

# Applications of manganocene in the synthesis of Mn(II) amide and imide cages

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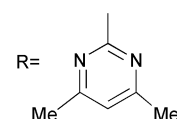
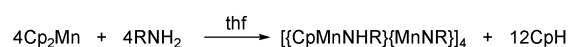
The reactions of manganocene, Cp<sub>2</sub>Mn (Cp = C<sub>5</sub>H<sub>5</sub>), with 2-aminopyrimidines give similar, octameric amido/imido cage complexes of general formulae [ $\{\text{CpMnNHR}\}\{\text{MnNR}\}_4$ ] [R = 4,6-Me<sub>2</sub>pm (**1a**), 4-MeO-6-Mepm (**1b**), 4,6-(MeO)<sub>2</sub>-pm (**1c**); pm = pyrimidinyl]. The structures of these complexes can be visualised as being composed of central Mn<sub>4</sub>N<sub>4</sub> imido cubane units that are coordinated at their peripheries by four [CpMnNHpm] monomers. In contrast, less acidic 2-aminopyridine (2-NH<sub>2</sub>py) and 8-aminoquinoline (8-NH<sub>2</sub>quin) are only singly deprotonated under similar conditions, giving the unusual hexanuclear amido complex [Cp<sub>2</sub>Mn<sub>3</sub>(NHpy)<sub>4</sub>]<sub>2</sub> (**2**) and the dimer [CpMn-(μ-8-HNquin)]<sub>2</sub> (**3**). *N,N'*-Dibenzylethylenediamine [(BnNHCH<sub>2</sub>)<sub>2</sub>] only forms the simple adduct [(η<sup>1</sup>-Cp)(η<sup>5</sup>-Cp)-Mn{(BnNHCH<sub>2</sub>)<sub>2</sub>}] (**4**) (Bn = CH<sub>2</sub>Ph) with Cp<sub>2</sub>Mn, in which no deprotonation of the organic acid has occurred. The X-ray structures of the new complexes **1b–c**, **3** and **4** are reported (**1a** and **2** having been communicated previously).

## Introduction

The potential applications of manganese carboxylate cluster compounds as precursors to molecule-based magnetic materials, or as molecular magnets in their own right, has attracted considerable interest in the past two decades.<sup>1</sup> Despite this, the chemistry and magnetic properties of related nitrogen-based manganese cluster compounds have been less explored, and so far only a handful of imido manganese cluster compounds (containing RN<sup>2-</sup> ligands) have been structurally characterised.<sup>2</sup> The majority of these species contain Mn in the v to vii oxidation states,<sup>2a</sup> the cationic species [Mn<sub>6</sub>(μ<sub>3</sub>-NPh)<sub>4</sub>(thf)<sub>4</sub>]<sup>4+</sup><sup>2b</sup> being the only structurally characterised Mn(II) imido complex. This situation contrasts with that for the amido Mn complexes (containing R<sub>2</sub>N<sup>-</sup> ligands) for which the solid-state structures of a relatively large number of Mn(II) complexes have been reported.<sup>3</sup> Our interest in this area has arisen from a general interest in the applications of main group and transition metal metallocenes as precursors in the synthesis of amido and imido compounds.<sup>4</sup> Although the lability and basicity of the C–metal bonds in stannocene (Cp<sub>2</sub>Sn) and related p-block metallocenes has long been appreciated,<sup>5</sup> the use of transition metal metallocenes as soluble sources of low-oxidation state metals has been investigated far less extensively. There is, nonetheless, ample evidence for the emergence of polarity in the C–metal bonds of many transition metal metallocenes (particularly those of the transition metal series). Thus, substitution of the Cp ligands by a range of organic nucleophiles is a characteristic of, for example, Cp<sub>2</sub>Ni, Cp<sub>2</sub>Mn<sup>6</sup> and [CpM·PR<sub>3</sub>] (M = Cu, Ag).<sup>7</sup> In addition, the deprotonation of weaker, oxygen- and nitrogen-based organic acids using Cp<sub>2</sub>Mn has also been reported.<sup>3a,8</sup> Although this application of Cp<sub>2</sub>Mn as a base has only been explored in a few limited studies, this reagent provides a more convenient precursor for metallo-organic Mn(II) derivatives than the use of highly air-sensitive compounds such as [Mn{N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub>.<sup>9</sup>

In a recent communication we showed for the first time that Cp<sub>2</sub>Mn is capable of doubly-deprotonating the NH<sub>2</sub> group of the moderately acidic 2-amino-4,6-dimethylpyrimidine frame-

work (Scheme 1, Fig. 1a), providing a potentially widely applicable route to high-nuclearity Mn(II) imido cage compounds.<sup>10</sup> This reactivity pattern contrasts with that of the less acidic 2-aminopyridine (2-NH<sub>2</sub>py) with Cp<sub>2</sub>Mn, which gives the hexanuclear complex [Cp<sub>2</sub>Mn<sub>3</sub>(NHpy)<sub>4</sub>]<sub>2</sub> (**2**) in which the NH<sub>2</sub>



**1a**  
Scheme 1

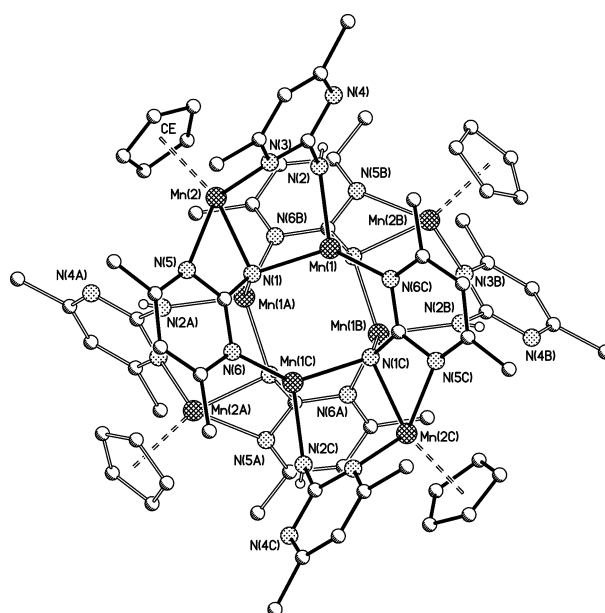
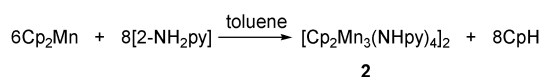


Fig. 1 Molecular structure of **1a**.

group of the amine has only been singly deprotonated (Scheme 2, Fig. 2).<sup>11</sup> We report here a full account of this work, including new studies of the reactions of a more extensive range of primary and bifunctional amines with Cp<sub>2</sub>Mn. In addition to the synthesis and structure of [ $\{\text{CpMnNH}(4,6\text{-Me}_2\text{pm})\}\{\text{MnN}(4,6\text{-Me}_2\text{pm})\}_4$ ] (1a)<sup>10</sup> (pm = pyrimidinyl) and [Cp<sub>2</sub>Mn<sub>3</sub>(NHpy)<sub>4</sub>]<sub>2</sub> (2),<sup>11</sup> which we have described previously, the syntheses and structures of the new Mn<sub>6</sub> cage complexes [ $\{\text{CpMnNH}(4\text{-MeO-6-Mepm})\}\{\text{MnN}(4\text{-MeO-6-Mepm})\}_4$ ] (1b) and [ $\{\text{CpMnNH}(4,6\text{-(MeO)}_2\text{pm})\}\{\text{MnN}(4,6\text{-(MeO)}_2\text{pm})\}_4$ ] (1c) (having similar structures to 1a), the dimer [CpMn(μ-8-Nquin)]<sub>2</sub> (3) (8-NH<sub>2</sub>quin = 8-aminoquinoline) and the adduct [(η<sup>1</sup>-Cp)(η<sup>5</sup>-Cp)Mn(BnNHCH<sub>2</sub>)<sub>2</sub>] (4) (Bn = benzyl) are reported. The characterisation of 1–4 allows an overall assessment of the scope (and limitations) of the use of Cp<sub>2</sub>Mn in the preparation of Mn(II) imido and amido complexes.



