

Tl(I) complexes of cymantrene-based tris(1-pyrazolyl)borates: polymers and macrocycles

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Cymantrene-based tris(1-pyrazolyl)borates have been synthesised from the reaction of CymBBr₂ and Cym'BBr₂ with pyrazole (Hpz) in the presence of triethylamine [Cym: cymantrenyl; Cym': (methyl)cymantrenyl]. The Tl(I) salts CymB(pz)₃Tl, **2a**, and Cym'B(pz)₃Tl, **2b**, have been structurally characterised by X-ray crystallography. Similar to the corresponding complex FcB(pz)₃Tl (Fc: ferrocenyl), CymB(pz)₃Tl features a polymeric structure with bridging [B(pz)₃] fragments in the solid state. Cym'B(pz)₃Tl shows a related oligomeric structure. This time a macrocyclic tetramer rather than a linear chain is observed. To provide a ligand of high solubility in non-polar solvents, compound Cym'B(pz^{4-R})₃Tl, [R = CH₂(C₆H₁₁)] **2d**, has been synthesised, which shows a reduced symmetry at the organometallic moiety, together with (cyclohexyl)methyl substituents in the 4-positions of all pyrazolyl rings.

Introduction

Tris(1-pyrazolyl)borates ("scorpionates") **A** were invented by Trofimenko more than 30 years ago and are today well-established as ligands in coordination chemistry (Fig. 1).^{1,2} In

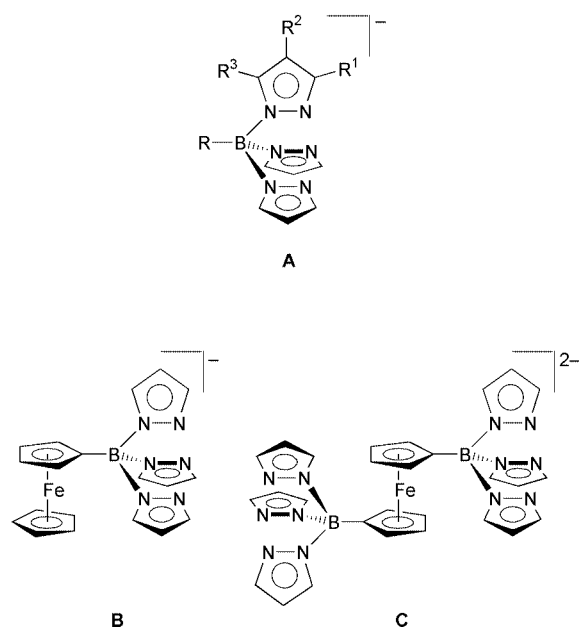


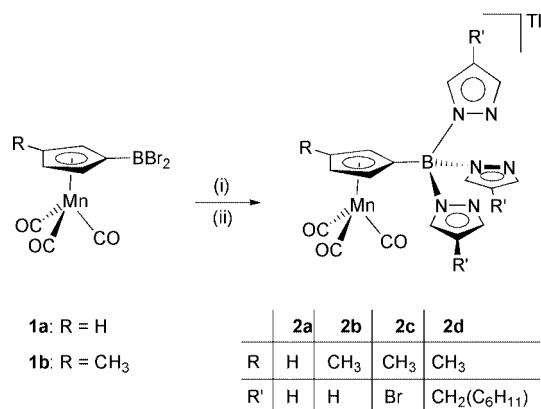
Fig. 1 Tris(1-pyrazolyl) borate **A** (substituents R¹–R³ on two of the three pyrazolyl rings are omitted for clarity) and its ferrocene-based derivatives **B** and **C**.

most complexes, the monoanionic molecules act as tripodal six-electron donors. Derivatives can be generated by varying the group R at boron or the substituents in the 3, 4 and 5 positions of the pyrazolyl rings. This gives rise to an enormous number of possible structural variations, permitting the design of scorpionate ligands with very specific steric and electronic features.

