

# Cymantrene-based tris(1-pyrazolyl)borates: synthesis and structural characterization of di- and trimetallic complexes

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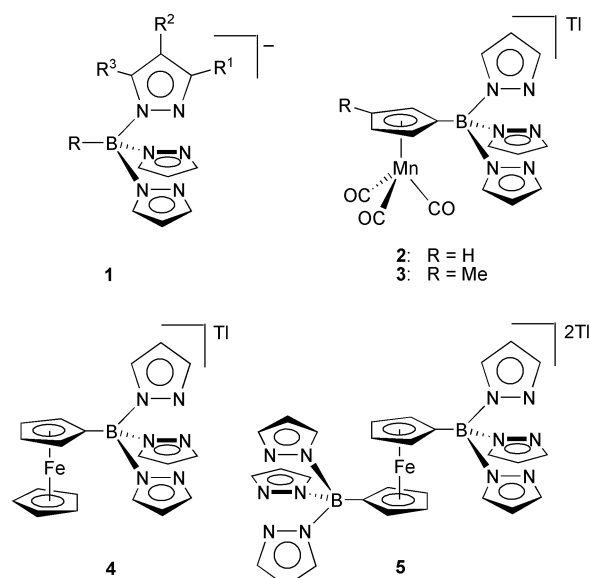
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The di- and trinuclear complexes  $\text{Mn}(\text{CO})_3[\text{CymB}(\text{pz})_3]$  **6**,  $\text{Mn}(\text{CO})_3[\text{CymB}(\text{pz})_2(\text{OH})]$  **7** and  $\text{Zn}[\text{CymB}(\text{pz})_3]_2$  **8** have been synthesized and structurally characterized by X-ray crystallography (Cym = cymantrenyl, pz = pyrazolyl). **6** and **8** are easily accessible from the corresponding  $\text{Ti}^{\text{I}}$  salt  $\text{Ti}[\text{CymB}(\text{pz})_3]$  **2** and  $\text{Mn}(\text{CO})_5\text{Br}$  or  $\text{ZnBr}_2$ , respectively. IR spectroscopy and X-ray crystallography on **6**, which features a cyclopentadienyl ring together with a scorpionate moiety in the same molecule, indicate both ligand types to exert a very similar electronic influence on the respective  $\text{Mn}(\text{CO})_3$  fragment. The heteroscorpionate complex **7** is obtained when the reaction of  $\text{Ti}[\text{CymB}(\text{pz})_3]$  **2** and  $\text{Mn}(\text{CO})_5\text{Br}$  is performed without exclusion of air and moisture. Complex **6** undergoes photolysis (with UV light,  $\lambda = 254 \text{ nm}$ ) leading to the liberation of carbon monoxide and the formation of larger aggregates of unknown molecular structure.

## Introduction

Tris(1-pyrazolyl)borates (“scorpionates”) **1**<sup>1,2</sup> (Fig. 1) have established themselves as a most important class of ligands in coordination chemistry, since they can readily be modified sterically and electronically through appropriate substitution both on the pyrazole rings ( $\text{R}^1$ – $\text{R}^3$ ) and on the boron centre (R). The denticity of scorpionate ligands ranges between one and three, and the bite angle is adjustable to the specific requirements of the coordinated metal complex fragment. Nowadays, scorpionates find applications in various fields such as analytical chemistry, homogeneous catalysis and materials science.<sup>3</sup>



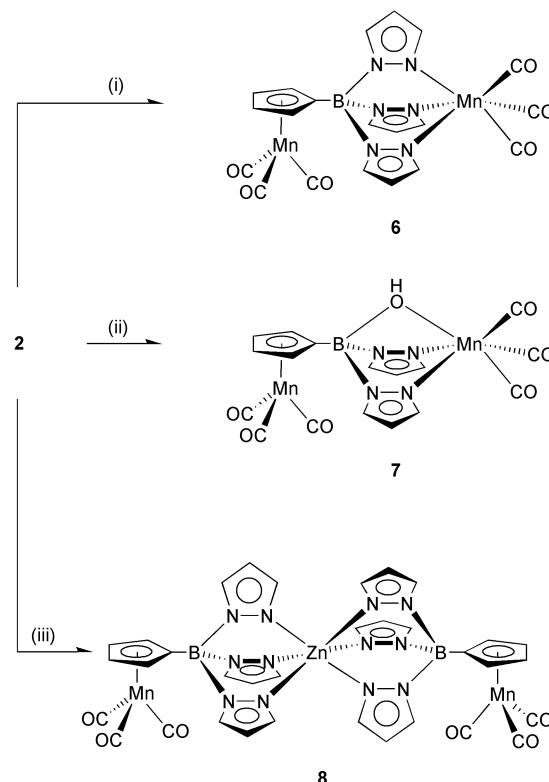
**Fig. 1** Tris(1-pyrazolyl)borate **1** (substituents  $\text{R}^1$ – $\text{R}^3$  on two of the three pyrazolyl rings are omitted for clarity) and its cymantrene- (**2**, **3**) and ferrocene-based derivatives (**4**, **5**).