Scheme 2

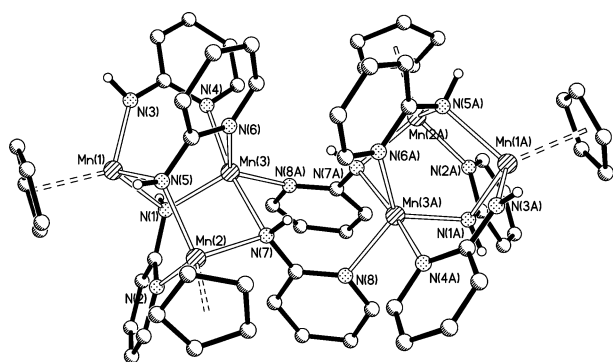
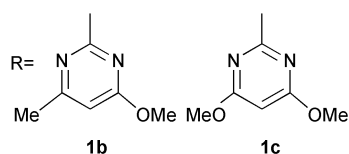
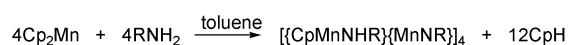


Fig. 2 Structure of the hexanuclear Mn<sub>6</sub> complex 2.

## Results and discussion

### Synthetic and structural studies

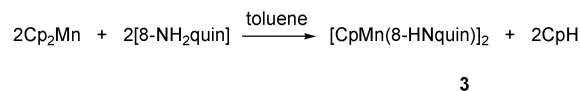
The reactions of 2-NH<sub>2</sub>(4-MeO-6-Mepm) and 2-NH<sub>2</sub>(4,6-(MeO)<sub>2</sub>pm) with Cp<sub>2</sub>Mn<sup>12</sup> (1 : 1 molar equivalents) at -78 °C in toluene, followed by storage at room temperature for 1–2 days give the new complexes [ $\{\text{CpMnNH}(4\text{-MeO-6-Mepm})\}\{\text{MnN}(4\text{-MeO-6-Mepm})\}_4$ ·6toluene (1b·6toluene) and [ $\{\text{CpMnNH}(4,6\text{-(MeO)}_2\text{pm})\}\{\text{MnN}(4,6\text{-(MeO)}_2\text{pm})\}_4$ ·6toluene (1c·6toluene). The first-batch yields of the crystalline complexes were 44% for 1b and 12% for 1c (Scheme 3, see Experimental section). Although it was shown by later structural investigations of 1b and 1c that there are six toluene molecules in the lattices of both compounds for each molecular unit, their isolation under vacuum (*ca.* 15 min, 10<sup>-1</sup> atm) resulted in loss of toluene in both cases. Elemental analysis suggests that there are *ca.* five toluene molecules remaining in isolated crystalline samples of 1b and *ca.* one toluene molecule in 1c. Relatively little information concerning the structures of the complexes could be gained from <sup>1</sup>H NMR spectroscopy, owing to the paramagnetic nature of the complexes and to their low solubility even in polar organic solvents such as DMSO. A further complication is the likely deaggregation of the complexes in



Scheme 3

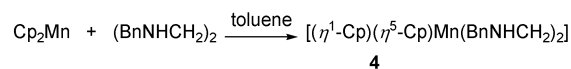
such a strong donor solvent, making it unlikely that the solution structures of the complexes are representative of those in the solid state. Significantly, however, the IR spectra of 1b and 1c reveal the presence of both N–H and Cp functionalities and therefore indicate that the deprotonation of the NH<sub>2</sub> group of the aminopyrimidines is incomplete, *i.e.*, that amido groups (RNH) are present in their structures. Similar spectroscopic features were reported for the related complex [ $\{\text{CpMnNH}(4,6\text{-Me}_2\text{pm})\}\{\text{MnN}(4,6\text{-Me}_2\text{pm})\}_4$ ] (1a).<sup>10</sup> The structural characterisation of 1b and 1c (discussed in detail later) showed that both RNH<sup>-</sup> (singly-deprotonated) and RN<sup>2-</sup> (doubly-deprotonated) groups are present in the solid state and that the structural arrangements of 1b and 1c are similar to that of 1a.

The reactivity pattern observed in the reactions of Cp<sub>2</sub>Mn with 2-aminopyrimidines contrasts with that found for 2-aminopyridine (2-NH<sub>2</sub>py), the isolated product from toluene solvent for the latter being the hexanuclear cage [Cp<sub>2</sub>Mn<sub>3</sub>(NHpy)<sub>4</sub>]<sub>2</sub> (2) in which only single deprotonation of the NH<sub>2</sub> group has occurred (Fig. 2). Full details of the synthesis and characterisation of 2 have been reported previously, so will not be discussed further here.<sup>11</sup> A similar result is observed in the reaction of Cp<sub>2</sub>Mn with 8-aminoquinoline (8-NH<sub>2</sub>quin), the product of the 1 : 1 stoichiometric reaction in toluene being the dimer [CpMn(μ-8-HNquin)]<sub>2</sub> (3) (Scheme 4) (isolated in 42% yield). Despite repeated attempts, the extreme air sensitivity and apparent thermal instability of solid 3 has made satisfactory elemental analysis on the complex impossible to obtain. Compound 3 was characterised by <sup>1</sup>H NMR and IR spectroscopy and by an X-ray structure determination. Two weak N–H stretching bands are observed in the infrared spectrum of 3 (3394, 3380 cm<sup>-1</sup>). Although the C–H stretching vibration for the Cp group in 3 could not be identified unambiguously in the infrared spectrum, the presence of Cp ligands in the complex is apparent in the <sup>1</sup>H NMR spectrum, with a broad resonance for this group being observed at 5.85 ppm. The <sup>1</sup>H NMR spectrum also suggests that the toluene molecules found in the crystal lattice of 3 (by X-ray structure determination) are removed by isolating the complex under vacuum (*ca.* 15 min, 10<sup>-1</sup> atm).