Scorpionates now find applications in a wide range of chemistry, from modelling the active site of metallo-enzymes, through analytical chemistry and organic synthesis to catalysis and materials science.^{2,3} Given this background, it is surprising to see that examples of redox-active⁴ or bifunctional⁵ scorpionate ligands are very rare. In order to fill this gap, we have recently synthesised the ferrocene-based scorpionate ligands **B** and **C** (Fig. 1).⁶ One aim is to use these species as building blocks for the generation of oligonuclear aggregates and metal-containing polymers.^{7–9} Numerous complexes of **B** have been characterised by X-ray crystallography. The Tl(I) salt of **B** provided the first example of a scorpionate complex featuring a polymeric structure in the solid state.⁶ In the meantime, other polymeric thallium scorpionates with bridging tris(1-pyrazolyl)borate units have been reported by Janiak *et al.*¹⁰ An important factor influencing the solid state structure of thallium scorpionates appears to be the degree of steric crowding around the boron centre.^{8,10} Ligand **B** in its tridentate coordination mode suffers from unfavourable steric interactions between the bulky ferrocenyl substituent and the hydrogen atoms in position 5 of the pyrazolyl rings. This steric stress can be substantially relieved if one of the three pyrazolyl rings is rotated by 90° about the B–N axis, which in turn switches the tris(1-pyrazolyl)borate moiety from a tridentate to a bridging coordination mode. However, it has to be taken into account that Tl–N bonds in scorpionate complexes are rather flexible. In a discussion of the respective solid state structures, crystal packing forces must therefore not be neglected.

In this paper, the syntheses and structural characterisations of scorpionate ligands bearing cyclopentadienyl manganese tricarbonyl (cymantrenyl: Cym) substituents at the boron centre are described (Scheme 1).

These species, which are conveniently accessible from borylated cymantrenes **1a** and **1b**,¹¹ will offer convenient access to kinetically stable, manganese containing heterooligometallic complexes. Moreover, the steric characteristics of the [(C₅H₅)Mn(CO)₃] unit are similar to those of the ferrocenyl substituent. It will therefore be revealing to compare the solid state structures of compounds **2** (Scheme 1) and the Tl(I) scorpionate **B** (Fig. 1).



Scheme 1 (i) + 3Hpz^{4-R'}, + 2NEt₃ in toluene; (ii) + TIOEt in toluene.

Results and discussion

Synthesis and spectroscopy

Cymantrene was borylated with boron tribromide in hexane as described previously by Siebert *et al.*¹¹ The resulting dibromoboryl derivative **1a** (Scheme 1) was obtained in moderate yield after prolonged heating. The use of (methyl)cymantrene led to shorter reaction times and improved yield (**1b**), which can be attributed to an increased reactivity towards electrophilic substitution due to the electron-releasing effect of the methyl group. Reaction of **1a** and **1b** with 3 equiv. of pyrazole and 2 equiv. of NEt₃ gave the corresponding free acids; subsequent deprotonation with TIOEt yielded the desired Tl(I) complexes **2a** and **2b**. In a similar way, the derivatives **2c** and **2d** have been synthesised. Metal complexes of **2c** are expected to provide single crystals of particularly good quality, while **2d** is highly soluble, even in hexane.

The ¹¹B NMR spectra of **2a–2d** show resonances in the range between –0.2 and 5.0 ppm, typical of tetracoordinate boron nuclei.¹² In the ¹H and ¹³C NMR spectra of **2a**, two resonances are observed for the cyclopentadienyl ring, whereas the pyrazolyl fragments give rise to three signals. This points towards a molecular structure of high average symmetry in solution. The ¹³C NMR resonance of the carbonyl ligands could not be detected. However, the IR spectrum of **2a** revealed three characteristic bands for the CO stretching modes at ν(CO) = 2019, 1944 and 1922 cm^{–1}. Similar signal patterns are found in the NMR and IR spectra of all other Tl(I) scorpionates under investigation here.

The resonances of the pyrazolyl protons, which are broad and poorly resolved at room temperature, sharpen up considerably, when the sample is heated. This effect has therefore to be attributed to a hindered rotation about the B–C bond, as has already been reported previously for the related ferrocene-based tris(1-pyrazolyl)borates.⁷ The barrier to rotation, however, appears to be smaller in the cymantrenyl scorpionates as compared to their ferrocene analogues.

Crystal structure determination

X-Ray quality crystals of **2a** and **2b** were grown from their toluene solutions at –25 °C (Table 1).

The cymantrene derivative forms polymeric chains in the solid state (Fig. 2), while cyclic tetramers are found in the case of the (methyl)cymantrene complex (Fig. 3).

