

# Donor-acceptor substituted ferrocenes. Novel structural motifs by intramolecular acid–base pairing <sup>☆</sup>

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Received 22 May 1995

## Abstract

On the basis of intramolecular donor–acceptor pairing, a convenient way to realize important structural motifs in organometallic chemistry is presented. Ferrocene, bearing a (phosphino)boryl substituent (–BR–PPh<sub>2</sub>) at each of its cyclopentadienyl rings, was found to establish a novel type of *ansa*-structure through interannular head-to-tail bonding (**1**). This B<sub>2</sub>P<sub>2</sub> bridge adopts an unusual non-planar conformation. For its two halves meeting in the B···B line the angle was found to be 45.0°. The cyclodiborataphosphoniane bridge shows a dynamic behaviour with an activation barrier  $\Delta G^\ddagger = 70 \text{ kJ mol}^{-1}$  for the breaking of a P–B bond. When the boron and phosphorus atoms are not directly attached to each other, but separated by an amino group (–BR–NPh–PPh<sub>2</sub>), no donor–acceptor pairing takes place (**2**, **3**). The ligand properties of **1** and **2** towards the Cr(CO)<sub>5</sub> fragment have been investigated.

**Keywords:** Boron; Ferrocenylboranes; Phosphinoboranes; Aminoboranes; Push-pull-systems; Dynamic NMR spectroscopy

## 1. Introduction

The chemical behaviour of a given transition metal centre largely depends on its ligand sphere. For the development of novel organometallic compounds with specific properties (e.g. catalytic activity) a sophisticated ligand design is thus of crucial importance [1]. This paper reports the synthesis, structure and reactivity of metal complexes combining both electron donor and electron acceptor functionalities in the same molecule.

It follows from isoelectronic principles that dative bonds between electron pair acceptors (e.g. boron) and donors (e.g. nitrogen, phosphorus) closely resemble carbon–carbon bonds in many respects [2]. In contrast to the latter, dative bonds can be established under very mild conditions. When donor and acceptor groups are incorporated in the ligand sphere of the same transition metal, they are likely to form intramolecular Lewis acid–base pairs. Therefore, it should be possible to establish certain important structural motifs (e.g. interannular bridges), which are often difficult to obtain via

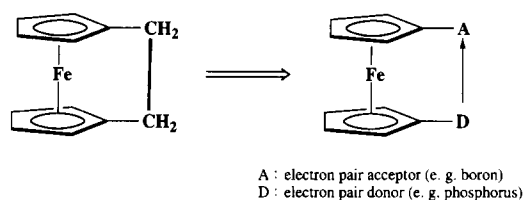
C–C-coupling, via the self-assembly of dative bonds (Scheme 1).

However, the strength of the prototype dative bond is only about one third the strength of the prototype covalent bond [3]. Moreover, dative bonds between atoms with different electronegativities are polar and therefore prone to nucleophilic or electrophilic attack. This may be exploited for the design of a ligand sphere, whose conformational rigidity can be altered on demand by the choice of solvent, Lewis acidic or basic additives and temperature. Examples of this new class of compounds are the ferrocene derivatives **1** (Scheme 3; Fig. 1).

It is important to note that **1** can be viewed in two different ways. On one hand, the ferrocene moiety represents a novel type of *ansa*-metallocene. On the other hand, depending on the stability of the B–P bonds and the ratio of the open-chain vs. the bridged conformer, **1** may be regarded as a potential ligand for other transition metals (e.g. Cr). The ferrocene moiety now merely provides a stereorigid backbone for these “push-pull-ligands”, L<sup>\*</sup>. Conventional ligands L only consist of Lewis basic centres D for the coordination of the Lewis acidic transition metal. The incorporation of additional Lewis acidic centres into L will result in a compound L<sup>\*</sup> that can be expected to show a distinctly

<sup>☆</sup> Dedicated to Professor Henri Brunner on the occasion of his 60th birthday.

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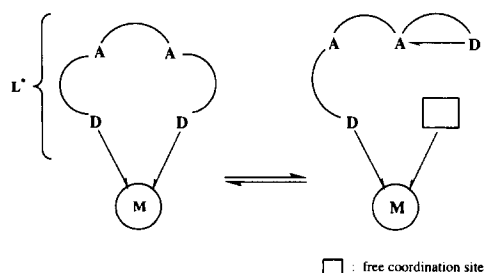


Scheme 1.

different coordinational behaviour. The dissociation of  $L^*$  from the transition metal M will be facilitated thermodynamically since part of the energy required for the breaking of the M–D bond is regained by D–A bond formation. When A competes with M for the lone pair of D the equilibrium of M–D dissociation will therefore be shifted towards the right side (Scheme 2).

The push-pull systems studied in this paper are derivatives of ferrocenylboranes, which have been described by Siebert et al. in 1974 [4]. Ferrocene can be borylated with  $BX_3$  (X = Cl, Br, I) up to four times [5] and therefore offers a convenient route for the synthesis of multifunctional boron compounds. The boron group represents an acceptor unit A whose Lewis acidity is adjustable over a wide range by varying the substitution pattern of boron. The Lewis acidity of the boron centre in ferrocenylboranes and the redox potential of the iron atom are mutually dependent [6]. As a consequence it should be possible to influence the strength of the acceptor unit of a given push-pull system electrochemically. Derivatives of diphenylphosphane were chosen as donor units D (Scheme 3) since arylphosphanes play an important role in the coordination chemistry of both boron [7] and transition metals [8].

The molecules 1–3 (Scheme 3) differ largely in the Lewis acidity of their boron centres and, therefore, represent two extremes on the scale of P–B adduct stability. In the case of 1 the most efficient way to supply the electron-deficient boron atoms with additional electron density lies in P–B adduct formation. The opposite is true for 2 and 3, which are derivatives of aminoboranes. Formally, these molecules are obtained when NR groups are inserted into the B–P bonds of 1. Like other aminoboranes, they possess a high degree of N–B- $\pi$  bonding, which leads to the stabilization of the three-coordinate boron centres. As a result 2