Scheme 4

The different outcomes of the reactions of the 2-aminopyrimidines, 2-aminopyridine and 8-aminoquinoline with Cp<sub>2</sub>Mn can be rationalised simply from the expected relative acidities of the organic acids, the presence of two electronegative N centres within the pyrimidinyl ring providing greater stabilisation of the negative charge. It is perhaps unsurprising then that reaction of Cp<sub>2</sub>Mn with the bifunctional secondary amine (BnNHCH<sub>2</sub>)<sub>2</sub> (Bn = benzyl) does not lead to any deprotonation of the two N–H groups. Instead, the simple adduct [(η<sup>1</sup>-Cp)(η<sup>5</sup>-Cp)Mn(BnNHCH<sub>2</sub>)<sub>2</sub>] (4) is isolated (Scheme 5). The infrared spectrum of 4 shows two N–H stretching bands at 3211 and 3192 cm<sup>-1</sup> as well as a doublet Cp–H stretching vibration at 3055 cm<sup>-1</sup>. Despite the paramagnetic nature of this complex (the Mn(II) centre having a formal electron count of 17 e), the resonances observed in the <sup>1</sup>H NMR spectrum are relatively sharp. Resonances due to the benzylic (PhCH<sub>2</sub>-) (δ 2.55) and –CH<sub>2</sub>–CH<sub>2</sub>– methylene groups (δ 2.04 and 1.73, respectively) are easily identified in DMSO, although the line-widths of these resonances result in loss of any coupling information.



Scheme 5

**Table 1** Crystal data for  $\{[\text{CpMnNH}(4\text{-MeO-6-Mepm})\{\text{MnN}(4\text{-MeO-6-Me-pm})\}_4 \cdot 6\text{toluene} (\mathbf{1b}\cdot 6\text{toluene})$ ,  $\{[\text{CpMnNH}(4,6\text{-(MeO)}_2\text{pm})\{\text{MnN}(4,6\text{-(MeO)}_2\text{pm})\}_4 \cdot 6\text{toluene} (\mathbf{1c}\cdot 6\text{toluene})$ ,  $[\text{CpMn}(\mu\text{-8-HNquin})]_2 \cdot 2\text{toluene} (\mathbf{3}\cdot 2\text{toluene})$  and  $[(\eta^1\text{-Cp})(\eta^5\text{-Cp})\text{Mn}(\text{BnNHCH}_2)_2] (\mathbf{4})$

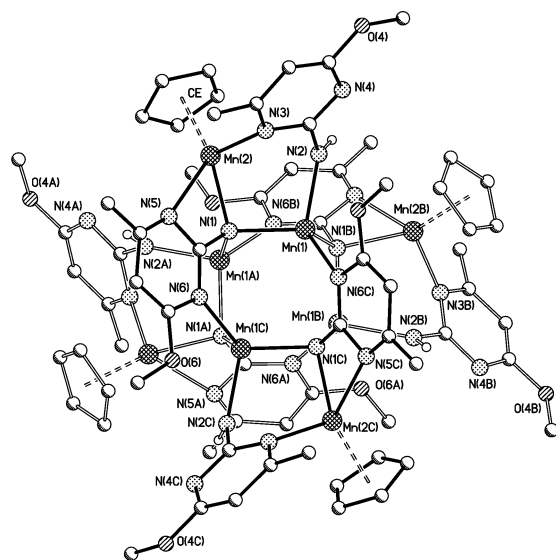
Compound <sup>a</sup>	<b>1b</b> ·6toluene	<b>1c</b> ·6toluene	<b>3</b> ·2toluene	<b>4</b>
Empirical formula	C <sub>110</sub> H <sub>128</sub> Mn <sub>8</sub> N <sub>24</sub> O <sub>8</sub>	C <sub>110</sub> H <sub>128</sub> Mn <sub>8</sub> N <sub>24</sub> O <sub>16</sub>	C <sub>43</sub> H <sub>40</sub> Mn <sub>2</sub> N <sub>4</sub>	C <sub>26</sub> H <sub>30</sub> MnN <sub>2</sub>
Formula weight	2353.88	2481.88	710.66	425.46
Crystal system	Tetragonal	Tetragonal	Monoclinic	Monoclinic
Space group	<i>I</i> <sub>4</sub> / <i>a</i>	<i>I</i> <sub>4</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	23.6528(8)	24.3007(12)	14.237 (3)	8.2142(4)
<i>b</i> /Å	—	—	10.815 (3)	14.7038(5)
<i>c</i> /Å	20.7070(6)	20.5467(11)	11.813 (2)	18.9720(11)
<i>a</i> /°	—	—	—	—
<i>β</i> /°	—	—	93.639 (14)	100.466(2)
<i>γ</i> /°	—	—	—	—
Cell volume/Å <sup>3</sup>	11584.6(6)	12133.3(11)	1815.2 (6)	2253.3(2)
<i>Z</i>	4	4	2	4
<i>ρ</i> /Mg m <sup>-3</sup>	1.347	1.359	1.300	1.254
Independent reflections ( <i>R</i> <sub>int</sub> )	5674 (0.063)	3934 (0.105)	2522 (0.022)	3970 (0.056)
<i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.057, <i>wR</i> <sub>2</sub> = 0.149	<i>R</i> <sub>1</sub> = 0.059, <i>wR</i> <sub>2</sub> = 0.140	<i>R</i> <sub>1</sub> = 0.040, <i>wR</i> <sub>2</sub> = 0.092	<i>R</i> <sub>1</sub> = 0.046, <i>wR</i> <sub>2</sub> = 0.101
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.099, <i>wR</i> <sub>2</sub> = 0.199	<i>R</i> <sub>1</sub> = 0.107, <i>wR</i> <sub>2</sub> = 0.201	<i>R</i> <sub>1</sub> = 0.0552, <i>wR</i> <sub>2</sub> = 0.0999	<i>R</i> <sub>1</sub> = 0.081, <i>wR</i> <sub>2</sub> = 0.156

<sup>a</sup> Data in common;  $\lambda = 0.71069$  Å; for **1b**, **1c** and **4** *T* = 180(2) K; for **3** *T* = 223(2) K.

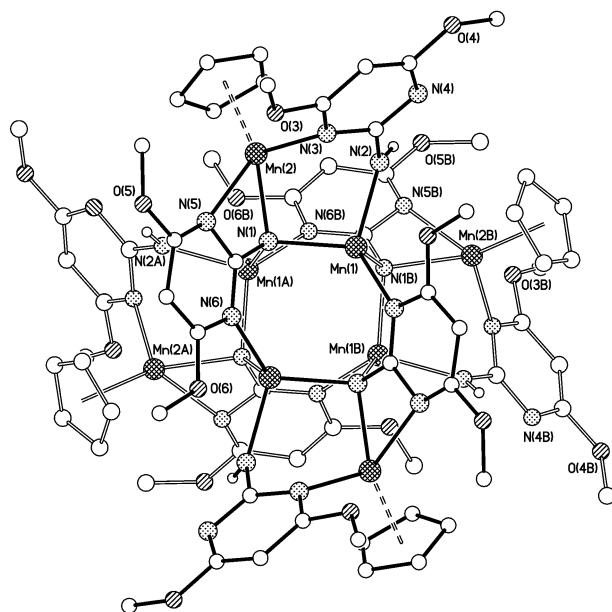
### Crystallographic studies

Low-temperature crystallographic studies were undertaken on complexes **1b**, **1c**, **3** and **4**. The structures of **1a** (Fig. 1) and **2** (Fig. 2) have been reported by us previously and it will not be appropriate to give a full account here. Details of the crystal data, data collections and refinements of the new complexes **1b**, **1c**, **3** and **4** are provided in Table 1. Key bond lengths and angles for the closely related Mn<sub>8</sub> cage compounds **1a**, **1b** and **1c** are listed in Table 2, for comparison. Selected bond lengths and angles for **3** and **4** are given in Tables 3 and 4, respectively.

