

# Synthesis and Coordination Chemistry of 1-Cymantrenyl-2,3,4,5-tetraphenylborole

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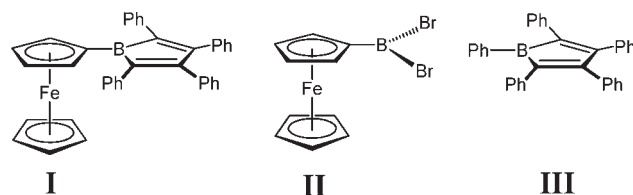
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Supporting Information

**ABSTRACT:** In this contribution, we report the synthesis of base-free 1-cymantrenyl-2,3,4,5-tetraphenylborole and two of its Lewis base adducts. In addition, the structural characterization and investigation of the photophysical properties are provided.

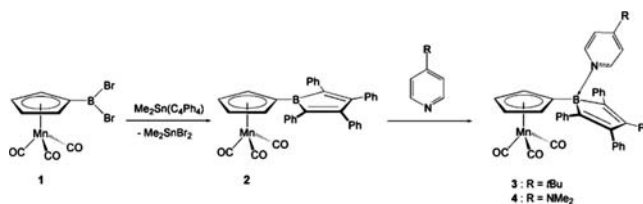
Because of their photophysical properties, borole derivatives are currently of tremendous interest, which is highlighted by an increasing number of publications in this field during the last couple of years.<sup>1</sup> The origin of the exceptional photophysical behavior is strongly related to the partial conjugation of the  $4\pi$  electrons of the butadiene backbone through the empty  $p_z$  orbital at boron, reason why boroles are considered antiaromatic systems.<sup>2</sup> Accordingly, the chromaticity of borole derivatives is caused by a small highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap, which, in turn, is highly dependent on the substituents at boron.<sup>3</sup> A large variety of different substituents has already been implemented, for instance, halides, aryl and amino groups, or metal fragments.<sup>1–4</sup> As a consequence of the pronounced Lewis acidity of the boron center, boroles have proven useful for the activation of small molecules and the coordination of even weak Lewis bases such as ethers or nitriles.<sup>2,5</sup> When sterically encumbered Lewis bases are employed, the formation of FLPs (Frustrated Lewis Pairs) can be observed, which also exhibit photophysical activity.<sup>6</sup> The high Lewis acidity of boroles was nicely illustrated for ferrocenylborole (**I**; Figure 1), the molecular structure of which features a significant bending of the boron moiety toward the iron center, which has been ascribed to a shift of electron density from the ferrocenyl unit to the unsaturated boron nucleus.<sup>3</sup> This characteristic feature has also been demonstrated for other boranes but is most distinct in the case of **I**. Similar electronic situations has been reported for cymantrenylboranes, and thus we focused our attention to the corresponding borole derivatives.<sup>7,8</sup>

Base-free 1-cymantrenyl-2,3,4,5-tetraphenylborole (**2**) was prepared by the stoichiometric reaction of cymantrenyldibromoborane (**1**) with 1,1-dimethyl-2,3,4,5-tetraphenylstannole (Scheme 1) via the well-known tin–boron exchange route.<sup>2</sup> Thus, **2** was isolated in good yield (70%) as a dark-orange, highly air- and moisture-sensitive solid. In accordance with the anticipated composition of **2**, the <sup>1</sup>H NMR spectrum features two multiplets at  $\delta$  4.67 and 4.86 for the Cp ring protons and a broad multiplet ( $\delta$  6.90–7.22) for the protons of the phenyl substituents. The boron nucleus could be detected as a rather broad resonance at  $\delta$  58 in the <sup>11</sup>B NMR spectrum, which appears downfield-shifted by 8.8 ppm with respect to **1**.<sup>9</sup> For structural



**Figure 1.** 1-Ferrocenyl-2,3,4,5-tetraphenylborole (**I**), ferrocenyldibromoborane (**II**), and pentaphenylborole (**III**).

## Scheme 1

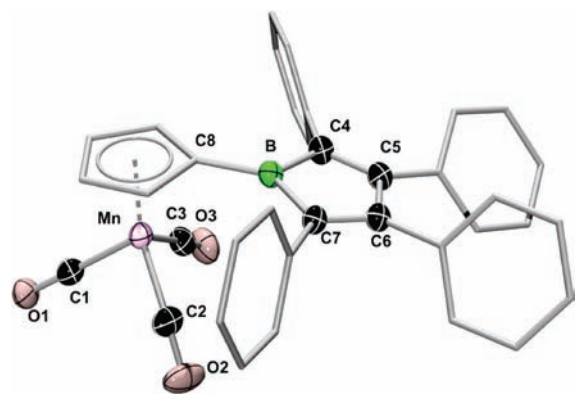


characterization, red crystals of **2**, obtained by the slow evaporation of a concentrated solution in CH<sub>2</sub>Cl<sub>2</sub>, were studied by X-ray diffraction (Figure 2).