This provides an impressive example of the way in which subtle changes at the periphery of a molecule can influence the crystal packing. On the other side, the structural motifs exhibited by the individual monomeric fragments of **2a** and **2b** are very similar [Note: the (methyl)cymantrenyl substituent of **2b** is disordered over two positions; occupancy factors: 0.568(5) and

Table 1 Selected bond lengths [Å], angles [°] and torsion angles [°] of **2a** and **2b**. N(6a) indicates that the atom belongs to a neighbouring molecule [*i.e.* Tl(1)–N(6a) is an intermolecular bond]

	2a	2b
B–C(10)	1.602(6)	1.650(13) [1.688(16)] ^b
B–N(1)	1.556(5)	1.515(12)
B–N(3)	1.566(5)	1.587(13)
B–N(5)	1.554(5)	1.538(12)
Tl–N(2)	2.654(3)	2.635(9)
Tl–N(4)	2.722(3)	2.582(9)
Tl–N(6a)	2.720(3)	2.682(7)
Tl ⋯ Tl ^a	5.101(1)	4.793(1)
N(1)–B(1)–N(3)	110.0(3)	110.3(6)
N(1)–B(1)–N(5)	105.4(3)	110.0(7)
N(3)–B(1)–N(5)	107.8(3)	105.0(8)
C(10)–B(1)–N(1)	113.8(3)	123.3(8) [96.9(9)] ^b
C(10)–B(1)–N(3)	106.3(3)	97.6(7) [120.3(9)] ^b
C(10)–B(1)–N(5)	113.4(3)	108.7(7) [113.9(8)] ^b
N(2)–Tl(1)–N(4)	70.4(1)	68.7(3)
N(2)–Tl(1)–N(6a)	87.3(1)	83.9(2)
N(4)–Tl(1)–N(6a)	83.2(1)	81.6(2)
C(10)–B–N(1)–N(2)	174.8(3)	173.6(8) [–174.8(9)] ^b
C(10)–B–N(3)–N(4)	168.0(3)	173.4(8) [–168.2(10)] ^b
C(10)–B–N(5)–N(6)	–76.8(4)	96.7(9) [66.6(11)] ^b
N(3)–B–C(10)–C(11)	–88.3(4)	–95.6(12) [–151.6(15)] ^b

^a 2a: Tl(1) ⋯ Tl(1a); 2b: Tl ⋯ TlB. ^b Values in brackets [] refer to the disordered (MeC₃H₃)Mn(CO)₃ unit.

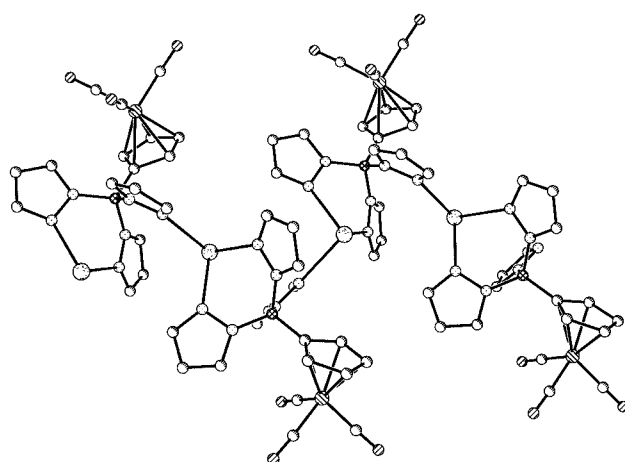


Fig. 2 Polymeric structure of **2a** in the solid state.

0.432(5)]. In both cases, each ligand binds to one Tl(I) ion in an η² fashion, while the third pyrazolyl ring is coordinated to another (symmetry-related) Tl(I) ion (Figs. 4 and 5).