In order to supply versatile building blocks for the generation of oligonuclear transition metal complexes, our group has recently prepared the cymantrenyl tris(1-pyrazolyl)borates **2** and **3**,<sup>4</sup> as well as the corresponding mono- (**4**) and difunctional (**5**) ferrocene-based derivatives (Fig. 1).<sup>5–8</sup>

## Results and discussion

### Synthesis and spectroscopy

The dinuclear manganese complex **6** is accessible in high yield from the reaction of  $\text{Mn}(\text{CO})_5\text{Br}$  with the  $\text{Ti}^{\text{I}}$  scorpionate **2** in dry THF at ambient temperature under an argon atmosphere (Scheme 1). X-Ray quality crystals of **6** were grown from  $\text{CDCl}_3$  in an NMR tube upon slow evaporation of the solvent. After the reaction had been performed without rigorous exclusion of air and moisture, the heteroscorpionate complex **7** was



**Scheme 1** Syntheses of **6–8**: (i) +  $\text{Mn}(\text{CO})_5\text{Br}$  in THF, r.t., inert gas atmosphere; (ii) +  $\text{Mn}(\text{CO})_5\text{Br}$  in THF, r.t., no inert gas atmosphere; (iii) + 0.5 equiv.  $\text{ZnBr}_2$  in THF, r.t., inert gas atmosphere.

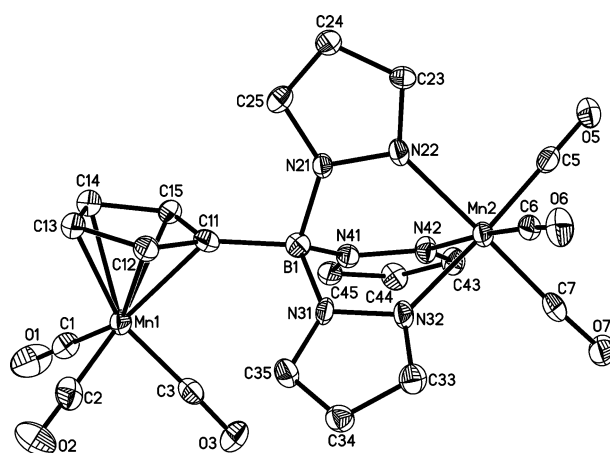
obtained in 32% yield. The compound crystallized from  $\text{CHCl}_3$  together with one equiv. of pyrazole ( $7 \cdot \text{pzH}$ ). Since THF solutions of **6** were found to be stable towards air and moisture, **7** is probably formed at an earlier stage *via* the hydrolysis of a reaction intermediate in which a  $\text{Mn}(\text{CO})_5$  [ $\text{Mn}(\text{CO})_4$ ] fragment is coordinated to only one [two] pyrazolyl ring[s] of the cymantrenyl scorpionate ligand. The heterotrimetallic compound **8** can be synthesized from two equiv. of **2** and one equiv. of  $\text{ZnBr}_2$  in THF in a very clean reaction.

The carbonyl ligands of parent cymantrene give rise to two bands in the infrared spectrum [ $A_1$ , E;  $\nu(\text{CO}) = 2035, 1949 \text{ cm}^{-1}$ ],<sup>9</sup> thereby indicating the  $\text{Mn}(\text{CO})_3$  fragment to possess local  $C_{3v}$  symmetry. Three rather than two bands appear in the IR spectrum of the cymantrenyl scorpionate complex **2** bearing a sterically demanding [Bpz<sub>3</sub>Tl] substituent on its cyclopentadienyl ring [**2**:  $\nu(\text{CO}) = 2019, 1944, 1922 \text{ cm}^{-1}$  (in TlBr)].<sup>4</sup> There is a pronounced red-shift of these frequencies compared to the bands recorded for cymantrene [see above; *cf.* methylcymantrene:<sup>9</sup>  $\nu(\text{CO}) = 2030, 1942 \text{ cm}^{-1}$ ; **3**:<sup>4</sup>  $\nu(\text{CO}) = 2003, 1933, 1917 \text{ cm}^{-1}$  (in TlBr)]. The  $\text{Mn}(\text{CO})_3$  complex **6** exhibits carbonyl bands at  $\nu(\text{CO}) = 2030, 2023, 1933$  (two shoulders at ca. 1945 and 1925) and  $1908 \text{ cm}^{-1}$  (in KBr). We tentatively assign the signal at  $\nu(\text{CO}) = 2030 \text{ cm}^{-1}$  to the  $\text{Mn}(\text{CO})_3$  fragment coordinated by the scorpionate ligand while the band at  $\nu(\text{CO}) = 2023 \text{ cm}^{-1}$  is likely due to the cymantrenyl substituent of **6** [*cf.*  $\text{Mn}(\text{CO})_3[\text{HB}(\text{pz})_3]$ :<sup>10</sup>  $\nu(\text{CO}) = 2041, 1941 \text{ cm}^{-1}$ ]. There is obviously only little difference between the CO stretching frequencies of the two manganese tricarbonyl units, which leads to the conclusion that the charge density on both manganese centres is rather similar. Broad and poorly resolved signals are obtained for the heteroscorpionate complex **7** [ $\nu(\text{CO}) = 2014, 1931$  (shoulder at *ca.*  $1905 \text{ cm}^{-1}$ ) while the expected set of three bands is observed in the case of the trinuclear  $\text{Mn}_2\text{Zn}$  aggregate **8** [ $\nu(\text{CO}) = 2021, 1944$  (shoulder at  $1934$ ),  $1918 \text{ cm}^{-1}$ ].