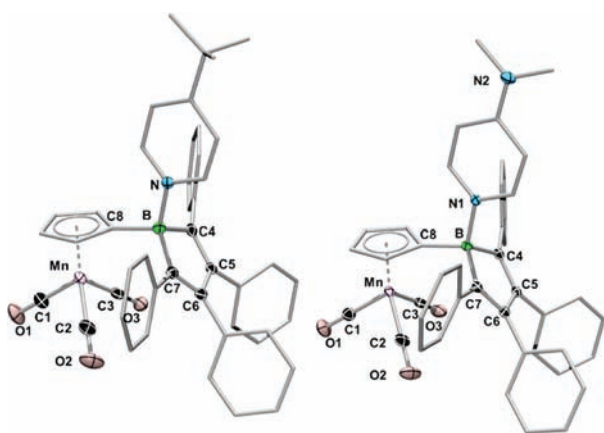
Structural features of **2** such as the propeller-like arrangement of the phenyl groups of the butadiene backbone are comparable to those found for other borole derivatives. The borole fragment is almost planar, as manifested by torsion angles between  $-2.3$  and  $3.1^\circ$ . In addition, the boracycle exhibits localized single and double bonds, which are related to the interaction of manganese with the unsaturated boron center. However, with a dip angle of  $11.4^\circ$ , this interaction is much less significant in **2** than that in **I** ( $29.4^\circ$ ),<sup>3</sup> which is most likely a result of the presence of three electron-withdrawing CO ligands. Moreover, the bending of the boron moiety in **2** toward the metal center is even less pronounced in comparison to those of the precursor **1** ( $11.7^\circ$ ) and the related methylcymantrene derivative  $[(\eta^5\text{-C}_5\text{H}_4(\text{Me}))(\text{CO})_3\text{Mn}\{\text{BBr}_2\}]$  ( $12.3^\circ$ ).<sup>7d,e,8</sup> This finding is rather surprising, keeping in mind that the dip angles in **II** ( $18.9$  and  $17.7^\circ$ )<sup>10</sup> are much smaller than that of the borole derivative **I**, a finding that highlights the pronounced Lewis acidity of boroles compared to the more common boranes. We propose that the bending of the borole moiety toward the manganese center is sterically hindered in **2** because of the presence of the CO groups. Consequently, the dip angle of **1** is greater than that in **2** based on the different sizes of the exocyclic BBr<sub>2</sub> and borole groups.

**Received:** March 18, 2011

**Published:** April 20, 2011

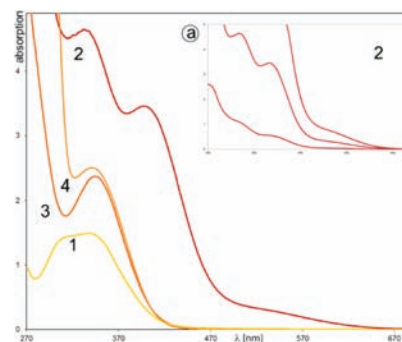


**Figure 2.** Molecular structure of **2** with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: B–C4 1.590(3), B–C7 1.583(3), B–C8 1.525(3), C4–C5 1.351(2), C5–C6 1.531(3), C6–C7 1.351(3).



**Figure 3.** Molecular structure of **3** (left) and **4** (right) with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] for **3**: B–N 1.619(3), B–C4 1.628(3), B–C7 1.624(3), B–C8 1.612(3), C4–C5 1.354(3), C5–C6 1.498(3), C6–C7 1.357(3). Selected bond lengths [Å] for **4**: B–N1 1.608(3), B–C4 1.633(3), B–C7 1.629(3), B–C8 1.608(3), C4–C5 1.358(3), C5–C6 1.500(3), C6–C7 1.357(3).

The coordination chemistry of **2** toward Lewis bases was studied exemplarily by mixing  $\text{CD}_2\text{Cl}_2$  solutions of **2** with 1 equiv of 4-*tert*-butylpyridine or 4-(dimethylamino)pyridine to afford **3** and **4**, respectively, as judged by NMR spectroscopy of the reaction mixtures (Scheme 1). Both species were isolated as yellow, moderately air- and moisture-sensitive solids in high yield (89–91%). Conclusive characterization was achieved by  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectroscopy in solution. Thus, **3** features a new set of signals in the  $^1\text{H}$  NMR spectrum with one singlet for the *tert*-butyl group ( $\delta$  1.47), two multiplets for the Cp protons ( $\delta$  4.15 and 4.60), two multiplets for the phenyl protons of the tetraphenylborole backbone ( $\delta$  6.55–6.57 and 6.95–7.09), and two multiplets for the aromatic protons of the pyridine base ( $\delta$  7.71–7.72 and 8.71–8.73). Most characteristically, the  $^{11}\text{B}$  NMR resonance of **3** is shifted significantly from 58 to 0.1 ppm, suggestive of a tetracoordinated boron center. The solution NMR spectra of **4** are comparable and are thus not discussed in detail here. The anticipated molecular compositions of **3** and **4** were substantiated by X-ray diffraction on single crystals