The main difference between the repeat units of **2a** and **2b** lies in the relative orientation of the pyrazolyl ring [N(5) to C(9)] with respect to the rest of the molecule, as evidenced by a torsion angle C(10)–B–N(5)–N(6) of –76.8(4)° in **2a** and 96.7(9)° [66.6(11)°] in **2b**. In both compounds, significant variations between the individual Tl–N bond lengths are observed [2a: Tl–N(2) = 2.654(3) Å, Tl–N(4) = 2.722(3) Å with Δ(Tl–N) = 0.068 Å; 2b: Tl–N(4) = 2.582(9) Å, Tl–N(6a) = 2.682(7) Å with Δ(Tl–N) = 0.100 Å]. The longest Tl–N distance [Tl–N(4)] in **2a** is found for the chelating fragment, while the longest bond in **2b** is established between the Tl(I) ion and the nitrogen atom of the η¹ coordinated pyrazole ring [Tl–N(6a)]. The Tl–N bonds thus appear to be weak, and the corresponding potential energy minima are probably rather shallow. This is in accord with the ¹H and ¹³C NMR signal patterns observed for **2a** and **2b** (see above), which suggest the scorpionate fragment to possess an average C₃ symmetry in solution. This can best be explained by the assumption that any oligomeric structures are restricted to

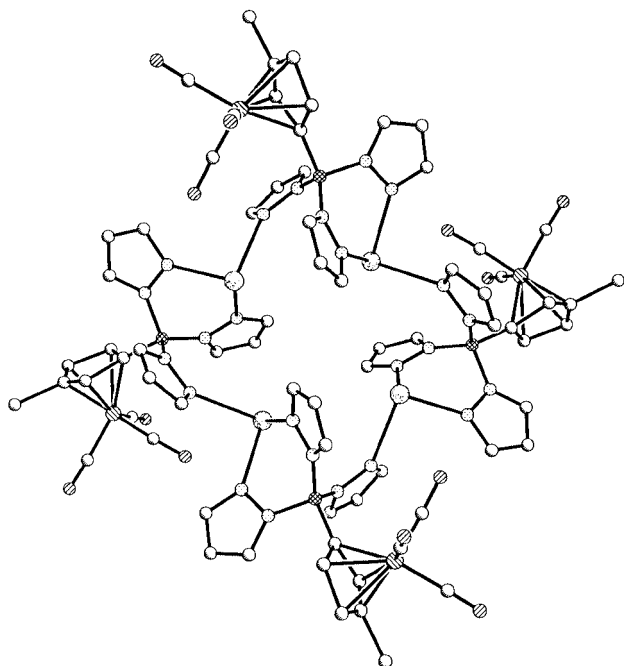


Fig. 3 Cyclic tetramer of **2b** in the solid state.

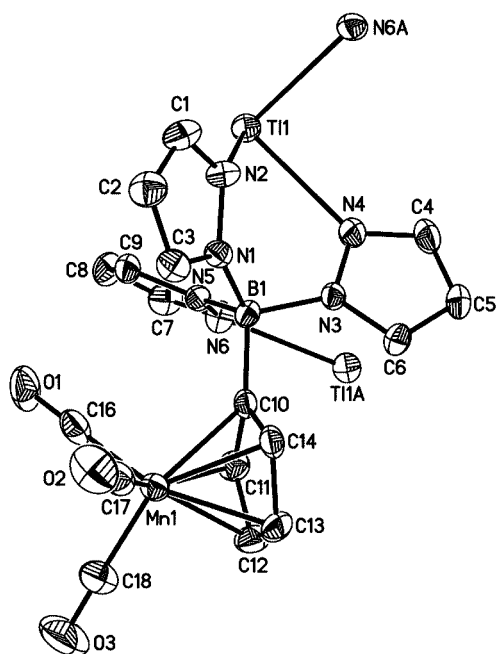


Fig. 4 Monomeric unit of **2a** in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Atom N6A corresponds to the symmetry operation $-x, y - \frac{1}{2}, \frac{1}{2} - z$.

the solid state, while monomeric thallium scorpionates are formed when **2a** and **2b** are dissolved in benzene or DMSO.

Conclusion

Cymantrene-based tris(1-pyrazolyl)borates are readily accessible from the reaction of CymBBR_2 and Cym'BBR_2 with various derivatives of pyrazole in the presence of triethylamine. Rather peculiar structures have been found for their Tl(I) complexes in the solid state. In the case of $[\text{CymB}(\text{pz})_3\text{Tl}]_\infty$ (**2a**, space group: $P2_1/c$), polymeric chains are formed, while the crystal lattice of $[\text{Cym'B}(\text{pz})_3\text{Tl}]_4$ (**2b**, space group: $I4_1/a$), consists of macrocyclic tetramers. In spite of considerable differences in the crystal packing, the individual monomeric units of **2a** and **2b** show very similar structural motifs. In both cases, each ligand binds