The <sup>11</sup>B NMR signals of **6**, **7** and **8** occur in a range typical of tetra-coordinated boron nuclei<sup>11</sup> [ $\delta(^{11}\text{B}, \text{CDCl}_3) = -2.2$  (**6**),  $0.7$  (**7**) and  $-1.6$  (**8**)]. In the <sup>1</sup>H NMR spectra of **6** and **8**, two resonances are found for the magnetically non-equivalent  $\alpha$  and  $\beta$  protons of the cyclopentadienyl ring(s) while the  $\text{C}_5\text{H}_4$  protons of **7** give rise to only one resonance possessing an intermediate shift value [*cf.* **6**:  $\delta(^1\text{H}, \text{CDCl}_3) = 4.87, 5.13$ ; **7**:  $\delta(^1\text{H}, \text{CDCl}_3) = 4.95$ ]. In all three molecules, the pyrazolyl rings give rise to the expected set of three resonances which appear in the usually observed spectral regions. The corresponding integral values are consistent with the assumption that **6** and **8** are cymantrenyl-substituted tris(1-pyrazolyl)borates, whereas **7** clearly contains only two pyrazolyl rings per molecule. A common feature of carbon atoms attached to a boron centre is an extreme broadening of their <sup>13</sup>C NMR signals, which has to be attributed to the quadrupolar relaxation of the boron nucleus.<sup>11</sup> Consequently, only two rather than three <sup>13</sup>C NMR resonances have been found for the cyclopentadienyl rings of **6**, **7** and **8**. Signals assignable to carbonyl ligands were also not detected in the <sup>13</sup>C NMR spectra of these molecules. The same is true for the Tl(i) salts **2** and **3**,<sup>4</sup> and even in the case of parent cymantrene <sup>13</sup>C(CO) resonances are not readily observed. However, IR spectroscopy (see above) as well as X-ray crystal structure analyses of **6**, **7** and **8** (see below) undoubtedly reveal the presence of three CO ligands on each of the manganese atoms. Only three <sup>13</sup>C NMR signals are visible for the pyrazolylborate groups of **6**, **7** and **8**, suggesting that the pyrazolyl rings are magnetically equivalent in these compounds, which is consistent with the proposed molecular structures (Scheme 1).

### Crystal structure determination

The dinuclear manganese complex **6** crystallizes from  $\text{CDCl}_3$  in the monoclinic space group  $P2_1$  with two crystallographically independent molecules (**6a**, **b**) in the asymmetric unit (Table 1, Fig. 2). Since there are no significant differences between



**Fig. 2** Structure plot of **6a** in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

corresponding bond lengths, angles and torsion angles of the two molecules, only **6a** will be discussed in detail here (Table 2). Contrary to the related Tl<sup>I</sup> salt **2**, which forms polymeric chains with bridging tris(1-pyrazolyl)borate ligands in the solid state, the scorpionate fragment of **6a** binds to the Mn(2) atom in an  $\eta^3$  fashion. One of the three pyrazolyl rings is placed in a position almost orthogonal to the cyclopentadienyl moiety [dihedral angle:  $94.8^\circ$ ]. The carbonyl ligand C(3)O(3) is pointing into the empty space between the two other pyrazolyl groups. The Mn–C as well as the C–O bond lengths of the two  $\text{Mn}(\text{CO})_3$  fragments are identical within experimental error (Table 2). This indicates a similar degree of Mn–CO back bonding in both cases as has already been deduced from the IR spectra of **6**. The manganese centre Mn(2) is surrounded by three nitrogen atoms and three carbon atoms in an almost perfect octahedral geometry [deviations from the ideal ligand–Mn(2)–ligand angles of  $180$  and  $90^\circ$  are smaller than  $5^\circ$ ]. The same is true for the pseudo-octahedral coordination sphere of Mn(1) [angles OC–Mn(1)–CO  $90.1(2)$ ,  $91.2(3)$  and  $91.5(3)^\circ$ ]. Compound **6a** contains a tetra-coordinated boron atom, which is in accord with the results obtained by <sup>11</sup>B NMR spectroscopy. Most likely due to steric repulsion, the angles C(11)–B(1)–N(31) and C(11)–B(1)–N(41) possess values of  $115.2(4)$  and  $114.7(4)^\circ$ , respectively, and are thus significantly larger than to be expected for a tetrahedral geometry.