**Figure 4.** UV–vis spectra of **1–4** in dichloromethane (**1** and **2**,  $c = 5 \times 10^{-4}$  mol/L; **3** and **4**,  $c = 3 \times 10^{-4}$  mol/L). (a) UV–vis spectra of **2** at concentrations between  $1.4 \times 10^{-3}$  and  $1.8 \times 10^{-4}$  mol/L.

obtained by the diffusion of hexane into dichloromethane solutions of **3** and **4**, respectively (Figure 3). The borole moiety in **3** and **4** is notably bent with respect to the Cp ring plane in comparison to **2**, for which the angle between C8, B, and the centroid of the borole ring is almost linear ( $178.5^\circ$ ). By contrast, the corresponding angles in **3** and **4** are significantly reduced to  $126.1$  and  $125.2^\circ$ , respectively (Figure 3), which is a result of the formation of  $\text{sp}^3$ -hybridized boron centers after coordination of the Lewis bases. In addition, a distinct elongation of the B–C8 distance is observed upon coordination of the bases [**1**, 1.520(5) Å; **2**, 1.525(3) Å; **3**, 1.612(3) Å; **4**, 1.608(3) Å]. While steric reasons most likely account for the unexpected longer bond length in **2** with respect to that in **1**, coordination of the nitrogen lone pair to the boron center, which is accompanied by a substantial decrease in the Lewis acidity, is responsible for the bond elongation in **3** and **4**. The decreasing Lewis acidity also results in an elongation of the other B–C bonds (B–C4 and B–C7) by ca. 4 pm for **3** and **4**. In addition, the borole moieties in **3** and **4** feature noticeably larger torsion angles ( $6.3$ – $7.5^\circ$  and  $5.8$ – $6.6^\circ$ ) than that of **2**, which highlights the sterically more congested situation after coordination of the Lewis bases. Structural differences between **3** and **4**, such as a slightly shorter B–N bond distance in **4**, are small and caused by the fact that 4-(dimethylamino)pyridine is a stronger Lewis base than 4-*tert*-butylpyridine.

As expected, the dip angles found in **3** and **4** ( $3.7$  and  $4.7^\circ$ ) are much smaller than that in **2**, which indicates the absence of any significant interaction of the manganese and boron nuclei upon the formation of a tetracoordinated boron center. The photo-physical properties of **1–4** were assessed by UV–vis spectroscopy in solution, which revealed substantial differences in the absorption behavior of the respective species. While two maxima ( $\lambda = 315$  and  $340$  nm) in the typical region for cymantrene<sup>11</sup> are observed for **1** (Figure 4), the absorption spectrum of **2** is significantly different, with peaks found at  $\lambda = 332$  and  $397$  nm. In addition, a broad shoulder is detected for the latter ( $\lambda = 515$  nm), which lies between the bands observed for **1** ( $390$  and  $485$  nm) and **III** ( $560$  nm) (Figure 1).<sup>3</sup> This finding indicates a smaller degree of electronic interaction between the metal and the boron center for the manganese borole complex **2** in comparison to the ferrocenylborole **I**. Moreover, larger extinction coefficients are found for **2** (Table 1) compared to **1**. Upon coordination of a Lewis base, i.e., upon formation of  $\text{sp}^3$ -hybridized boron centers, the absorption spectra are again significantly altered, and **3** and **4** feature only one absorption

**Table 1.** List of Absorption Maxima ( $\lambda$  [nm]) and Extinction Coefficients ( $\epsilon$  [L/mol·cm])

2	3	4	1
332 nm, 8509 L/mol·cm	345 nm, 7251 L/mol·cm	342 nm, 7196 L/mol·cm	315 nm, 2973 L/mol·cm
397 nm, 6491 L/mol·cm			340 nm, 3160 L/mol·cm
515 nm, 622 L/mol·cm			

maximum each ( $\lambda = 345$  and  $342$  nm), thus lying in the area typically observed for adducts between boroles and strong Lewis bases.<sup>2,3</sup>

In summary, **2** has been prepared by tin–boron exchange and its structural characterization in the solid state revealed a significant electronic interaction between the electron-deficient boron center and the cymantrenyl moiety, which to some extent, however, appears to be attenuated by steric congestion. This manganese–boron interaction also leads to the characteristic photophysical properties of the title compound as assessed by UV–vis spectroscopy, which further highlights the subtle and tunable influence of the substituent at boron. A striking change in the absorption behavior was observed upon coordination of Lewis bases to the unsaturated boron center of **2**, which is also well documented for related species such as ferrocenylboranes.<sup>12</sup> Two different adducts have been prepared and fully characterized in solution and in the solid state. Further, related systems are subject to current studies in our laboratories.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Experimental procedures, spectroscopic and crystallographic data, UV–visible spectra, and crystallographic material in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ ACKNOWLEDGMENT

This work was supported by the GRK1221.

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