The low-temperature X-ray studies of complexes **1b** (Fig. 3) and **1c** (Fig. 4) show that they both have similar octameric, Mn<sub>8</sub> cage structures in the solid state of formulae  $[(\eta\text{-Cp})\text{Mn}(2\text{-NHR})\cdot\text{Mn}(2\text{-NR})]_4$  [*R* = 4-MeO-6-Mepm (**1b**), 4,6-(MeO)<sub>2</sub>pm (**1c**)] possessing exact *-4* symmetry. This arrangement is the same as that observed previously in the Mn<sub>8</sub> cage of **1a** (Fig. 1). However, unlike **1a** where there are five thf molecules in the lattice per molecule, in **1b** and **1c** six toluene molecules reside in the lattice for each molecule of the complexes. The structures of **1a–c** are best regarded as co-complexes of four Mn(II) imido [Mn{2-NR}] and four organo/amido [(η-Cp)Mn{2-NHR}] monomer units. The common core arrangements and numbering schemes for **1a**, **1b** and **1c** are shown in Fig. 5a and 5b, respectively. The central cores of the molecules are formed from



**Fig. 3** Molecular structure of  $[(\eta\text{-Cp})\text{MnNH}(4\text{-MeO-6-Mepm})\{\text{MnN}(4\text{-MeO-6-Me-pm})\}_4 (\mathbf{1b})$ . H-atoms, except those attached to N, and lattice toluene molecules have been omitted for clarity.



**Fig. 4** Molecular structure of  $[(\eta\text{-Cp})\text{MnNH}(4,6\text{-(MeO)}_2\text{pm})\{\text{MnN}(4,6\text{-(MeO)}_2\text{pm})\}_4 (\mathbf{1c})$ . H-atoms, except those attached to N, and lattice toluene molecules have been omitted for clarity.

the association of four [Mn{2-NR}] units, giving similar distorted tetrahedral arrangements of the Mn centres [in **1a** Mn(1) ... Mn(1A,1B) 3.1594(8), Mn(1) ... Mn(1C) 3.543(1) Å; in **1b** Mn(1) ... Mn(1A,1B) 3.219(1), Mn(1) ... Mn(1C) 3.689(1) Å; in **1c** Mn(1) ... Mn(1A,1B) 3.223(1), Mn(1) ... Mn(1C) 3.724(1) Å]. This central fragment can be visualised as a highly distorted Mn<sub>4</sub>N<sub>4</sub> cubane unit, in which four opposite edges [defined by Mn(1) ... N(1C), Mn(1A) ... N(1B), Mn(1B) ... N(1A) and Mn(1C) ... N(1)] have been broken. The anionic imido-N centres of the 2-NR ligands in these units bridge the symmetry-related Mn atoms of the core [in **1a** Mn(1)–N(1) 2.085(3), Mn(1)–N(1B) 2.110(3) Å; in **1b** Mn(1)–N(1) 2.075(3), Mn(1)–N(1B) 2.097(3) Å; in **1c** Mn(1)–N(1) 2.088(5), Mn(1)–N(1B) 2.101(5) Å], with one of the neutral N centres of each pm ring spanning the four broken edges of the Mn<sub>4</sub>N<sub>4</sub> core *via* longer donor interactions [in **1a** Mn(1)–N(6C) 2.160(3) Å; in **1b** Mn(1)–N(6C) 2.150(3) Å; in **1c** Mn(1)–N(6C) 2.144(5) Å]. As a result, the Mn centres of the core attain a highly distorted tetrahedral geometry. The [(η-Cp)Mn{2-NHR}] units in **1a–c** are located at the periphery of the cages [in **1a** Mn(1) ... Mn(2) 3.2335(7) Å; in **1b** Mn(1) ... Mn(2) 3.2609(8) Å; in **1c** Mn(1) ... Mn(2) 3.300(1) Å]. The

**Table 2** Selected bond lengths (Å) and bond angles (°) for [ $\{\text{CpMnNH}(4\text{-MeO-6-Mepm})\}\{\text{MnN}(4\text{-MeO-6-Mepm})\}_4\cdot 6\text{toluene}$ ] (**1b**·6toluene), and [ $\{\text{CpMnNH}(4,6\text{-(MeO)}_2\text{pm})\}\{\text{MnN}(4,6\text{-(MeO)}_2\text{pm})\}_4\cdot 6\text{toluene}$ ] (**1c**·6toluene) compared with those reported for **1a**·5thf

	<b>1a</b>	<b>1b</b>	<b>1c</b>
Mn(1)–N(1)	2.085(3)	2.075(3)	2.088(5)
Mn(1)–N(1B)	2.110(3)	2.097(3)	2.101(5)
Mn(1)–N(2)	2.117(3)	2.095(3)	2.095(5)
Mn(1)–N(6C)	2.160(3)	2.150(3)	2.144(5)
Mn(2)–N(1)	2.208(3)	2.183(3)	2.154(5)
Mn(2)–N(3)	2.200(3)	2.195(4)	2.190(5)
Mn(2)–N(5)	2.262(3)	2.300(3)	2.347(5)
Mn(2)···Cp <sub>centroid</sub>	2.23	2.19	2.20
Mn(1)···Mn(1A)	3.1594(8)	3.2187(9)	3.223(1)
Mn(1)···Mn(2)	3.2335(7)	3.2609(8)	3.300(1)
Mn(1)···Mn(1C)	3.543(1)	3.689(1)	3.724(1)
N(1)–Mn(1)–N(1B)	106.1(1)	108.9(1)	111.4(2)
N(1)–Mn(1)–N(2)	100.3(1)	100.1(1)	101.4(2)
N(1)–Mn(1)–N(6C)	122.7(1)	118.3(1)	116.8(2)
Mn(1)–N(1)–Mn(1A)	97.7(1)	101.0(1)	100.6(2)
N(2)–Mn(1)–N(1B)	102.3(1)	103.0(1)	100.5(2)
N(1B)–Mn(1)–N(6C)	109.8(1)	106.3(1)	105.2(2)
N(1)–Mn(2)–N(3)	104.7(1)	106.2(1)	103.9(2)
N(1)–Mn(2)–N(5)	61.9(1)	61.5(1)	61.2(2)
N(3)–Mn(2)–N(5)	102.6(1)	103.1(1)	102.9(2)

The atom labels refer to the following symmetry operations: A  $-0.25 - y, -0.25 + x, -0.25 - z$ ; B  $0.25 + y, -0.25 - x, -0.25 - z$ ; C  $-x, -y - 0.5, z$ .