Compound  $7 \cdot \text{pzH}$  crystallizes from  $\text{CHCl}_3$  in the monoclinic space group  $C2/c$  (Table 1). The molecule has to be addressed as a heteroscorpionate complex in which the Mn(2) centre is coordinated by two pyrazolyl rings and one hydroxy substituent. In the solid state, each molecule of **7** is linked to a second molecule of **7** *via* two bridging pyrazole heterocycles and by four N–H–O hydrogen bonds. Two different structural types of these dimeric aggregates are observed. One, which is depicted in Fig. 3, possesses an inversion centre while the building blocks of the other dimer are not symmetry related. This results in an overall number of three crystallographically independent molecules **7a**·pzH, **7b**·pzH and **7c**·pzH in the asymmetric unit. A schematic sketch of the arrangement of these molecules in the crystal lattice is given in Fig. 4. **7a**·pzH, **7b**·pzH and **7c**·pzH exhibit very similar structural parameters. Any further structure description will therefore be restricted to molecule **7c**·pzH (Table 2, Fig. 3). The molecular structure of **7c**·pzH closely resembles that of **6a** apart from the fact that a hydroxy group is substituted for the pyrazolyl ring N(21)N(22)C(23)C(24)C(25). Again, the octahedral coordination sphere around Mn(2) is largely unperturbed, except of the bond angle O(8)–Mn(2)–C(7) which is reduced to a value of  $168.0(2)$ . There are no significant differences between the structural features of the C(7)O(7) ligand located in a position *trans* to the hydroxy donor [Mn(2)–C(7)  $1.787(5) \text{ \AA}$ , C(7)–O(7)  $1.155(5) \text{ \AA}$ ] and the other two carbonyl groups that coordinate *trans* to a pyrazolyl

**Table 1** Crystallographic data for **6**, **7**·pzH and **8**

Compound	<b>6</b>	<b>7</b> ·pzH	<b>8</b>
Formula	C <sub>20</sub> H <sub>13</sub> BMn <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	C <sub>20</sub> H <sub>15</sub> BMn <sub>2</sub> N <sub>6</sub> O <sub>7</sub>	C <sub>34</sub> H <sub>26</sub> B <sub>2</sub> Mn <sub>2</sub> N <sub>12</sub> O <sub>6</sub> Zn
<i>M</i>	554.05	572.07	895.54
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>C</i> 2/ <i>c</i>	<i>P</i> 1̄
<i>a</i> /Å	9.3830(9)	56.691(4)	8.5125(6)
<i>b</i> /Å	22.907(2)	13.2772(6)	8.6745(6)
<i>c</i> /Å	10.5301(9)	19.5660(10)	12.3157(9)
<i>α</i> /°	90	90	98.556(6)
<i>β</i> /°	105.298(7)	103.776(5)	96.647(6)
<i>γ</i> /°	90	90	92.171(6)
<i>V</i> /Å <sup>3</sup>	2183.1(3)	14303.6(14)	891.84(11)
<i>Z</i>	4	24	1
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.686	1.594	1.667
<i>F</i> (000)	1112	6912	452
<i>μ</i> (Mo-Kα)/cm <sup>-1</sup>	0.1209	0.1113	0.1430
2 $\theta$ <sub>max</sub> /°	51.06	52.48	64.32
Measured reflections	22577	74118	35033
Unique reflections ( <i>R</i> <sub>int</sub> )	7920 (0.0651)	14138 (0.1263)	6175 (0.0597)
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	6496	7786	5233
Parameters refined	631	997	259
<i>R</i> 1 [ <i>I</i> > 2σ( <i>I</i> )]	0.0415	0.0462	0.0498
<i>wR</i> 2 [ <i>I</i> > 2σ( <i>I</i> )]	0.0794	0.0650	0.1551
GOOF on <i>F</i> <sup>2</sup>	0.939	0.817	1.068
Largest diff. peak and hole/e <sup>-</sup> Å <sup>-3</sup>	0.605, -0.519	0.473, -0.359	0.563, -1.965

**Table 2** Selected bond lengths (Å), angles (°) and torsion angles (°) of **6a**, **7c**·pzH and **8**; *x*: in the case of **7c**·pzH