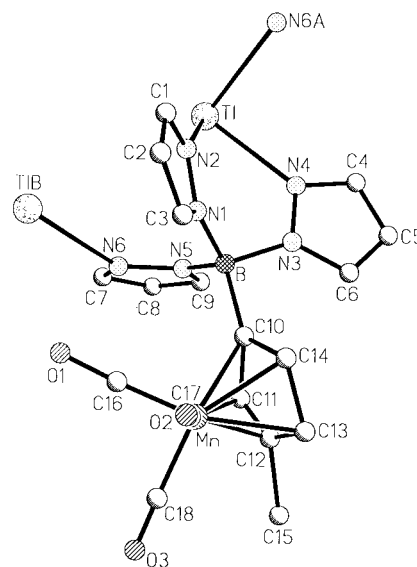


Fig. 5 Monomeric unit of **2b** in the solid state. Atoms N6A and TlB correspond to the symmetry operations $\frac{3}{4} + y, \frac{1}{4} - x, \frac{1}{4} - z$ and $\frac{1}{4} - y, -\frac{3}{4} + x, \frac{1}{4} - z$, respectively.

to one Tl(I) ion in an η^2 fashion, while the third pyrazolyl ring is coordinated to another Tl(I) ion. The results of the X-ray crystal structure determinations of **2a** and **2b** nicely support our previous interpretation of the solid state structures of various ferrocenyl scorpionates.⁸ Bulky substituents attached to the boron centre apparently disfavour an η^3 binding mode of the scorpionate ligand, probably due to steric congestion. As a consequence, oligomeric structures may be established in complexes with weak metal–nitrogen bonds.

Even though the carbonyl ligands of cymantrene are easily replaceable either thermally or photochemically by various Lewis bases,¹³ the scorpionate complexes **2a–2d** are stable at ambient temperature and upon exposure to daylight. No self-polymerisation with Mn–pyrazole adduct formation and CO liberation is observed.

Experimental

General considerations

All reactions and manipulations of air-sensitive compounds were carried out in dry, oxygen-free argon using standard Schlenk apparatus. Toluene and hexane were freshly distilled under N_2 from potassium–benzophenone prior to use. NMR: Bruker ACP 200, Bruker DPX 250, Bruker AMX 400 spectrometers. Abbreviations: s = singlet; d = doublet; t = triplet; vtr = virtual triplet; mult = multiplet; n.r. = multiplet expected in the ^1H NMR spectrum but not resolved; n.o. = signal not observed; Cym = cymantrenyl, Cym' = (methyl)cymantrenyl, Cp = cyclopentadienyl, Cp' = (methyl)cyclopentadienyl, Cyh = cyclohexyl, pz = pyrazolyl. Elemental analyses were performed by the microanalytical laboratory of the University of Frankfurt.

Complexes **1a** and **1b**,¹¹ 4-bromopyrazole¹⁴ and 4-(cyclohexyl)methylpyrazole¹⁵ have been synthesised according to literature procedures.

Syntheses

Synthesis of 2a. A toluene solution (20 ml) of pyrazole (1.00 g, 14.69 mmol) was added dropwise with stirring to a toluene (30 ml) solution of **1a** (1.83 g, 4.90 mmol) at -78°C . Afterwards, neat NEt_3 (0.99 g, 9.78 mmol) was added, the reaction mixture was allowed to warm to room temperature and stirred overnight. Insoluble material was removed using a filter cannula, the filtrate was cooled to 0°C , treated with neat TIOEt

Table 2 Crystallographic data for **2a** and **2b** [(MeC₅H₃)Mn(CO)₃ disordered over two positions]

Compound	2a	2b
Formula	C ₁₇ H ₁₃ BMnN ₆ O ₃ Tl·0.5C ₇ H ₈	C ₁₈ H ₁₅ BMnN ₆ O ₃ Tl·C ₇ H ₈
<i>M</i>	665.52	725.61
Crystal system	Monoclinic	Tetragonal
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>I</i> 4 ₁ / <i>a</i>
<i>a</i> /Å	10.2126(8)	15.2801(10)
<i>b</i> /Å	9.6558(5)	15.2801(10)
<i>c</i> /Å	22.902(2)	45.333(7)
β /°	94.674(5)	90
<i>V</i> /Å ³	2250.9(3)	10584.5(18)
<i>Z</i>	4	16
<i>D</i> /g cm ^{−3}	1.964	1.821
<i>F</i> (000)	1268	5600
μ (Mo-K α)/cm ^{−1}	77.46	65.97
$2\theta_{\max}$ /°	58.06	63.22
Measured reflections	35811	96081
Unique reflections (<i>R</i> _{int})	5330 (0.0397)	8270 (0.0909)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	4637	4367
Parameters refined	307	323
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0322	0.0873
<i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0574	0.1997
GOOF on <i>F</i> ²	1.149	1.825
Largest diff. peak and hole/e Å ^{−3}	0.99, −0.75	4.08, −2.49