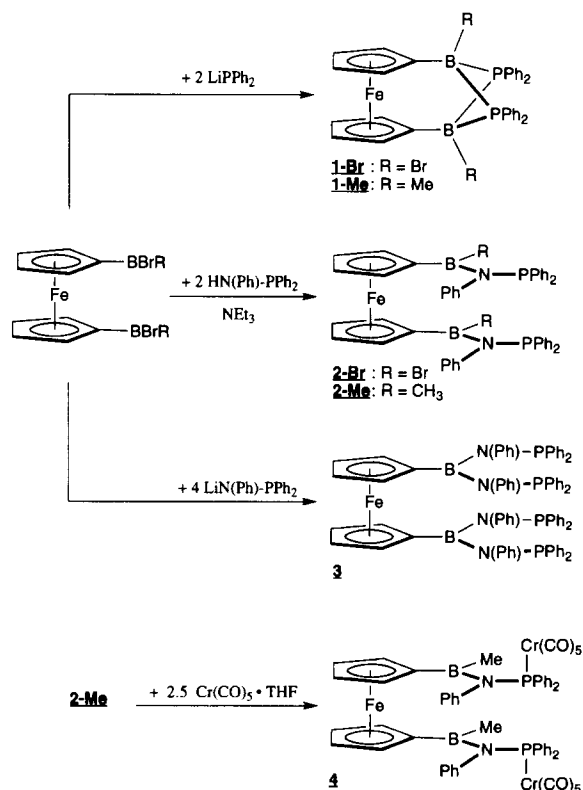
Scheme 2.

and 3 should have a much weaker tendency towards intramolecular P–B coordination than 1. Consequently, they can be expected to be strongly coordinating phosphino ligands for a variety of transition metals. The question arises whether 1-Me and 1-Br can serve as phosphino ligands as well, and under which circumstances a coordinatively unsaturated transition metal centre is able to compete with the boron atoms for the coordinating  $PPh_2$  moiety. It follows from a comparison of the bond energies [9], that in many cases a P–B bond is less favourable than a P–M bond, but differences are small and an equilibrium between both bonding states can therefore be expected.

## 2. Results and discussion

### 2.1. Synthesis

The reaction of 1,1'-bis[bromo(methyl)boryl]ferrocene [10] and 1,1'-bis(dibromoboryl)ferrocene [5,10] with lithiumdiphenylphosphide in toluene gives the ferrocenophanes 1-Me and 1-Br in about 80% and 60% yield, respectively (Scheme 3). Instead of  $LiPPh_2$ ,  $Me_3SiPPh_2$  or  $HPPH_2/NEt_3$  can be employed with similar results. 1-Me crystallizes from toluene/hexane as soft yellow platelets, which are extremely sensitive to air and moisture.



Scheme 3.

**2-Me** and **2-Br** are synthesized from 1,1'-bis[bromo(methyl)boryl]- and 1,1'-bis(dibromoboryl)ferrocene with (anilino)diphenylphosphane/triethylamine [11] in 70% yield. Recrystallization from toluene/hexane leads to the analytically pure substances. For the synthesis of **3**, 1,1'-bis(dibromoboryl)ferrocene was reacted with four equivalents of the lithiumphosphinoamide LiN(Ph)PPh<sub>2</sub> [12]. **4** was obtained almost quantitatively from **2-Me** with an excess of Cr(CO)<sub>5</sub>·THF in toluene. **2–4** are much easier to handle than **1**, but are still sensitive to air and moisture (Scheme 3).

## 2.2. NMR data

Mutual assignments of <sup>1</sup>H and <sup>13</sup>C resonance signals are based on 2D heteronuclear shift correlations. Together with <sup>1</sup>H/<sup>1</sup>H COSY and <sup>1</sup>H NOE difference spectra an almost complete assignment of the resonances of **1–4** was achieved.

The <sup>11</sup>B NMR spectrum of **1-Me** shows a broad resonance at  $\delta = -3.4$  ( $h_{1/2} = 600$  Hz). This value indicates a four-coordinate rather than a three-coordinate boron [13]. In the <sup>31</sup>P NMR spectrum a single resonance for both PPh<sub>2</sub> groups is found which is remarkably broadened due to the quadrupolar relaxation of the boron nucleus ( $\delta = -17.5$ ;  $h_{1/2} = 100$  Hz). The observed shift is comparable to those normally seen for dimeric phosphinoboranes with a four-coordinate phosphorus centre [14–19]. The <sup>1</sup>J(BP) coupling is not resolved in both the <sup>11</sup>B and the <sup>31</sup>P NMR spectrum.

The <sup>1</sup>H{<sup>31</sup>P} NMR spectrum shows one singlet for the methyl groups attached to boron ( $\delta = 1.30$ ). In the ferrocene region two virtual triplets are observed for H<sub>2,5</sub> ( $\delta = 3.93$ ) and H<sub>3,4</sub> ( $\delta = 3.98$ ) corresponding to an A<sub>2</sub>B<sub>2</sub> spin system where vicinal and cross-ring coupling constants are approximately equal and considerably smaller than the chemical shift difference between unlike protons. The resonance that was assigned to H<sub>2,5</sub> shows an NOE effect of +20% upon *ortho*-PPh<sub>2</sub> proton irradiation. When phosphorus coupling is admitted the methyl groups at boron appear as a triplet (<sup>3</sup>J(PH) = 13.1 Hz) whereas the proton signals of the ferrocene moiety become broader, completely losing their fine structure.

A common feature of carbon atoms adjacent to a boron centre is an extreme broadening of their <sup>13</sup>C resonances [13]. This has again to be attributed to the quadrupolar relaxation of the boron nucleus. Consequently the methyl groups in **1-Me** appear as a broad hump at  $\delta = 9.7$  and the C<sub>1,1'</sub> atoms of the ferrocene subunit could not be detected at all. C<sub>3,4</sub> and C<sub>2,5</sub> show singlet ( $\delta = 70.2$ ) and triplet ( $\delta = 74.6$ ; <sup>3</sup>J(PC) = 9 Hz) resonances, respectively. The four phenyl substituents in **1-Me** give two sets of resonances, each of them consisting of four signals (C<sub>i,o,m,p</sub>). With the exception of the para carbon atoms all resonances of the

phenyl rings appear as virtual triplets due to phosphorus coupling. The structure of **1-Me** in solution, as deduced from the NMR data, is given in scheme 3. From the symmetry of **1-Me** it is evident that all four B–P bonds are identical and no distinction has to be made between dative and covalent bonding.