**Table 3** Selected bond lengths (Å) and bond angles (°) for [ $\text{CpMn}(\mu\text{-8-HNquin})_2$ ] (**3**)

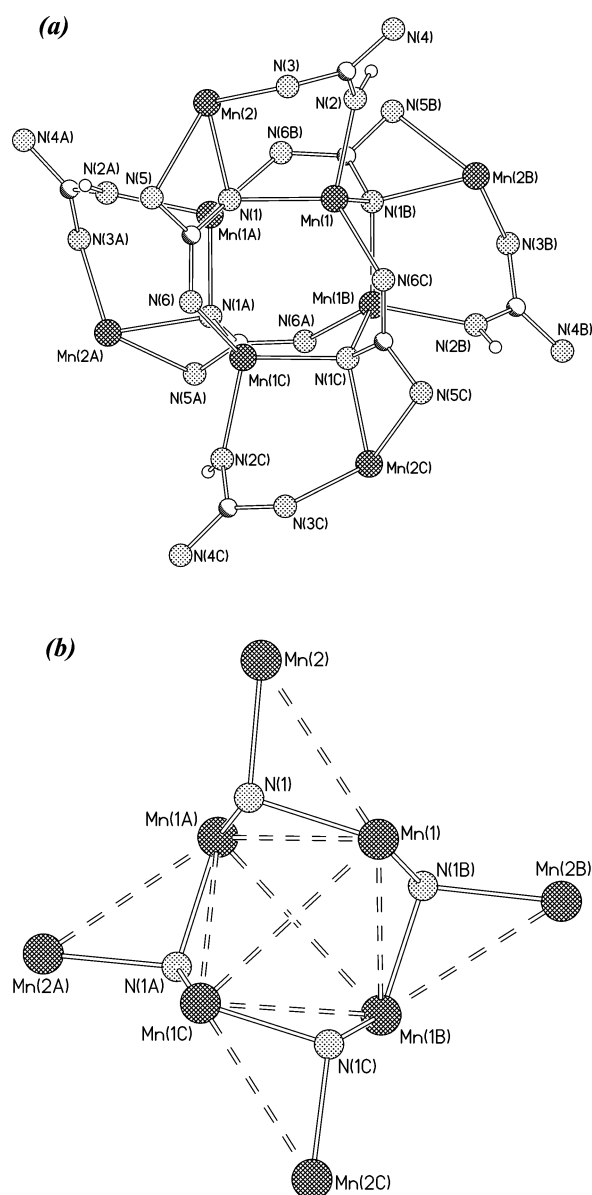
Mn(1)–N(2)	2.143(3)	Mn(1)···Cp <sub>centroid</sub>	2.18
Mn(1)–N(2A)	2.197(3)	Mn(1)···Mn(1A)	2.944(1)
Mn(1)–N(1)	2.219(2)		
N(2)–Mn(1)–N(2A)	94.6(1)	N(2A)–Mn(1)–N(1)	96.60(9)
N(2)–Mn(1)–N(1)	76.28(9)	Mn(1)–N(2)–Mn(1A)	85.4(1)

The atom labels refer to the following symmetry operations: A  $1 - x, 2 - y, -z$ .

MnCp fragments of these monomer units are chelated by the imido N centre [in **1a** Mn(2)–N(1) 2.208(3) Å; in **1b** Mn(2)–N(1) 2.183(3) Å; in **1c** Mn(2)–N(1) 2.154(5) Å] and the second N centre [in **1a** Mn(2)–N(5) 2.262(3) Å; in **1b** Mn(2)–N(5) 2.300(3) Å; in **1c** Mn(2)–N(5) 2.347(5) Å] of each of the 2-NR ligands of the central Mn<sub>4</sub>N<sub>4</sub> core. The 2-NHR groups of the  $[(\eta\text{-Cp})\text{Mn}\{2\text{-NHR}\}]$  units adopt a similar chelating bonding mode to that found for the 2-NR groups within the Mn<sub>4</sub>N<sub>4</sub> cores of **1a–c**, with the anionic N(H) centres and one of the pm ring N centres being involved in bridging the core Mn and Mn(Cp) atoms [in **1a** Mn(1)–N(2) 2.117(3), Mn(2)–N(3) 2.200(3) Å; in **1b** Mn(1)–N(2) 2.095(3), Mn(2)–N(3) 2.195(4) Å; in **1c** Mn(1)–N(2) 2.095(5), Mn(2)–N(3) 2.190(5) Å]. The Mn atoms within each  $[(\eta\text{-Cp})\text{Mn}\{2\text{-NHR}\}]$  monomer therefore obtain a ‘piano-stool’ coordination geometry similar to that found in metal carbonyls such as  $[\text{CpMn}(\text{CO})_3]$ .<sup>13</sup> However, the Mn centres in **1a–c** are clearly high-spin (formally 17 e) in **1a–c** at 180 K. This conclusion is supported by the long C–Mn distances involved [in **1a** range 2.408(5)–2.616(5) Å; in **1b** 2.455(6)–2.508(4) Å; in **1c** 2.464(8)–2.515(9) Å; cf. 2.33–2.65 Å

**Table 4** Selected bond lengths (Å) and angles (°) for  $[(\eta^1\text{-Cp})(\eta^5\text{-Cp})\text{Mn}(\text{BnNHCH}_2)_2]$  (**4**)

Mn(1)–N(1)	2.226(2)	Mn(1)–C(6–11)	2.450(2)–2.555(2)
Mn(1)–N(2)	2.261(2)	Cp <sub>centroid</sub> ···Mn(1)	2.21
Mn(1)–C(1)	2.331(2)		
N(1)–Mn(1)–N(2)	79.22(7)	N(1)–Mn(1)–Cp <sub>centroid</sub>	121.0(1)
C(1)–Mn(1)–Cp <sub>centroid</sub>	121.8(1)	N(2)–Mn(1)–Cp <sub>centroid</sub>	114.3(1)



**Fig. 5** Core structure of **1a–c** (a) showing connectivity of guanidide units, (b) the Mn<sub>8</sub> arrangement and shortest Mn···Mn contacts.

for high spin<sup>14,15</sup>, within the range of 2.33–2.65 Å observed for high spin and significantly greater than the values expected for low-spin Mn(II) (ca. 2.11–2.14 Å).<sup>14,15</sup>

A noticeable trend can be discerned in the core Mn···Mn distances on going from **1a** to **1b** and **1c**. There is a large expansion in the key Mn···Mn distances defining the cores of the complexes as one moves from **1a** to **1c**. Within the central Mn<sub>4</sub>N<sub>4</sub> cubane units the nearest neighbouring distance expands from Mn(1)···Mn(1A) 3.1594(8) Å in **1a** to Mn(1)···Mn(1A) 3.2187(9) Å in **1b**, to Mn(1)···Mn(1A) 3.223(1) Å in **1c**,<sup>16</sup> at the same time the Mn···Mn separation across this unit increases from Mn(1)···Mn(1C) 3.543(1) Å in **1a**, to Mn(1)···Mn(1C) 3.689(1) Å in **1b**, to Mn(1)···Mn(1C) 3.724(1) Å in **1c**. In addition, the Mn···Mn separation between the independent Mn centres in the asymmetric units [Mn(1) and Mn(2)] increases from Mn(1)···Mn(2) 3.2335(7)