Compound	<b>6a</b>	<b>7c</b> ·pzH	<b>8</b>
Mn(1)–C(1)	1.796(6)	1.772(4)	1.800(2)
Mn(1)–C(2)	1.801(6)	1.804(5)	1.802(2)
Mn(1)–C(3)	1.788(6)	1.796(5)	1.805(2)
Mn(2)–C(5)	1.819(6)	1.816(5)	–
Mn(2)–C(6)	1.790(6)	1.810(5)	–
Mn(2)–C(7)	1.809(5)	1.787(5)	–
C(1)–O(1)	1.165(7)	1.175(4)	1.147(3)
C(2)–O(2)	1.153(7)	1.148(5)	1.148(3)
C(3)–O(3)	1.155(6)	1.154(5)	1.153(3)
C(5)–O(5)	1.140(7)	1.146(5)	–
C(6)–O(6)	1.171(6)	1.161(5)	–
C(7)–O(7)	1.160(6)	1.155(5)	–
B(1)–C(11)	1.602(7)	1.594(6)	1.605(3)
B(1)–N(21)[O(8) <sup>x</sup> ]	1.548(6)	1.496(5)	1.567(3)
B(1)–N(31)	1.559(7)	1.557(6)	1.557(3)
B(1)–N(41)	1.559(7)	1.542(5)	1.567(3)
Mn(2)–N(22)[O(8) <sup>x</sup> ]	2.035(4)	2.090(3)	–
Mn(2)–N(32)	2.046(5)	2.047(3)	–
Mn(2)–N(42)	2.058(4)	2.055(3)	–
Zn(1)–N(22)	–	–	1.995(2)
Zn(1)–N(32)	–	–	2.002(2)
Zn(1)–N(42)	–	–	1.988(2)
C(11)–B(1)–N(21)[O(8) <sup>x</sup> ]	107.0(4)	112.2(4)	107.1(2)
C(11)–B(1)–N(31)	115.2(4)	114.4(3)	115.4(2)
C(11)–B(1)–N(41)	114.7(4)	115.4(3)	114.0(2)
N(31)–B(1)–N(21)[O(8) <sup>x</sup> ]	107.5(4)	103.9(3)	106.6(1)
N(41)–B(1)–N(21)[O(8) <sup>x</sup> ]	106.5(4)	102.0(3)	106.6(2)
N(41)–B(1)–N(31)	105.5(4)	107.7(4)	106.5(2)
C(12)–C(11)–B(1)–N(21)[O(8) <sup>x</sup> ]	77.3(6)	–79.7(5)	89.9(2)
C(12)–C(11)–B(1)–N(31)	–42.1(6)	38.3(6)	–28.7(3)
C(12)–C(11)–B(1)–N(41)	–164.9(4)	164.1(4)	–152.4(2)
C(11)–B(1)–N(21)–N(22)	–177.3(4)	–	175.3(2)
C(11)–B(1)–N(31)–N(32)	175.1(4)	162.6(3)	168.3(2)
C(11)–B(1)–N(41)–N(42)	–171.3(4)	–161.8(4)	–176.3(2)

ring [Mn(2)–C(5) 1.816(5) Å, C(5)–O(5) 1.146(5) Å; Mn(2)–C(6) 1.810(5) Å, C(6)–O(6) 1.161(5) Å]. As already observed for **6a**, the bond angles C(11)–B(1)–N(31) and C(11)–B(1)–N(41) of **7c**·pzH are stretched to values of 114.4(3) and 115.4(3)°, respectively. The C(11)–B(1)–O(8) angle is also quite large [112.2(4)°], which is clearly due to the fact that the small μ-hydroxy bridge has to span the same distance between B(1) and Mn(2) as the much bigger μ-pyrazolyl ligands. The conformation of the heteroscorpionate fragment in **7c**·pzH and the

tris(1-pyrazolyl)borate ligand in **6a** relative to their adjacent cymantrenyl units is very similar [torsion angles: C(12)–C(11)–B(1)–O(8) –79.7(5)° (**7c**·pzH); C(12)–C(11)–B(1)–N(21) 77.3(6)° (**6a**)].

The heterotrinnuclear complex **8** crystallizes from C<sub>6</sub>D<sub>6</sub> in the triclinic space group *P*1̄ (Table 1, Fig. 5). The Zn<sup>II</sup> ion is located at a crystallographic inversion centre and coordinated by the six nitrogen atoms of two cymantrenyl scorpionate ligands [Zn(1)–N(22) 1.995(2) Å, Zn(1)–N(32) 2.002(2) Å, Zn(1)–N(42)

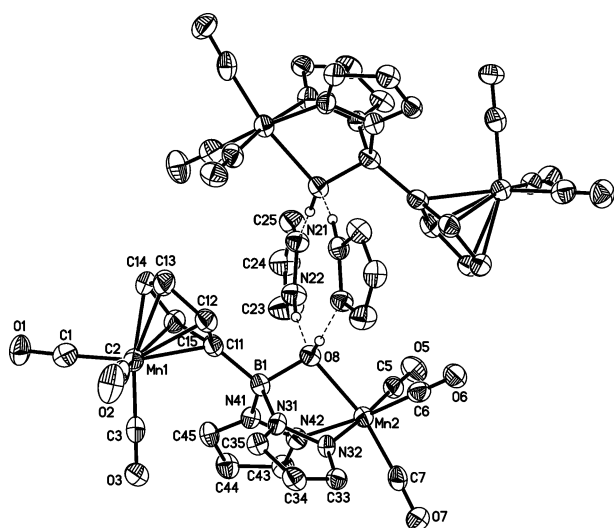


Fig. 3 Structure plot of **7c**·pzH in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

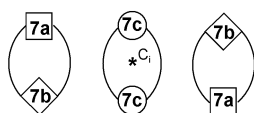


Fig. 4 Crystal packing scheme of **7c**·pzH. **7a**–**c**: Three crystallographically independent molecules in the asymmetric unit;  $C_i$ : inversion centre.