To investigate the stability of the cyclodiborataphosphoniane bridge of **1-Me**, high temperature NMR spectra have been measured in toluene-d<sup>8</sup>. The <sup>11</sup>B and <sup>31</sup>P NMR spectra do not show any significant changes in the temperature range from room temperature to 100°C. In the <sup>1</sup>H NMR spectrum the triplet splitting of the methyl resonance of **1-Me** is preserved whereas the two sets of ortho protons, H<sub>0</sub> and H<sub>0'</sub>, were found to coalesce at T<sub>c</sub> = 65°C. From the latter observation it can be concluded that a continuous breaking and reforming of B–P bonds takes place. When one B–P bond is cleaved, the PPh<sub>2</sub> moiety is free to rotate around the remaining one. This facile interconversion of both phenyl rings effectively averages the magnetic environments of the protons associated with each phenyl group producing magnetical equivalence on the <sup>1</sup>H NMR time scale. From T<sub>c</sub> a value of 70 kJ mol<sup>-1</sup> was calculated for the activation barrier  $\Delta G^\ddagger$  of this process ( $\Delta G^\ddagger = RT_c (22.96 + \ln(T_c/\delta\nu))$  [J mol<sup>-1</sup>]) [20]. The fluxional behaviour of **1-Me** was further studied with the help of the Forsén-Hoffman spin saturation transfer method [21]. This method is based on observation of the absorption signal intensity in one of the sites of an exchange system, when another site is saturated by a second rf field. In the case of **1-Me** the two sets of ortho-protons, H<sub>0'</sub> and H<sub>0</sub>, represent the two sites of the exchange system. We have determined the relaxation time T<sub>1</sub> for both H<sub>0</sub> and H<sub>0'</sub> at different temperatures as well as the decrease in the absorption intensity of H<sub>0</sub> upon irradiation into the resonance frequency of H<sub>0'</sub> at each of these temperatures (Table 1). From these data an activation barrier for the breaking of a B–P bond of  $\Delta G^\ddagger = 70$  kJ mol<sup>-1</sup> was obtained. This is in accordance with the value determined by the line shape method (see above). The thermodynamic parameters  $\Delta H^\ddagger = 45$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger = -90$  J (Kmol)<sup>-1</sup> of this exchange process were obtained from an Eyring plot [20].

Table 1

T (K)	I <sub>0</sub> (ref) <sup>a</sup>	I <sub>0</sub> (irr) <sup>b</sup>	$\tau$ (sec)	thermodynamic data
268	1.79	1.43	4.4	$\Delta G^\ddagger = 70 \pm 1$ kJ mol <sup>-1</sup>
278	1.78	1.08	1.7	$\Delta H^\ddagger = 45 \pm 5$ kJ mol <sup>-1</sup>
288	1.78	0.77	0.8	$\Delta S^\ddagger = -90 \pm 15$ J (Kmol) <sup>-1</sup>
298	1.94	0.65	0.5	

<sup>a</sup> Integral of signal H<sub>0</sub> compared to the ferrocene protons without saturation of H<sub>0'</sub>.

<sup>b</sup> Integral of signal H<sub>0</sub> compared to the ferrocene protons with saturation of H<sub>0'</sub>.

It has to be emphasized that no spectroscopically detectable concentration of the open-chain form of **1-Me** is present. We conclude that even at elevated temperatures the time required for the actual ring exchange process is much shorter than the lifetime of the  $B_2P_2$  entity. Nevertheless, because of this dynamic behaviour of the  $B_2P_2$  moiety the question remains unanswered as to which of the phenyl rings has to be assigned to the dashed set of  $^1H$  and  $^{13}C$  resonances.

The NMR spectra of **1-Me** and **1-Br** exhibit the same general features. The most remarkable difference between both derivatives is manifested in a significant upfield shift of the  $^{31}P$  resonance of **1-Br** ( $\delta = -36.4$ ) as well as in the better shielding of both its ipso carbon atoms,  $C_i$  and  $C_j$ .

From the results of the dynamic NMR studies it becomes evident that the equilibrium between the  $B_2P_2$  bridged conformation of the push-pull-systems **1-Me** and **1-Br** and their open-chain structures lies almost exclusively on the side of the intramolecular adduct. To find out whether this is also true in the presence of a transition metal complex with weakly bound ligands, **1-Br** was treated with two equivalents of  $Cr(CO)_5 \cdot (THF)$  in toluene. Upon addition of the chromium complex, the colour of the solution turned slowly from orange to deep red. The reaction was monitored by  $^{31}P$  and  $^{11}B$  NMR spectroscopy and the resonances of **1-Br** were found to vanish gradually over a period of several hours. In the end, the NMR spectra indicated a mixture of several products, which could not be separated from each other. Their chemical composition is still unknown.

When a solution of **1-Br** in  $CD_2Cl_2$  is treated with a small amount of pyridine, the coordinating  $PPh_2$  groups are substituted cleanly and smoothly by two molecules of pyridine such that the boron centres remain four coordinate ( $\delta(^{11}B) = 9.4$ ,  $\delta(^{31}P) = -25.0$ ). In the  $^1H$ - and  $^{13}C$  NMR spectra of **1-Br**·2Py only one set of resonances for all four phenyl groups is found. The carbon resonances of the  $PPh_2$  moieties now appear no longer as triplets, but as doublets, indicating that coupling occurs with only one rather than with two phosphorus atoms. The cleavage of the  $B_2P_2$  bridge is highly selective and gives only one of the two possible diastereomers. It is very likely that two B–P bonds, which are located at opposite edges of the  $B_2P_2$  ring are cleaved. This implies that the rac and not the meso diastereomer is formed.

After the reaction with pyridine, both  $PPh_2$  moieties are free to act as ligands for transition metal centres. This indicates, how easily the ligand properties of **1-Me** and **1-Br** can be influenced by the choice of solvent or of Lewis basic additives.

For the aminoborane **2-Me**, a value of  $\delta(^{11}B) = 46.5$  is observed which is typical for three-coordinate boron nuclei [13]. The  $^{31}P$  resonance appears at 60.3 ppm,

significantly shifted to lower field compared to the parent aminophosphane  $Ph_2PNHPh$  ( $\delta = 28.5$ ). This is probably the result of a high degree of N–B- $\pi$  bonding in **2-Me**, which decreases the electron density at nitrogen and further polarizes the N–P bond. In the  $^1H$  NMR spectrum of **2-Me** the resonances for  $H_{2,5}$  as well as for the methyl groups are extremely broadened at room temperature. A gradual sharpening of these signals is observed with increasing temperature while the  $^{11}B$  and  $^{31}P$  spectra remain unchanged. The line broadening at r.t. has therefore to be attributed to a hindered rotation in **2-Me** that may have either steric or electronic reasons. Since the bis(amino)borane **3** (see below) exhibits a narrow  $H_{2,5}$  resonance even though it is more hampered by sterical overcrowding, the hindered rotation in **2-Me** is probably a consequence of the pronounced double bond character of its B–N bond. The more electron density is transferred into the empty orbital of boron, the less negative charge can be delocalised into the nitrogen bound phenyl ring. Consequently, its ortho and para  $^{13}C$  resonances are shifted to lower field in **2-Me** compared to the parent aminophosphane (from 116.0 (d) and 119.4 ppm (s) in  $Ph(H)N-PPh_2$  to 129.3 (s) and 125.3 (s) in **2-Me**). In the case of (anilino)diphenylphosphane, the ortho carbon atoms of the NPh moiety appear as doublets ( $^3J(PC) = 13$  Hz) due to phosphorus coupling. This coupling vanishes upon borylation of the nitrogen atom, which may be interpreted in terms of a decreased PN bond order in **2** and **3**.