Å in **1a**, to Mn(1) ⋯ Mn(2) 3.2609(8) Å in **1b**, to Mn(1) ⋯ Mn(2) 3.300(1) Å in **1c**. The origin of this trend may, in part, be due to increased steric crowding resulting from the presence of more demanding MeO groups around the core. The presence of electron-releasing MeO substituents in the 4- and 6-positions of the pm framework should also have an impact on the hybridisation and/or charge at the ring-N and anionic 2-N atoms of the pmNH<sup>-</sup> and pmN<sup>2-</sup> ligands. Although it is difficult to delineate the potential steric and electronic contributions by a simple comparison of the key Mn–N bond lengths and angles found in **1a–c** (presented in Table 2), the major effect of changing the substituents appears to be felt by the imido pmN<sup>2-</sup> ligands. Thus, whereas the majority of the bond lengths and angles associated with Mn–N cores in **1a–c** remain largely unaltered (within the crystallographic errors), there are significant changes occurring in Mn(2)–N(5) (*ca.* 0.08 Å increase) and N(1)–Mn(1)–N(6C) (*ca.* 6° decrease), N(1B)–Mn(1)–N(6C) (*ca.* 4° decrease) in going from **1a** to **1b** to **1c**.

As noted in the introduction to this paper, although amido Mn(II) compounds (containing R<sub>2</sub>N<sup>-</sup> anions) are more common, very few Mn imido compounds like **1a–c** have been structurally characterised.<sup>2</sup> Of these the majority are Mn(V–VII) complexes such as the nitrido anion [Mn<sup>VII</sup>(N)(N<sup>t</sup>Bu)<sub>3</sub>]<sup>2-</sup> and the dimers [Mn<sup>V</sup>(R)(N<sup>t</sup>Bu)(μ-N<sup>t</sup>Bu)]<sub>2</sub> (R = CH<sub>2</sub>CMe<sub>3</sub>, CH<sub>2</sub>Ph), prepared by transmetallation reactions of [Mn(N<sup>t</sup>Bu)<sub>3</sub>Cl].<sup>2a</sup> The only previously structurally authenticated example of a Mn(II) imido compound is the hexanuclear adamantane-like cation [Mn<sub>6</sub>(μ<sub>3</sub>-NPh)<sub>4</sub>(thf)<sub>4</sub>]<sup>4+</sup>, obtained by the transmetalation reaction of [Mg(NPh)(thf)<sub>6</sub>] with MnBr<sub>2</sub> in thf.<sup>2b</sup> Interestingly, the Mn–N(imido) bond lengths [2.035(9)–2.080(9) Å] in [Mn<sub>6</sub>(μ<sub>3</sub>-NPh)<sub>4</sub>(thf)<sub>4</sub>]<sup>4+</sup> are at the lower end of those found in the Mn<sub>4</sub>N<sub>4</sub> cores of **1a–c** 2.075(3)–2.110(3) Å,<sup>2b</sup> probably resulting from the overall positive charge of the [Mn<sub>6</sub>(μ<sub>3</sub>-NPh)<sub>4</sub>(thf)<sub>4</sub>]<sup>4+</sup> cation. The common structure adopted by **1a–c** contains many novel features. Not least, the complexes are the highest nuclearity imido Mn cages to be structurally characterised. The incorporation of four CpMn units within these cage arrangements is also unprecedented. The most closely related situation is found in [(CpMn)<sub>3</sub>(μ<sub>2</sub>-NO)<sub>3</sub>(μ<sub>3</sub>-NO)], containing three CpMn fragments.<sup>17</sup>

The solid-state structure of [CpMn(μ-8-HNquin)]<sub>2</sub> (**3**) (Fig. 6) is that of a centrosymmetric dimer in which each Mn centre is bonded to a terminal η<sup>5</sup>-Cp ligand [Mn(II) ⋯ Cp<sub>centroid</sub> 2.18 Å] and is further bonded to a μ-NH centre within the central Mn<sub>2</sub>N<sub>2</sub> ring unit [Mn(1)–N(2) 2.143(3) Å, Mn(1)–N(2A) 2.197(3) Å]. There are two toluene molecules present in the lattice of the complex. The Mn<sub>2</sub>N<sub>2</sub> core of **3** is diamond shaped, with angles of 94.6(1)° for N(2)–Mn(1)–N(2A) and 85.4(1)° for Mn(1)–N(2)–Mn(1A). Each Mn centre then forms longer

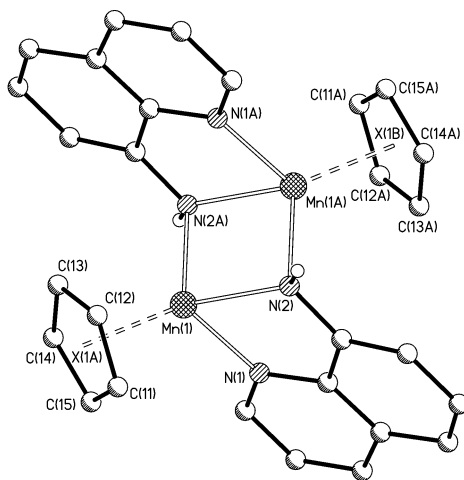


Fig. 6 Structure of the dimer [CpMn(μ-8-HNquin)]<sub>2</sub> (**3**). H atoms, except those attached to N, have been omitted for clarity.

bonds to the N centres within the quinoline ligands [N(1)–Mn(1) 2.219(2) Å]. The Mn–C bond lengths [range 2.429(4)–2.515(4) Å] are indicative of high-spin Mn(II) [normally in the range 2.33–2.65 Å<sup>14,15</sup>] and the Mn(II) centres have a formal electron count of 17 e. The Mn ⋯ Mn separation across the dimer unit appears to be short [Mn(1) ⋯ Mn(1A) 2.9440(10) Å]; *cf.* Mn<sub>2</sub>(CO)<sub>10</sub> *ca.* 2.90 Å.<sup>16</sup> However, a search of the Cambridge Crystallographic Data Base (CCDC) reveals that Mn ⋯ Mn separations within related Mn<sub>2</sub>N<sub>2</sub> dimers (*ca.* 2.39–2.64 Å) are generally significantly shorter than in **3**.<sup>18</sup> Thus, it is unlikely that there is any degree of Mn ⋯ Mn bonding in the complex. The previously reported complex **2** and the new species **3** are rare examples of a primary-amido Mn(II) complex (containing RNH<sup>-</sup> ligands), the trinuclear, heteroleptic complex [(Me<sub>3</sub>Si)<sub>2</sub>NMn(μ-NHDipp)<sub>2</sub>]<sub>2</sub>Mn] (Dipp = 4,6-<sup>t</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) being one of the few simple primary-amido Mn(II) complexes to be reported prior to our studies.<sup>19</sup> Most other structurally characterised examples contain secondary-amido ligands (R<sup>1</sup>R<sup>2</sup>N<sup>-</sup>).<sup>3</sup>