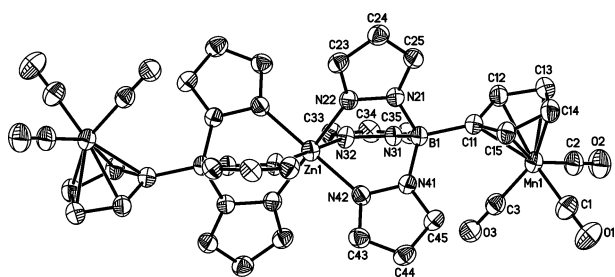


Fig. 5 Structure plot of **8** in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

1.988(2) Å; average value 1.996 Å; Table 2]. There is only negligible deviation from an ideal octahedral coordination sphere around the zinc atom. The conformation of the cymantrenyl scorpionate moiety in **8** is similar to that observed in the case of **6a** [cf. torsion angles: C(12)–C(11)–B(1)–N(21) 89.9(2)° (**8**), 77.3(6)° (**6a**)], and the overall molecular structure of **8** closely resembles that of the related Cu<sup>II</sup> complex Cu[FcB(pz\*)]<sub>2</sub> [Fc = ferrocenyl; pz\* = (cyclohexylmethyl)pyrazolyl].<sup>8</sup>

**Reactivity of 6.** A solution of **6** in CHCl<sub>3</sub>, which was exposed to air over a period of several days, did not show signs of hydrolysis or oxidative decomposition (IR and NMR spectroscopic monitoring). Upon irradiation of a CD<sub>3</sub>CN solution of **6** with UV light ( $\lambda = 254$  nm) in an NMR tube, a pale yellow microcrystalline precipitate formed. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the supernatant did not give any signals except those of the solvent molecules. The precipitate proved to be insoluble in all common organic solvents. Its IR spectrum in KBr revealed absorption bands at  $\nu(\text{CO}) = 2019, 1933$  (very broad) and  $1862 \text{ cm}^{-1}$  [cf. **6**:  $\nu(\text{CO}) = 2030, 2023, 1933$  (two shoulders at ca. 1945 and 1925),  $1908 \text{ cm}^{-1}$ ; in KBr]. The complex (MeC<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>2</sub>CH<sub>3</sub>CN exhibits a signal at  $\nu(\text{CO}) = 1886 \text{ cm}^{-1}$  in the IR spectrum.<sup>12</sup> Thus, the infrared data obtained for the precipitate indicate the presence of Mn(CO)<sub>2</sub>Do fragments in the photolysis product(s) of **6** (Do: CD<sub>3</sub>CN or another  $\sigma$ -donor, most likely pyrazole). When the experiment was repeated in the presence of 1 equiv. of PPh<sub>3</sub>, qualitatively similar results were obtained [absorption bands of the precipitate in

KBr:  $\nu(\text{CO}) = 2019, 1948, 1927, 1913, 1856 \text{ cm}^{-1}$ ; cf. (C<sub>5</sub>H<sub>5</sub>)–Mn(CO)<sub>2</sub>PPh<sub>3</sub>:<sup>13</sup>  $\nu(\text{CO}) = 1931, 1864 \text{ cm}^{-1}$ , in CH<sub>2</sub>Cl<sub>2</sub>].

MALDI mass spectra of **6** gave peaks at  $m/z = 488$  [ $M^+ - 3 \text{ CO} + \text{H}_2\text{O}$ ], 771, 1056, 1338, 1625 and 1910 (6-aza-2-thiothymine matrix). A peak assignable to [ $M^+$ ] ( $m/z = 554$ ) was not observed. The signal intensities decrease continuously with increasing ion masses. It is interesting to note that the differences between the  $m/z$  values of adjacent peaks are 283, 285, 282, 287 and 285, thereby indicating that the heavier ions may be generated by the consecutive addition of always the same molecular fragment. Since complex **6** possesses a strong absorption band in the UV/vis spectrum at the wavelength of the laser beam ( $\lambda = 337$  nm), the experiment was repeated with neat **6** which was not embedded into a polymer matrix. In this spectrum, the peaks at  $m/z = 488, 771$  and 1056 occurred again. Given the fact that (i) **6** contains six carbonyl ligands at two different sites in the molecule, (ii) the molecular mass of a pyrazolyl ring [ $m/z$  (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>) = 67] is similar to that of the cyclopentadienyl group [ $m/z$  (C<sub>5</sub>H<sub>4</sub>) = 64] and (iii) water molecules may become attached to the ions in the course of the measurement, an unambiguous assignment of the peaks was found to be rather difficult. It is, however, obvious that **6** has a pronounced tendency to form larger aggregates, as has already been observed in the case of the Tl<sup>I</sup> complexes **2** and **3**.<sup>4</sup>