The  $^{31}P$  resonance of **4** exhibits the expected downfield shift upon complexation ( $\delta = 120.5$  [4];  $\delta = 60.3$  [**2-Me**]). In the  $^{13}C$  NMR spectrum of **4** two resonances for the equatorial ( $\delta = 216.6$ ;  $^2J(PC) = 13$  Hz) and axial ( $\delta = 221.2$ ;  $^2J(PC) = 6$  Hz) carbonyl ligands are observed with the latter possessing the smaller PC coupling constant.

### 2.3. X-ray structure of **1-Me**

The structure of **1-Me** in the solid state was investigated by single crystal X-ray diffraction methods (Fig. 1).

Until now, nine other derivatives of dimeric phosphinoboranes have been structurally characterized [14–19,22,23]. Only two of them (i.e.  $[Ph_2P-BI_2]_2$ , **A** [22], and *cis*- $[^tBu_2P-BH^tBu]_2$ , **B** [18]) show a non-planar configuration of the cyclodiboraphosphonane ring while the others are all planar. Therefore, a noteworthy feature of **1-Me** is the extremely bent  $B_2P_2$  ring. The dihedral angle between the two halves of the ring, which meet in the  $P \cdots P$  line is  $41.6^\circ$  (**A**:  $29.8^\circ$ , **B**:  $19.1^\circ$ ), for the two halves meeting in the  $B \cdots B$  line the angle was found to be  $45.0^\circ$  (**A**:  $29.7^\circ$ ). In the case of **A** and **B** the ring skeleton is believed [18,22] to be bent for sterical reasons, while the non-planarity of **1-Me** is presumably caused by the ferrocene link. Moreover, a smaller degree of bending of the  $B_2P_2$  ring

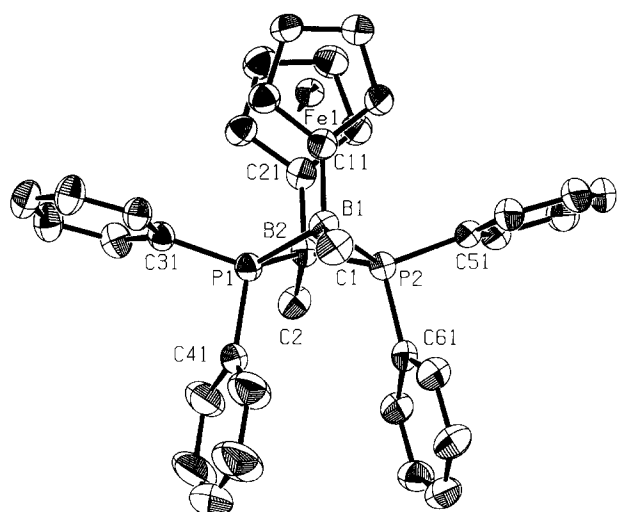


Fig. 1. PLATON [25] drawing of 1,1'-Fc[B(CH<sub>3</sub>)PPh<sub>2</sub>]<sub>2</sub> (**1-Me**). Elements are represented by thermal ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)–B(1) 2.036(4), P(1)–B(2) 2.033(4), P(2)–B(1) 2.032(4), P(2)–B(2) 2.059(4), P(1)–C(31) 1.824(3), P(1)–C(41) 1.827(3), P(2)–C(51) 1.831(3), P(2)–C(61) 1.833(3), B(1)–C(1) 1.604(5), B(1)–C(11) 1.602(5), B(2)–C(2) 1.596(5), B(2)–C(21) 1.593(5); C(1)–B(1)–C(11) 112.3(3), C(11)–B(1)–P(1) 108.5(2), C(11)–B(1)–P(2) 108.1(2), C(1)–B(1)–P(1) 121.5(3), C(1)–B(1)–P(2) 121.0(3), P(1)–B(1)–P(2) 81.5(1), C(2)–B(2)–C(21) 113.7(3), C(21)–B(2)–P(1) 108.5(2), C(21)–B(2)–P(2) 108.1(2), P(1)–B(2)–P(2) 81.0(1), C(2)–B(2)–P(1) 119.7(3), C(2)–B(2)–P(2) 121.4(2), B(1)–P(1)–B(2) 90.7(2), B(1)–P(2)–B(2) 90.1(2).

would lead to an increase of unfavourable nonbonding interactions between the ferrocene moiety and two of the phenyl rings. There are several other evidences which indicate a considerably higher B<sub>2</sub>P<sub>2</sub> ring strain in **1-Me** compared to **A** (Fig. 2).

The CBB angles in **1-Me** (C<sub>11</sub>–B<sub>1</sub> ··· B<sub>2</sub>: 93.6°; C<sub>21</sub>–B<sub>2</sub> ··· B<sub>1</sub>: 93.7°) are 7° and 15° smaller than the two IBB angles in **A** (I<sub>1</sub>–B<sub>1</sub> ··· B<sub>2</sub>: 101.0°; I<sub>2</sub>–B<sub>2</sub> ··· B<sub>1</sub>: 108.6°). The distance between the two phosphorus atoms in

**1-Me** was found to be 0.12 Å smaller than in **A** (**1-Me**: 2.656 Å; **A**: 2.777 Å), whereas the two boron atoms are further apart from each other (**1-Me**: 2.896 Å; **A**: 2.769 Å). **1-Me** shows B–P bond lengths (Fig. 1) that are very similar to those of the other structurally characterized cyclodiborataphosponianes, but greater than in the adducts H<sub>3</sub>PBH<sub>3</sub> and MeH<sub>2</sub>PBH<sub>3</sub> [24] which have B–P bonds of about 1.93 Å. The observed BPB and PBP angles are comparable to those normally seen for both planar and non-planar cyclodiborataphosponiane derivatives (Fig. 1). In the ferrocene moiety the two cyclopentadienyl rings are slightly tilted with an angle between both planes of 7.4°.

### 3. Conclusion

1,1'-Bis[(amino)boryl]ferrocenes were found to possess three-coordinate boron atoms rather than intramolecular B–N–B bridges [26]. In contrast to these results, we obtained with the 1,1'-bis[(phosphino)boryl]ferrocenes a novel type of ferrocenophanes with a cyclodiborataphosponiane moiety spanning both cyclopentadienyl rings. This different chemical behaviour is a consequence of the larger covalent radius of phosphorus, which results in a smaller degree of P–B π bonding and favours P–B σ adduct formation. We are currently attempting to use these findings for the facile synthesis of tailor-made, self-assembling ligand environments.

