2	last-squares on F^2
Data / parameters / restrains	2789 / 136 / 0	6825 / 379 / 0
Goodness-of-fit on F^2	1.122	1.026
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0319$.	$R_1 = 0.0455.$
	$wR^2 = 0.0749$	$w R^2 = 0.0908$
R indices (all data)	$R_2 = 0.0450$.	$R_2 = 0.1060$.
	$w\bar{R}^2 = 0.0831$	$w\bar{R}^2 = 0.1075$
Maximum/minimum residual	1.124 / -0.962	0.690 / -0.627
electron density /e $\cdot Å^{-3}$		

Table 2 Crystal data and refinement parameters for the compounds 1 and 7.

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