(1.22 g, 4.89 mmol) and stirred at room temperature for 12 h, whereupon a colourless precipitate gradually formed. The crude product was collected on a frit, triturated with hexane (2 × 15 ml) and recrystallised from toluene to yield analytically pure **2a**. Yield: 2.22 g (73%). IR (KBr, cm^{−1}): ν (CO) 2019 (vs), 1944 (vs), 1922 (vs). ¹¹B NMR (128.3 MHz, C₆D₆): δ −0.2 (*h*_{1/2} = 70 Hz). ¹H NMR (400 MHz, C₆D₆): δ 4.16, 4.40 (2 × n.r., 2 × 2H, Cp-H), 6.14 (n.r., 3H, pz-H4), 7.28, 7.69 (2 × n.r., 2 × 3H, pz-H3,5). ¹³C NMR (100.5 MHz, C₆D₆): δ 84.4, 89.3 (Cp-C), 105.0 (pz-C4), 135.6, 139.7 (pz-C3,5); n.o.: Cp-C1, CO. MS(ESI): *m/z* 620 (12) [M]⁺, 415 (45) [M − Ti]⁺. Calc. for C₁₇H₁₃BMnN₆O₃Tl [619.46]: C, 32.96; H, 2.12; N, 13.57. Found: C, 32.91; H, 2.47; N, 13.94%.

Synthesis of 2b. **2b** was prepared similarly to **2a** from **1b** (0.98 g, 2.53 mmol), pyrazole (0.52 g, 7.64 mmol), NEt₃ (0.51 g, 5.04 mmol) and TIOEt (0.63 g, 2.53 mmol). Yield: 1.22 g (76%). IR (TiBr, cm^{−1}): ν (CO) 2003 (vs), 1933 (vs), 1917 (vs). ¹¹B NMR (128.3 MHz, [D₆]DMSO): δ 0.2 (*h*_{1/2} = 70 Hz). ¹H NMR (250 MHz, C₆D₆): δ 1.50 (s, 3H, CH₃), 4.09, 4.34 (vtr, mult, 1H, 2H, Cp'-H2,4,5), 6.14 (vtr, 3H, *J*_{HH} = 2.0 Hz, pz-H4), 7.28, 7.76 (2 × d, *J*_{HH} = 1.4, 2.5 Hz, pz-H3,5). Significantly different chemical shifts are observed in [D₆]DMSO, e.g. δ 4.62, 4.86, 5.09 (3 × n.r., 3 × 1H, Cp'-H2,4,5). ¹³C NMR (100.5 MHz, [D₆]DMSO): δ 12.9 (CH₃), 78.9, 81.2, 89.5, 90.3 (Cp'-C2,3,4,5), 102.2 (pz-C4), 132.6, 138.2 (pz-C3,5); n.o.: Cp'-C1, CO. MS(ESI): *m/z* 429 (100) [M − Ti]⁺. Calc. for C₁₈H₁₅BMnN₆O₃Tl [633.47]: C, 34.13; H, 2.39; N, 13.27. Found: C, 34.44; H, 2.65; N, 13.47%.