To get more insight into the thermal stability of **6**, differential thermal scans (DSC)<sup>14</sup> and thermogravimetric measurements (TG)<sup>15</sup> were performed [heating rate: 10 K min<sup>-1</sup>; inert gas flow: Ar]. The compound loses about 45% of its original weight in the temperature range between 165 °C and 400 °C. Four well-resolved steps are clearly visible which correspond to weight losses of 8.5% ( $T = 165\text{--}190$  °C), 8.5% ( $T = 205\text{--}245$  °C), 12% ( $T = 285\text{--}320$  °C) and 16% ( $T = 340\text{--}400$  °C). Since liberation of two CO ligands from **6** leads to a mass reduction of 10%, the first three steps in the TG curve are likely due to the consecutive loss of all six carbonyl groups. This interpretation is further supported by the fact that no carbonyl bands appear in the infrared spectrum of the material obtained from the crucible after the DTA–TG measurements. It is interesting to note in this context that the endothermic peak in the DTA curve, which is associated with the loss of the first two CO ligands, is significantly smaller than in the case of the other two CO liberation steps.

## Conclusion

The di- and trinuclear complexes Mn(CO)<sub>3</sub>[CymB(pz)<sub>3</sub>] **6**, Mn(CO)<sub>3</sub>[CymB(pz)<sub>2</sub>(OH)] **7** and Zn[CymB(pz)<sub>3</sub>] **8** have been synthesized and structurally characterized by X-ray crystallography (Cym = cymantrenyl, pz = pyrazolyl). **7** represents a rare example of a heteroscorpionate ligand featuring a hydroxy donor functionality. In contrast to the corresponding cymantrene-based Tl<sup>I</sup> scorpionates **2** and **3**, which form polymeric chains and cyclic tetramers with bridging tris(1-pyrazolyl)borate moieties in the solid state, a tridentate coordination mode is preferred by the scorpionate ligands in **6–8**. The compounds are stable towards air and moisture. Irradiation of **6** with UV light in the presence of acetonitrile or PPh<sub>3</sub> leads to substitution reactions within the carbonyl ligand spheres. We have not been able to identify the molecular structure and precise chemical composition of the reaction product(s) but rather obtained microcrystalline precipitates which proved to be insoluble in all common organic solvents. MALDI mass spectrometry indicates the removal of carbonyl ligands from **6** to be accompanied by the formation of larger aggregates.

## Experimental

### General considerations

All reactions and manipulations of air-sensitive compounds were carried out in dry, oxygen-free argon using standard

Schlenk ware unless mentioned otherwise. Solvents were freshly distilled under argon from Na/benzophenone (THF, hexane, C<sub>6</sub>D<sub>6</sub>) or passed through a 4 Å molecular sieves column (CHCl<sub>3</sub>, CDCl<sub>3</sub>) prior to use. IR: Nicolet MAGNA-IR 550. Abbreviations: w = weak, m = medium, s = strong, sh = shoulder. NMR: Bruker AMX 250, AMX 400, Bruker DPX 250. <sup>11</sup>B NMR spectra were reported relative to external BF<sub>3</sub>·Et<sub>2</sub>O. Abbreviations: d = doublet; n.r. = multiplet expected in the <sup>1</sup>H NMR spectrum but not resolved; n.o. = signal not observed; Cym = cymantrenyl; pz = pyrazolyl. MS: Fisons, VG Tofspec. Elemental analyses were performed by the micro-analytical laboratory of the University of Frankfurt.

Tl[CymB(pz)<sub>3</sub>] **2** has been synthesized according to a literature procedure.<sup>4</sup>

## Syntheses

**Synthesis of 6.** A mixture of Tl[CymB(pz)<sub>3</sub>] **2** (0.61 g, 0.99 mmol) and Mn(CO)<sub>5</sub>Br (0.27 g, 0.99 mmol) in dry THF (40 ml) was stirred at room temperature for 24 h, whereupon a colourless precipitate formed (TlBr). The insoluble material was collected on a frit and the yellow filtrate evaporated to dryness *in vacuo*. The resulting yellow residue was triturated with hexane (10 ml) and dried *in vacuo* again. Yield: 0.44 g (80%). X-Ray quality crystals of **2** were obtained from CDCl<sub>3</sub> at ambient temperature.