Our results indicate that the Lewis acidity of e.g. the Cr(CO)<sub>5</sub> fragment is high enough to compete successfully with the boron atom in **1** for the lone pair of the coordinating PPh<sub>2</sub> group. However, **1** does not yet meet the requirements of a push-pull-ligand, which should be able to coordinate reversibly either its own boron moiety or a transition metal and to form well-defined

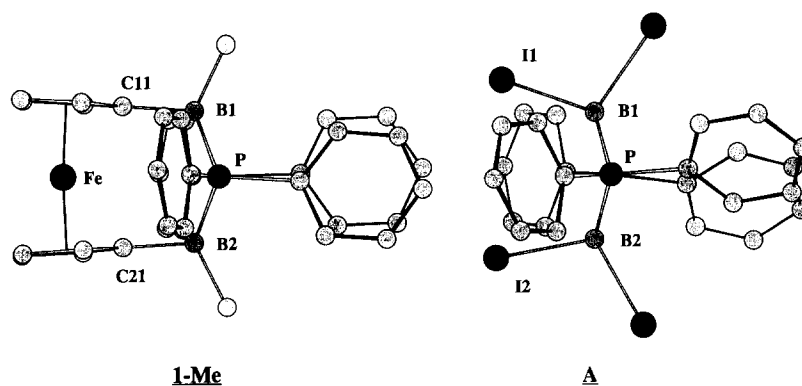


Fig. 2. Ball and stick drawing of **1-Me** and **A** [22]. Comparison of selected interatomic distances (Å), angles (deg) and angles between planes (deg): **1-Me**: P(1) ··· P(2) 2.656, B(1) ··· B(2) 2.896; C(11)–B(1) ··· B(2) 93.6, C(21)–B(2) ··· B(1) 93.7; B(1)P(1)P(2)/B(2)P(1)P(2) 41.6, P(1)B(1)B(2)/P(2)B(1)B(2) 45.0. **A**: P(1) ··· P(2) 2.777, B(1) ··· B(2) 2.769; I(1)–B(1) ··· B(2) 101.0, I(2)–B(2) ··· B(1) 108.6; B(1)P(1)P(2)/B(2)P(1)P(2) 29.8, P(1)B(1)B(2)/P(2)B(1)B(2) 29.7.

adducts in both cases. Problems arise presumably from the sensitivity of the covalent B–P bonds which have therefore to be replaced by more stable entities like B–N–P, B–O–P or B–C–P. As reported in this paper, the B–N–P link gives less sensitive compounds (**2**, **3**), which at room temperature exclusively exist in the open-chain form. Further investigations of the B–O–P and B–C–P analogues are in progress.

#### 4. Experimental details

All reactions and manipulations were carried out in dry, oxygen-free argon using standard Schlenkware or in an argon-filled drybox. Solvents were freshly distilled under N<sub>2</sub> from Na/K alloy-benzophenone (toluene, hexane, THF) prior to use. IR spectra were recorded as toluene solutions (organic and organometallic compounds) using a Perkin-Elmer 1650 FTIR spectrometer. The organic syntheses were assisted by gas chromatographic analyses using a Hewlett-Packard HP5890 instrument coupled with a mass selective detector HP5970. NMR spectra were recorded on a JEOL JMN-GX 400 and a Bruker DPX 400 spectrometer. All <sup>31</sup>P NMR spectra were referenced to external 85% H<sub>3</sub>PO<sub>4</sub>, and <sup>11</sup>B NMR spectra were referenced to external BF<sub>3</sub> · Et<sub>2</sub>O. Elemental analyses were performed by the microanalytical laboratory of the Technische Universität München.

**General remarks:** The assignment of NMR resonances follows the common numbering scheme for substituted ferrocenes (Fc), whereas the ortho, meta, para nomenclature is used for the phenyl rings (abbreviations: s = singlet, d = doublet, tr = triplet, vtr = virtual triplet, mult = multiplet). Satisfactory elemental analyses were obtained for all compounds described in this paper. Neither the CI nor the EI method gave mass spectra of any diagnostic value.

##### 4.1. (Anilino)diphenylphosphane

(Anilino)diphenylphosphane was synthesized according to the method of Wiegräbe [11]. Since a complete NMR spectroscopical characterization has not been published so far, its NMR data are given below.

NMR (CDCl<sub>3</sub>, RT): δ<sup>31</sup>P = 28.5; δ<sup>1</sup>H = 4.42 (d, 1H, NH), 6.87 (tr, 1H, <sup>3</sup>J(HH) = 7.3 Hz, NPh-*p*), 7.07 (d, 2H, <sup>3</sup>J(HH) = 7.3 Hz, NPh-*o*), 7.25 (vtr, 2H, <sup>3</sup>J(HH<sub>o</sub>) = <sup>3</sup>J(HH<sub>p</sub>) = 7.3 Hz, NPh-*m*), 7.41 (mult, 6H, PPh-*m,p*), 7.51 (mult, 4H, PPh-*o*); δ<sup>13</sup>C = 116.0 (d, <sup>3</sup>J(PC) = 13 Hz, NPh-*o*), 119.4 (s, NPh-*p*), 128.5 (d, <sup>3</sup>J(PC) = 7 Hz, PPh-*m*), 129.1 (s, PPh-*p*), 129.2 (s, NPh-*m*), 131.2 (d, <sup>2</sup>J(PC) = 20 Hz, PPh-*o*), 140.2 (d, <sup>1</sup>J(PC) = 13 Hz, PPh-*i*), 146.5 (d, <sup>2</sup>J(PC) = 18 Hz, NPh-*i*).

##### 4.2. 1,1'-Fc[B(Me)PPh<sub>2</sub>]<sub>2</sub> (**1-Me**)

A solution of 0.93 g (2.4 mmol) of 1,1'-Fc(BBrMe)<sub>2</sub> in 10 ml of toluene was slowly added to a slurry of 0.90 g (4.5 mmol) of LiPPh<sub>2</sub> in 30 ml of toluene at –78°C with stirring. The slurry became orange-red and after 30 min it was allowed to warm to room temperature and stirred for 12 h. The mixture was then filtered through a fine-porosity frit and the precipitated LiBr was extracted twice with 20 ml of toluene. The toluene solvent was removed from the orange filtrates in vacuo leaving a yellow solid coated with an orange oil. Recrystallization from toluene/hexane gave yellow platelets of **1-Me**. Yield: 1.12 g, 1.9 mmol (79%).