Synthesis of 2c. **2c** was prepared similarly to **2a** from **1b** (1.30 g, 3.35 mmol), 4-bromopyrazole (1.48 g, 10.06 mmol), NEt₃ (0.68 g, 6.72 mmol) and TIOEt (0.84 g, 3.37 mmol). Yield: 1.93 g (66%). IR (TiBr, cm^{−1}): ν (CO) 2016 (vs), 1933 (vs), 1917 (shoulder). ¹¹B NMR (128.3 MHz, [D₆]DMSO): δ 5.0 (*h*_{1/2} = 250 Hz). ¹H NMR (250 MHz, C₆D₆): δ 1.36 (s, 3H, CH₃), 3.92, 3.98, 4.07 (3 × n.r., 3 × 1H, Cp'-H2,4,5), 7.16, 7.68 (2 × s, 2 × 3H, pz-H3,5). ¹³C NMR (62.9 MHz, [D₆]DMSO): δ 13.5 (CH₃), 82.1, 89.9, 90.5 (Cp'-C2,4,5), 90.1 (pz-C4), 133.0, 139.4 (pz-C3,5); n.o.: Cp'-C1,3, CO. MS(ESI): *m/z* 663 (100) [M − Ti]⁺. Calc. for C₁₈H₁₂BBr₃MnN₆O₃Tl [870.08]: C, 24.85; H, 1.38; N, 9.66. Found: C, 24.84; H, 1.67; N, 9.38%.

Synthesis of 2d. **2d** was prepared similar to **2a** from **1b** (1.47 g, 3.80 mmol), 4-(cyclohexyl)methylpyrazole (1.87 g, 11.40 mmol),

NEt₃ (0.77 g, 7.60 mmol) and TIOEt (0.95 g, 3.80 mmol). Yield: 1.47 g (42%). IR (TiBr, cm^{−1}): ν (CO) 2012 (vs), 1926 (vs), 1914 (shoulder). ¹¹B NMR (128.3 MHz, C₆D₆): δ 1.1 (*h*_{1/2} = 450 Hz). ¹H NMR (250 MHz, C₆D₆): δ 0.83–0.92, 1.04–1.18, 1.31–1.49 (3 × mult, 6H, 9H, 3H, Cyh-H), 1.54 (s, 3H, CH₃), 1.61–1.74 (mult, 15H, Cyh-H), 2.32 (d, 6H, *J*_{HH} = 6.9 Hz, CH₂), 4.17, 4.54 (2 × vtr, 1H, 2H, Cp'-H2,4,5), 7.24, 7.71 (2 × s, 2 × 3H, pz-H3,5). ¹³C NMR (62.9 MHz, C₆D₆): δ 13.3 (CH₃), 26.6 (Cyh-C3,5), 26.9 (Cyh-C4), 32.6 (CH₂), 33.4 (Cyh-C2,6), 39.6 (Cyh-C1), 83.9, 88.5, 89.6 (Cp'-C2,4,5), 118.4 (pz-C4), 134.8, 140.0 (pz-C3,5); n.o.: Cp'-C1,3, CO. MS(ESI): *m/z* 717 (30) [M − Ti]⁺. Calc. for C₃₉H₅₁BMnN₆O₃Tl [921.92]: C, 50.81; H, 5.57; N, 9.11. Found: C, 50.50; H, 5.29; N, 8.86%.

Crystal structure determinations of 2a and 2b

X-Ray quality crystals were grown by storing a toluene solution of **2a** or **2b** at −25 °C for one week. Crystal data and details of the structure determinations are summarised in Table 2; plots of the molecular structures of **2a** and **2b** are shown in Figs. 2 and 3. Compound **2a** crystallises together with 0.5 equiv. of toluene, compound **2b** crystallises together with one equiv. of toluene. The measurements were performed at 173 K (**2a**) and 144 K (**2b**) using a SIEMENS SMART CCD diffractometer with graphite-monochromated Mo-K α radiation (λ = 0.71073 Å). A pale yellow plate with dimensions 0.12 × 0.18 × 0.38 mm was used for **2a**, an orange block with dimensions 0.24 × 0.60 × 0.68 mm was used for **2b**. Empirical absorption corrections were made. The structures were determined by direct methods using the program SHELXS¹⁶ (**2a**) and the program SIR-92¹⁷ (**2b**). Hydrogen atoms were placed at calculated positions and were not refined. All atoms of the [(MeC₅H₃)Mn(CO)₃] fragment of **2b** were refined with a split atom model, since this entire group was found to be disordered over two possible positions; the occupancy factor was 0.568(5) vs. 0.432(5). Distance constraints were used for the disordered [(MeC₅H₃)Mn(CO)₃] fragment and the toluene solvate groups.

CCDC reference numbers 165815 and 165816.

See <http://www.rsc.org/suppdata/dt/b1/b105692c/> for crystallographic data in CIF or other electronic format.

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