The result of the attempted reaction of (BnNHCH<sub>2</sub>)<sub>2</sub> with Cp<sub>2</sub>Mn is simple complexation of the Mn(II) centre (without deprotonation of the NH functionality). The composition of the product [(η<sup>1</sup>-Cp)(η<sup>5</sup>-Cp)Mn(BnNHCH<sub>2</sub>)<sub>2</sub>] (**4**) (Fig. 7) is similar to that of other donor complexes of Cp<sub>2</sub>Mn with various mono- and bi-dentate O, N and P ligands.<sup>20</sup> Similar η<sup>1</sup>- and η<sup>5</sup>-bonding of the Cp ligands to that in **4** occurs in the only other N-donor adduct of manganocene, [(η<sup>1</sup>-Cp)(η<sup>5</sup>-Cp)Mn(TMEDA)].<sup>20a</sup> The Mn–N bond lengths in the latter [2.338(5) and 2.354(5) Å] are similar to those in **4** [2.226(2) and 2.261(2) Å]. In contrast to **4** and [(η<sup>1</sup>-Cp)(η<sup>5</sup>-Cp)Mn(TMEDA)], the Cp ligands in [Cp<sub>2</sub>Mn·thf],<sup>20d</sup> [Cp<sub>2</sub>Mn·PR<sub>3</sub>]<sup>20b,c</sup> and [Cp<sub>2</sub>Mn·Me<sub>2</sub>-PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>]<sup>20c</sup> all adopt η<sup>5</sup>-Cp coordination modes. Although the steric demands of the Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub> ligand are greater than that of the (BnNHCH<sub>2</sub>)<sub>2</sub> ligand, making a change in the hapticity of the Cp ligands more likely, the decisive factor is the shortness of Mn–N bonds compared to Mn–P bonds. Thus, the resulting closer approach of the (BnNHCH<sub>2</sub>)<sub>2</sub> ligand to the Cp<sub>2</sub>Mn monomer unit in fact produces a greater disruption of the Cp–Mn bonding than the Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub> ligand. Despite the shortness of the Mn–O bond in [Cp<sub>2</sub>Mn·thf], the coordinated ligand has low steric demands so that the η<sup>5</sup>-Cp coordination is retained. Further evidence of steric congestion within the structure of **4** is seen in the asymmetry of the coordination of the two N centres of the (BnNHCH<sub>2</sub>)<sub>2</sub> ligand [the Mn(1)–N bonds differing by *ca.* 0.35 Å]. The observation that Cp<sub>2</sub>Mn does not deprotonate (BnNHCH<sub>2</sub>)<sub>2</sub> can be compared to the formation of the complex [(Dipp(N)CH<sub>2</sub>CH<sub>2</sub>N(H)Dipp)<sub>2</sub>Mn] (Dipp = 4,6-<sup>t</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in the reaction of Mn{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> with DippN(H)CH<sub>2</sub>CH<sub>2</sub>N(H)Dipp (the product resulting from deprotonation of just one of the N–H groups of the organic acid).<sup>21</sup> Apart from the obvious difference in the Mn(II) base employed in this reaction, the major difference is the likely greater acidity of DippN(H)CH<sub>2</sub>CH<sub>2</sub>N(H)Dipp compared to that of (BnNHCH<sub>2</sub>)<sub>2</sub>.

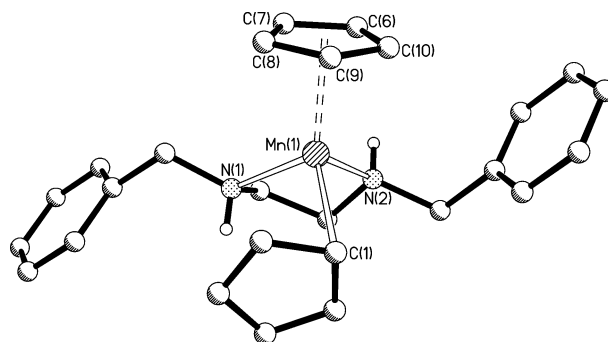


Fig. 7 Structure of the adduct [(η<sup>1</sup>-Cp)(η<sup>5</sup>-Cp)Mn(BnNHCH<sub>2</sub>)<sub>2</sub>] (**4**). H atoms, except those attached to N, have been omitted for clarity.

## Conclusions

The results presented in this paper show that the reactions of aromatic primary amines with  $\text{Cp}_2\text{Mn}$  can be used in the preparation of imido and amido  $\text{Mn}(\text{II})$  cage compounds. In order for complete deprotonation of the  $\text{NH}_2$  functionality to occur, however, organic aromatic substituents possessing more than one ring N atom are required in order to stabilise the negative charge within an imido group. The more acidic 2-aminopyrimidines can be doubly deprotonated even in the presence of electron-donating MeO and Me substituents, while only single deprotonation of 2-aminopyridines and related aromatic amines occurs under the reaction conditions employed. So far studies have only investigated room-temperature reactions of these species. Future studies will investigate higher temperature reactions of primary amines, in an attempt to effect complete deprotonation, and the reactions of primary phosphines with  $\text{Cp}_2\text{Mn}$ . Although limited, magnetic studies of **1a** and **2** have been reported in preliminary publications,<sup>10,11</sup> the studies presented in this paper have focused only on the synthetic scope of the use of manganocene as a base. Detailed magnetic and electronic measurements of the new complexes will be the subject of a future paper.

## Experimental

### General

Manganocene and the new compounds **1b**, **1c**, **3** and **4** are highly air- and moisture-sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques and under dry/oxygen-free argon.<sup>22</sup> The pyrimidine and pyridine starting materials were used as supplied (Aldrich). Toluene, thf and hexane were dried by distillation over sodium/benzophenone prior to the reactions. Manganocene was prepared using the method of Wilkinson *et al.*<sup>12</sup> Complexes **1–5** were isolated and characterised with the aid of a nitrogen-filled glove box fitted with a Belle Technology  $\text{O}_2$  and  $\text{H}_2\text{O}$  internal recirculation system and equipped with an  $\text{O}_2$  meter (reading *ca.* 1–10 ppm while in use). Melting points (uncorrected) were determined by using a conventional apparatus and sealing samples in capillaries under argon. IR spectra were recorded as Nujol mulls using NaCl plates and were run on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer. Elemental analyses were performed by first sealing the samples under argon in airtight aluminium boats (1–2 mg) and C, H and N content was analysed using an Exeter Analytical CE-440.  $^1\text{H}$  NMR spectra were recorded on a Bruker AM400 MHz spectrometer in dry deuterated  $\text{D}_6$ -DMSO (using the solvent resonances as the internal reference).