NMR (CDCl<sub>3</sub>, RT): δ<sup>11</sup>B = –3.4 (*h*<sub>1/2</sub> = 600 Hz); δ<sup>31</sup>P = –17.5 (*h*<sub>1/2</sub> = 100 Hz); δ<sup>1</sup>H = 1.30 (tr, 6H, <sup>3</sup>J(PH) = 13.1 Hz, CH<sub>3</sub>), 3.93 (vtr, 4H, <sup>3</sup>J(HH) = <sup>4</sup>J(HH) = 1.7 Hz, H<sub>2,5</sub>), 3.98 (vtr, 4H, <sup>3</sup>J(HH) = <sup>4</sup>J(HH) = 1.7 Hz, H<sub>3,4</sub>), 6.91 (vtr, 4H, <sup>3</sup>J(HH<sub>o</sub>) = <sup>3</sup>J(HH<sub>p</sub>) = 7.3 Hz, H<sub>m</sub>), 6.98 (tr, 2H, <sup>3</sup>J(HH) = 7.3 Hz, H<sub>p</sub>), 7.39 (mult, 6H, H<sub>m,p</sub>), 7.56 (mult, 4H, <sup>3</sup>J(HH) = 7.3 Hz, H<sub>o</sub>), 7.87 (mult, 4H, H<sub>o</sub>); δ<sup>13</sup>C = 9.7 (broad, CH<sub>3</sub>), 70.2 (s, C<sub>3,4</sub>), 74.6 (vtr, <sup>3</sup>J(PC) = 9 Hz, C<sub>2,5</sub>), 127.6 (vtr, <sup>3</sup>J(P<sub>a</sub>C) = <sup>5</sup>J(P<sub>b</sub>C) = 4 Hz, C<sub>m</sub>), 128.3 (s, C<sub>p</sub>), 128.7 (vtr, <sup>3</sup>J(P<sub>a</sub>C) = <sup>5</sup>J(P<sub>b</sub>C) = 5 Hz, C<sub>m</sub>), 129.7 (s, C<sub>p</sub>), 133.0 (vtr, <sup>2</sup>J(P<sub>a</sub>C) = <sup>4</sup>J(P<sub>b</sub>C) = 3 Hz, C<sub>o</sub>), 133.2 (vtr, <sup>2</sup>J(P<sub>a</sub>C) = <sup>4</sup>J(P<sub>b</sub>C) = 3 Hz, C<sub>o</sub>), 136.0 (vtr, <sup>1</sup>J(P<sub>a</sub>C) = <sup>3</sup>J(P<sub>b</sub>C) = 16 Hz, C<sub>i</sub>), 138.9 (vtr, <sup>1</sup>J(P<sub>a</sub>C) = <sup>3</sup>J(P<sub>b</sub>C) = 36 Hz, C<sub>i</sub>), n.o. (C<sub>1,r</sub>).

##### 4.3. 1,1'-Fc[B(Br)PPh<sub>2</sub>]<sub>2</sub> (**1-Br**)

At –78°C Ph<sub>2</sub>PLi (0.89 g, 4.6 mmol) in 20 ml of toluene was treated dropwise with a solution of 1,1'-Fc(BBr<sub>2</sub>)<sub>2</sub> (1.21 g, 2.3 mmol) in 20 ml of toluene. The slurry became pale red and after 30 min it was allowed to warm to room temperature and stirred for 12 h. After filtration through a fine-porosity frit the precipitated LiBr was extracted twice with 10 ml of toluene. The solution was cooled to –25°C to give **1-Br** as a yellow microcrystalline solid. Yield: 0.88 g, 1.2 mmol (53%). NMR (CDCl<sub>3</sub>, RT): δ<sup>11</sup>B = –5.7 (*h*<sub>1/2</sub> = 400 Hz); δ<sup>31</sup>P = –36.4 (*h*<sub>1/2</sub> = 180 Hz); δ<sup>1</sup>H = 4.10 (s, 8H, H<sub>2,3,4,5</sub>), 6.97 (vtr, 4H, <sup>3</sup>J(HH<sub>o</sub>) = <sup>3</sup>J(HH<sub>p</sub>) = 7.3 Hz, H<sub>m</sub>), 7.06 (tr, 2H, <sup>3</sup>J(HH) = 7.3 Hz, H<sub>p</sub>), 7.49 (mult, 6H, H<sub>m,p</sub>), 8.11 (mult, 4H, H<sub>o</sub>), 8.22 (mult, 4H, H<sub>o</sub>); δ<sup>13</sup>C = 72.2 (s, C<sub>3,4</sub>), 74.9 (vtr, <sup>3</sup>J(PC) = 8 Hz, C<sub>2,5</sub>), 127.5 (vtr, <sup>3</sup>J(P<sub>a</sub>C) = <sup>5</sup>J(P<sub>b</sub>C) = 5 Hz, C<sub>m</sub>), 129.2 (vtr, <sup>3</sup>J(P<sub>a</sub>C) = <sup>5</sup>J(P<sub>b</sub>C) = 6 Hz, C<sub>m</sub>), 129.5 (s, C<sub>p</sub>), 131.1 (s, C<sub>p</sub>), 131.9 (vtr, <sup>1</sup>J(P<sub>a</sub>C) = <sup>3</sup>J(P<sub>b</sub>C) = 22 Hz, C<sub>i</sub>), 132.9 (vtr, <sup>2</sup>J(P<sub>a</sub>C) = <sup>4</sup>J(P<sub>b</sub>C) = 4 Hz, C<sub>o</sub>), 133.4 (vtr, <sup>2</sup>J(P<sub>a</sub>C) = <sup>4</sup>J(P<sub>b</sub>C) = 2 Hz, C<sub>o</sub>), 134.8 (vtr, <sup>1</sup>J(P<sub>a</sub>C) = <sup>3</sup>J(P<sub>b</sub>C) = 38 Hz, C<sub>i</sub>), n.o. (C<sub>1,r</sub>).