IR (CDCl<sub>3</sub>, cm<sup>-1</sup>): ν(CO) 2036 (w), 2023 (s), 1942 (s; sh at *ca.* 1935); IR (KBr, cm<sup>-1</sup>): ν(CO) 2030 (m), 2023 (s), 1933 (s; with two sh at *ca.* 1945 and 1925), 1908 (w). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128.3 MHz): δ -2.2 (*w*<sub>1/2</sub> = 90 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 4.87, 5.13 (2 × n.r., 2 × 2H, C<sub>5</sub>H<sub>4</sub>), 6.24 (n.r., 3H, pz-H4), 7.65, 7.89 (2 × n.r., 2 × 3H, pz-H3,5). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz): δ 86.4, 86.7 (C<sub>5</sub>H<sub>4</sub>), n.o. (Cp-CB), 105.9 (pz-C4), 135.0, 144.9 (pz-C3,5), n.o. (CO). Calc. for C<sub>20</sub>H<sub>13</sub>-BMn<sub>2</sub>N<sub>6</sub>O<sub>6</sub> (554.05): C, 43.36; H, 2.37; N, 15.17. Found: C, 43.01; H, 2.22; N, 14.95%.

**Synthesis of 7.** Complex **7** was prepared similarly to **6**, but without exclusion of air and moisture. Tl[CymB(pz)<sub>3</sub>] **2** (0.31 g, 0.50 mmol), Mn(CO)<sub>5</sub>Br (0.14 g, 0.51 mmol), THF (20 ml). Yield: 0.09 g (32%). Yellow X-ray quality crystals of **7**·pzH were obtained from CHCl<sub>3</sub> at ambient temperature.

IR (KBr, cm<sup>-1</sup>): ν(CO) 2014 (s), 1931 (s; sh at *ca.* 1905). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128.3 MHz): δ 0.7 (*w*<sub>1/2</sub> = 100 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 4.95 (n.r., 4H, C<sub>5</sub>H<sub>4</sub>), 6.26 (n.r., 2H, pz-H4), 7.57, 7.85 (2 × d, 2 × 2H, *J*<sub>HH</sub> = 2.2 Hz, pz-H3,5). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz): δ 84.8, 87.0 (C<sub>5</sub>H<sub>4</sub>), n.o. (Cp-CB), 106.7 (pz-C4), 132.3, 142.8 (pz-C3,5), n.o. (CO). Calc. for C<sub>17</sub>H<sub>11</sub>BMn<sub>2</sub>N<sub>4</sub>O<sub>7</sub> (503.99)·C<sub>3</sub>H<sub>4</sub>N<sub>2</sub> (68.08): C, 41.99; H, 2.64; N, 14.69. Found: C, 41.55; H, 2.60; N, 14.43%.

**Synthesis of 8.** A mixture of Tl[CymB(pz)<sub>3</sub>] **2** (0.090 g, 0.145 mmol) and ZnBr<sub>2</sub> (0.016 g, 0.071 mmol) in dry THF (20 ml) was stirred at room temperature for 30 h, whereupon a colourless precipitate formed (TlBr). The insoluble material was collected on a frit and the yellow filtrate evaporated to dryness *in vacuo*. The yellow residue was triturated with hexane (2 × 15 ml) and dried *in vacuo* again. Yield: 0.054 g (85%). X-Ray quality crystals of **8** were grown by slow evaporation of its solution in C<sub>6</sub>D<sub>6</sub> at ambient temperature.

IR (CDCl<sub>3</sub>, cm<sup>-1</sup>): ν(CO): 2021 (s), 1944 (s, sh at *ca.* 1934), 1918 (s). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128.3 MHz): δ -1.6 (*w*<sub>1/2</sub> = 200 Hz).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 5.07, 5.18 (2 × n.r., 2 × 4H, C<sub>5</sub>H<sub>4</sub>), 6.09 (n.r., 6H, pz-H4), 7.14, 7.75 (2 × n.r., 2 × 6H, pz-H3,5). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 86.1, 87.7 (C<sub>5</sub>H<sub>4</sub>), n.o. (Cp-CB), 103.6 (pz-C4), 133.9, 139.7 (pz-C3,5), n.o. (CO). CI-MS: *m/z* 895 [M<sup>+</sup>]. Calc. for C<sub>34</sub>H<sub>26</sub>B<sub>2</sub>Mn<sub>2</sub>N<sub>12</sub>O<sub>6</sub>Zn (895.54): C, 45.60; H, 2.93; N, 18.77. Found: C, 45.28; H, 2.74; N, 18.59%.

**Crystal structure determinations of 6, 7 and 8.** Crystal data and details of the structure determinations are summarised in Table 1. Plots of the molecular structures of **6a**, **7c**·pzH and **8** are shown in Figs. 2, 3 and 5. The measurements were performed at 100 K using a STOE-IPDS-II two-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were made.<sup>16,17</sup> The structures were determined by direct methods using the programs SHELXS and SHELXL.<sup>18,19</sup> Hydrogen atoms bonded to C were placed at calculated positions and were not refined. Hydrogen atoms bonded to O and N were refined isotropically.

CCDC reference numbers 196636 (**6**), 196635 (**7c**·pzH) and 196637 (**8**).

See <http://www.rsc.org/suppdata/dt/b2/b212356h/> for crystallographic data in CIF or other electronic format.

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