### Syntheses

$[(\eta^5\text{-Cp})\text{Mn}\{2\text{-NH}(4\text{-MeO-6-Mepm})\}]\text{Mn}\{2\text{-N}(4\text{-MeO-6-Mepm})\}]_4$  (**1b**). A solution of 2-amino-4-methoxy-6-methylpyrimidine (0.075 g, 0.54 mmol) in toluene (30 ml) was added dropwise to a solution of  $\text{Cp}_2\text{Mn}$  (0.10 g, 0.54 mmol) in toluene (15 ml) at  $-78^\circ\text{C}$ . The reaction mixture initially became very dark but after stirring for 5 min at  $-78^\circ\text{C}$  and then allowing the temperature to increase to  $5^\circ\text{C}$ , a series of colour changes finally led to a yellow solution. A precipitate was formed which was dissolved by addition of 10 ml of toluene and heating gently. The bright yellow solution was stored at room temperature for 2 days. Orange crystals were produced. Although later X-ray structure determination shows that there are six toluene molecules in the lattice of **1b**, isolation of crystalline samples under vacuum ( $10^{-1}$  atm, 15 min) gives material in which there are only five toluene molecules per molecule of **1b**. The following data refer to this material. Yield 0.07 g (44%). Decomp.  $164^\circ\text{C}$  to black solid. IR (Nujol, NaCl windows),  $\nu/\text{cm}^{-1} = 3341$  (w, N–H str.), 3060 (vw, Cp–H str.), 1575 (w, C=N str.).  $^1\text{H}$

NMR (400.16 MHz,  $+25^\circ\text{C}$ ,  $\text{D}_6$ -DMSO,  $\delta/\text{ppm} = 7.19$  (s, aryl C–H), 6.93 (s, br, Cp–H) 2.47 (s, MeO), 2.24 (s, Me). Elemental analysis; found C 54.8, H 5.5, N 14.6; cald. for **1b**·5toluene C 54.7, H 5.4, N 14.6%.

$[(\eta^5\text{-Cp})\text{Mn}\{2\text{-NH}(4,6\text{-(MeO)}_2\text{pm})\}]\text{Mn}\{2\text{-N}(4,6\text{-(MeO)}_2\text{pm})\}]_4$  (**1c**). A solution of 2-amino-4,6-dimethoxypyrimidine (0.155 g, 1.0 mmol) in toluene (40 ml) was added dropwise to a solution of  $\text{Cp}_2\text{Mn}$  (0.185 g, 1.0 mmol) in toluene (20 ml) at  $-78^\circ\text{C}$ . The solution became dark brown. It was stirred at  $-78^\circ\text{C}$  for five minutes then allowed to warm to  $5^\circ\text{C}$ , turning light brown. The solution was stored at room temperature for 2 days. Light brown crystals of **1c** were produced. Although later X-ray structure determination shows that there are six toluene molecules in the lattice of **1c**, isolation of crystalline samples under vacuum ( $10^{-1}$  atm, 15 min) gives material in which there is only one toluene per molecule of **1c**. The following data refer to this material. Yield 0.03 g (12%). Decomp  $178^\circ\text{C}$  to black solid. IR (Nujol, NaCl windows),  $\nu/\text{cm}^{-1} = 3347$ , 3298 (w, N–H str.), *ca.* 3060 (vw, Cp–H str.), 1589 (w, C=N str.).  $^1\text{H}$  NMR (400.16 MHz,  $+25^\circ\text{C}$ ,  $\text{D}_6$ -DMSO)  $\delta/\text{ppm} = 7.08$  (s, aryl C–H), 5.25 (s, Cp), 2.23 (s, MeO). Elemental analysis; found C 43.5, H 4.5, N 15.4; cald. for **1c**·toluene C 44.6, H 4.4, N 16.6%.

$[\text{CpMn}(\mu\text{-8-HNquin})]_2$  (**3**). A solution of 8-aminoquinoline (0.14 g, 1.0 mmol) in toluene (10 ml) was added dropwise to a solution of  $\text{Cp}_2\text{Mn}$  (0.19 g, 1.0 mmol) in toluene (15 ml) at  $-78^\circ\text{C}$ . The mixture turned orange and a precipitate was formed. It was stirred (5 min) and warmed to room temperature. A dark orange solution was obtained on brief, gentle heating and stored at room temperature (24 h), resulting in the formation of brown crystals of **3** (0.14 g, 42%). Decomp.  $90^\circ\text{C}$ , to a black solid. IR (Nujol, NaCl windows),  $\nu/\text{cm}^{-1} = 3394$ , 3380 (w, N–H str.), 1613 (w, C=N str.), 1592 (m, C=C str.).  $^1\text{H}$  NMR (400.16 MHz,  $+25^\circ\text{C}$ ,  $\text{D}_6$ -DMSO)  $\delta/\text{ppm} = 8.67$ , 8.13, 7.17 (br s, C–H aromatic), 5.85 (br s, Cp), 3.28 (br s, NH).

$[(\eta^1\text{-Cp})(\eta^5\text{-Cp})\text{Mn}\{\text{BnNHCH}_2\}_2]$  (**4**). A solution of *N,N'*-dibenzylethylenediamine (0.23 ml, 1.0 mmol) in thf (10 ml) was added dropwise to a solution of  $\text{Cp}_2\text{Mn}$  (0.185 g, 1.0 mmol) in thf (10 ml) at  $-78^\circ\text{C}$ . The reaction mixture turned dark brown and was stirred at  $-78^\circ\text{C}$  for five min then allowed to warm to room temperature, finally becoming light brown. After briefly bringing the reaction to reflux, it was stirred for another hour. A white solid was formed, which dissolved on heating. Storage at room temperature (4 days) produced colourless crystals of **4**. Yield 0.14g (33%). IR (Nujol, NaCl windows),  $\nu/\text{cm}^{-1} = 3211$ , 3192 (m, N–H str.), 3082 (m), 3069 (m), 3055 (d, m; Cp–H str.), 3025 (m, aryl C–H), other major bands at 1181 (s), 1090 (s), 1080 (s), 1027 (s), 1003 (s), 965 (s), 747 (vs), 732 (vs), 696 (vs).  $^1\text{H}$  NMR (400.16 MHz,  $+25^\circ\text{C}$ ,  $\text{D}_6$ -DMSO)  $\delta/\text{ppm} = 7.27$  (s), 7.19 (s, aromatic C–H), 3.82 (s, Cp), 2.55 (s,  $\text{PhCH}_2$ ), 2.04 (s), 1.73 (s) ( $\text{CH}_2\text{CH}_2$ ). Elemental analysis; found C 71.6, H 6.8, N 7.1; cald. for **4** C 73.4, H 7.1, N 6.6%.

### X-Ray crystallography

Crystals of **1b**, **1c**, **3** and **4** were mounted directly from the mother solution under nitrogen at room temperature, a perfluorocarbon oil being used to protect them from atmospheric air and moisture.<sup>23</sup> Data for **1b**, **1c** and **4** were collected using a Nonius Kappa CCD diffractometer, and for **3** on a Bruker *P4* four-circle diffractometer. The structures were solved by direct methods and refinement carried out using full-matrix least squares on  $F^2$  (SHELXL-97 **1b**; SHELXL-93 **1c**, **3** and **4**).<sup>24</sup> The crystals of **1b** and **1c** were isomorphous and in both crystals 1.5 toluene molecules were disordered in the asymmetric unit (*i.e.*, per two independent manganese atoms). It was not possible to locate the toluene methyl groups so these were assumed to be disordered over all carbons of the ring; hydrogen

atoms of  $\frac{5}{6}$  occupancy were assigned to the six ring carbon atoms of the complete toluene solvate molecules. In **3** and **4** the hydrogen atoms of the cyclopentadienyl groups were directly located, and were included in the observed positions, without refinement in **3** and refined freely in **4**. In all four structures anisotropic displacement parameters were assigned to all full occupancy non-hydrogen atoms.

CCDC reference numbers 207480–207483.

See <http://www.rsc.org/suppdata/dt/b3/b303727b/> for crystallographic data in CIF or other electronic format.

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