##### 4.4. 1,1'-Fc[B(Me)(NPh)PPh<sub>2</sub>]<sub>2</sub> (**2-Me**)

1,1'-Fc(BBrMe)<sub>2</sub> (0.69 g, 1.7 mmol) in 15 ml of toluene was added to a solution of HNPh(PPh<sub>2</sub>) (0.97 g,

3.5 mmol) in 35 ml of toluene at  $-78^{\circ}\text{C}$  with stirring. The resulting orange solution was then treated with 0.49 ml (0.35 g, 3.5 mmol) of  $\text{NEt}_3$ , stirred at  $-78^{\circ}\text{C}$  for 5 min and gently warmed to room temperature. After 12 h of stirring  $\text{HNEt}_3\text{Br}$  was separated from the orange solution with a filter cannula. From the filtrate all volatiles were removed in vacuo whereupon an orange oil was obtained. Upon treatment with 20 ml of hexane the oil solidified to give a yellow precipitate. The precipitate was washed twice with 10 ml of hexane and then dried in vacuo to give 1.18 g (1.5 mmol, 90%) of **2-Me**.

NMR ( $\text{CDCl}_3$ , RT):  $\delta^{11}\text{B} = 46.5$  ( $h_{1/2} = 1500$  Hz);  $\delta^{31}\text{P} = 60.3$  ( $h_{1/2} = 30$  Hz);  $\delta^1\text{H} = 1.13$  (broad, 6H,  $\text{CH}_3$ ), 3.53 (broad, 4H,  $\text{H}_{2,5}$ ), 4.27 (s, 4H,  $\text{H}_{3,4}$ ), 6.58 (d, 4H,  $^3J(\text{HH}) = 7.3$  Hz, NPh-*o*), 6.96 (vtr, 4H,  $^3J(\text{HH}_o) = ^3J(\text{HH}_p) = 7.3$  Hz, NPh-*m*), 7.02 (tr, 2H,  $^3J(\text{HH}) = 7.3$  Hz, NPh-*p*), 7.28 (tr, 8H,  $^3J(\text{HH}_o) = ^3J(\text{HH}_p) = 7.3$  Hz, PPh-*m*), 7.33 (tr, 4H,  $^3J(\text{HH}) = 7.3$  Hz, PPh-*p*), 7.35 (mult, 8H,  $^3J(\text{HH}) = 7.3$  Hz, PPh-*o*);  $\delta^{13}\text{C} = 6.1$  (broad,  $\text{CH}_3$ ), 71.9 (broad,  $\text{C}_{1,1'}$ ), 73.1 (s,  $\text{C}_{3,4}$ ), 76.0 (broad,  $\text{C}_{2,5}$ ), 125.3 (s, NPh-*p*), 127.9 (d,  $^3J(\text{PC}) = 6$  Hz, PPh-*m*), 128.0 (s, NPh-*m*), 128.8 (s, PPh-*p*), 129.3 (s, NPh-*o*), 133.3 (d,  $^2J(\text{PC}) = 22$  Hz, PPh-*o*), 138.3 (d,  $^1J(\text{PC}) = 20$  Hz, PPh-*i*), 146.9 (d,  $^2J(\text{PC}) = 9$  Hz, NPh-*i*).

#### 4.5. $1,1'\text{-Fc}[\text{B}(\text{Br})(\text{NPhPPH}_2)]_2$ (**2-Br**)

**2-Br** was synthesized similar to **2-Me** from  $1,1'\text{-Fc}(\text{BBr}_2)_2$  (0.59 g, 1.1 mmol),  $\text{HNPh}(\text{PPh}_2)$  (0.62 g, 2.3 mmol) and  $\text{NEt}_3$  (0.31 ml, 0.23 g, 2.3 mmol). Yield: 0.82 g, 0.9 mmol (83%).

NMR ( $\text{CDCl}_3$ , RT):  $\delta^{11}\text{B} = 42.5$  ( $h_{1/2} = 1500$  Hz);  $\delta^{31}\text{P} = 70.1$  ( $h_{1/2} = 180$  Hz);  $\delta^1\text{H} = 3.90$  (broad, 4H,  $\text{H}_{2,5}$ ), 4.42 (s, 4H,  $\text{H}_{3,4}$ ), 6.57 (d, 4H,  $^3J(\text{HH}) = 7.3$  Hz, NPh-*o*), 6.96 (vtr, 4H,  $^3J(\text{HH}_o) = ^3J(\text{HH}_p) = 7.3$  Hz, NPh-*m*), 7.05 (tr, 2H,  $^3J(\text{HH}) = 7.3$  Hz, NPh-*p*), 7.31 (mult, 20H, PPh-*o,m,p*);  $\delta^{13}\text{C} = \text{n.o.}$  ( $\text{C}_{1,1'}$ ), 75.1 (s,  $\text{C}_{3,4}$ ), 78.0 (broad,  $\text{C}_{2,5}$ ), 126.2 (s, NPh-*p*), 128.0 (d,  $^3J(\text{PC}) = 6$  Hz, PPh-*m*), 128.2 (s, NPh-*m*), 129.1 (s, PPh-*p*), 129.3 (s, NPh-*o*), 133.5 (d,  $^2J(\text{PC}) = 23$  Hz, PPh-*o*), 136.7 (d,  $^1J(\text{PC}) = 20$  Hz, PPh-*i*), 147.0 (d,  $^2J(\text{PC}) = 9$  Hz, NPh-*i*).

#### 4.6. $1,1'\text{-Fc}[\text{B}(\text{NPhPPH}_2)]_2$ (**3**)

A solution of 1.37 g (2.6 mmol) of  $1,1'\text{-Fc}(\text{BBr}_2)_2$  in 15 ml of toluene was added to a slurry of 10.4 mmol of  $\text{LiNPhPPH}_2$  in 40 ml of toluene at  $-78^{\circ}\text{C}$  with stirring. The  $\text{LiNPhPPH}_2$  was generated from 3.00 g (10.8 mmol) of  $\text{HNPhPPH}_2$  according to a literature procedure [12]. Upon warming to room temperature the reaction mixture first turned brown and finally adopted an orange-red colour. After 24 h the mixture was filtered through a fine-porosity frit to remove most of the precipitated

$\text{LiBr}$ . The volume of toluene was reduced to 20 ml and the cloudy solution was filtered again to separate from residual  $\text{LiBr}$ . Toluene was evaporated and the resulting orange solid was dried in vacuo. Recrystallization from toluene/hexane (2:1) gave pale orange crystals of **3** (Yield: 2.66 g; 2.0 mmol; 77%).

NMR ( $\text{CDCl}_3$ , RT):  $\delta^{11}\text{B} = 45$  (very broad);  $\delta^{31}\text{P} = 51.5$  ( $h_{1/2} = 250$  Hz);  $\delta^1\text{H} = 3.62$  (s, 4H,  $\text{H}_{2,5}$ ), 3.82 (s, 4H,  $\text{H}_{3,4}$ ), 6.83 (mult, 20H, NPh-*o,m,p*), 7.20 (mult, 24H, PPh-*m,p*), 7.48 (mult, 16H, PPh-*o*);  $\delta^{13}\text{C} = 68.7$  (broad,  $\text{C}_{1,1'}$ ), 73.0 (s,  $\text{C}_{3,4}$ ), 77.7 (s,  $\text{C}_{2,5}$ ), 123.8 (s, NPh-*p*), 127.7 (s, PPh-*m*), 127.8, 127.9 (s, s, NPh-*o,m*), 128.2 (s, PPh-*p*), 132.7 (mult, PPh-*o*), 138.8 (mult, PPh-*i*), 146.3 (vtr,  $^2J(\text{PC}) = ^4J(\text{PC}) = 4$  Hz, NPh-*i*).

#### 4.7. $1,1'\text{-Fc}[\text{B}(\text{Me})(\text{NPhPPH}_2 \cdot \text{Cr}(\text{CO})_5)]_2$ (**4**)

1.40 g (6.4 mmol) of  $\text{Cr}(\text{CO})_6$  were irradiated for 24 h in 140 ml of THF with a mercury broad band UV lamp. The evolution of 150 ml of CO was observed. 0.31 g (0.4 mmol) of **2-Me** were dissolved in 20 ml of toluene and 26 ml (1.2 mmol) of the calibrated  $\text{Cr}(\text{CO})_5 \cdot \text{THF}$  solution (excess) were added at room temperature with stirring. After stirring for 1 h the solvents were evaporated in vacuo leaving a pale red solid behind. The solid was extracted twice with 10 ml of toluene and dried completely in vacuo to yield the chromium complex **4** almost quantitatively.

NMR ( $\text{CDCl}_3$ , RT):  $\delta^{11}\text{B} = 48$  (very broad);  $\delta^{31}\text{P} = 120.5$  (broad);  $\delta^1\text{H} = 0.50$  (s, 6H,  $\text{CH}_3$ ), 3.17 (4H,  $\text{H}_{2,5}$ ), 4.07 (4H,  $\text{H}_{3,4}$ ), 6.91 (d, 4H,  $^3J(\text{HH}) = 6.8$  Hz, NPh-*o*), 7.13 (vtr, 4H,  $^3J(\text{HH}_p) = ^3J(\text{HH}_o) = 6.8$  Hz, NPh-*m*), 7.17 (tr, 2H,  $^3J(\text{HH}) = 6.8$  Hz, NPh-*p*), 7.30 (mult, 8H, PPh-*m*), 7.35 (mult, 4H, PPh-*p*), 7.42 (mult, 8H, PPh-*o*);  $\delta^{13}\text{C} = 9.9$  (d,  $^3J(\text{PC}) = 5$  Hz,  $\text{CH}_3$ ), 72.2 (broad,  $\text{C}_{1,1'}$ ), 73.0 (s,  $\text{C}_{3,4}$ ), 75.3 (s,  $\text{C}_{2,5}$ ), 126.9 (s, NPh-*p*), 128.1 (d,  $^3J(\text{PC}) = 9$  Hz, PPh-*m*), 129.0 (s, NPh-*m*), 130.1 (s, PPh-*p*), 130.9 (d,  $^3J(\text{PC}) = 3$  Hz, NPh-*o*), 131.9 (d,  $^2J(\text{PC}) = 12$  Hz, PPh-*o*), 137.8 (d,  $^1J(\text{PC}) = 33$  Hz, PPh-*i*), 145.5 (s, NPh-*i*), 216.6 (d,  $^2J(\text{PC}) = 13$  Hz,  $\text{CO}_{\text{eq}}$ ), 221.2 (d,  $^2J(\text{PC}) = 6$  Hz,  $\text{CO}_{\text{ax}}$ ).

IR (toluene;  $\text{cm}^{-1}$ ): 2062 (m,  $\text{A}_1$ ), 1981 (w,  $\text{B}_2$ ), 1940 (vs,  $\text{A}_1/\text{E}$ ).

#### 4.8. X-ray crystal structure determination of (**1-Me**)

A yellow crystal of **1-Me** was selected in a perfluorinated oil and mounted in a glass capillary on an Image Plate Diffraction System (IPDS, STOE). Final lattice parameters were obtained by least squares refinement of 1280 reflections (graphite monochromator,  $\lambda = 71.073$  pm -  $\text{Mo K}\alpha$ ). Monoclinic system, space group  $\text{P}2_1/\text{n}$  (I.T.-No.: 14),  $a = 1319.4(3)$  pm,  $b = 1679.2(3)$  pm,  $c = 1633.0(4)$  pm,  $\beta = 98.34(2)^\circ$ ,  $V = 3580 \cdot 10^6$  pm<sup>3</sup>,  $\rho_{\text{calc}} = 1.296$  g cm<sup>-3</sup>,  $Z = 4$ . The crystal contains one additional solvent molecule (toluene) in the asymmetric

unit, which is disordered. Data were collected at  $-80(\pm 0.3)^{\circ}\text{C}$ , distance from crystal to image plate 80 mm ( $7.1^{\circ} < 2\theta < 48.4^{\circ}$ ), 360 images collected,  $0^{\circ} < \varphi < 360^{\circ}$ ,  $\Delta\varphi = 1^{\circ}$ , exposure time 10 min. Data were corrected for Lorentz and polarization terms. 41547 data measured, 12 overflows, 0 overlaps, 822 reflections systematically absent, 40725 data merged ( $R = 0.065$ ), 5629 independent reflections, 411 with negative intensity, 5186 reflections with  $I > 0.01 \cdot \sigma(I)$  used for refinement. The structure was solved by the Patterson method [27] and refined with standard difference Fourier techniques [28]. All hydrogens bonded to non-disordered carbon atoms were located in difference Fourier maps and refined isotropically. 520 parameters refined, 9.97 data per parameter, weighting scheme according to Tukey and Prince [29] shift/error  $< 0.001$  in the last cycle of refinement, residual electron density  $+0.45 \text{ e}\text{\AA}^{-3}$  37 pm near C86,  $-0.56 \text{ e}\text{\AA}^{-3}$ ,  $R = 0.061$ ,  $R_w = 0.050$ , minimized function was  $\sum w(|F_o| - |F_c|)^2$  [30].

### Acknowledgements

The authors wish to thank Prof. Dr. W.A. Herrmann (Technische Universität München) for his generous support. We are grateful to Prof. Dr. H. Nöth (Ludwig-Maximilians-Universität München) for a gift of  $\text{BBr}_3$ . Financial support from the ‘‘Bayerisches Forschungsprogramm Katalyse’’ (FORKAT) and from the ‘‘Fonds der Chemischen Industrie’’ (Ph.D. fellowship for M.M.) is appreciated.

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