FULL PAPER

Syntheses, structures and magnetic properties of Mn(II) dimers $[CpMn(\mu-X)]_2$ ($Cp = C_5H_5$; X = RNH, R^1R^2N , $C \equiv CR$)[†]

Carmen Soria Alvarez,^{*a*} Sally R. Boss,^{*a*} Jonathan C. Burley,^{*a*} Simon M. Humphry,^{*a*} Richard A. Layfield,^{*a*} Richard A. Kowenicki,^{*a*} Mary McPartlin,^{*b*} Jeremy M. Rawson,^{**a*} Andrew E. H. Wheatley,^{**a*} Paul T. Wood^{**a*} and Dominic S. Wright^{**a*}

^a Chemistry Department, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: dsw1000@cus.cam.ac.uk; Fax: +0044 1223 336362

^b Department of Health and Biological Science, London Metropolitan University, London, UK N7 8DB

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Manganocene, Cp_2Mn , has been employed as a precursor in the synthesis of a range of Mn(II) dimers of the type $[CpMn(\mu-X)]_2 [X = 8-NHC_9H_6N (1), N(Ph)(C_5H_4N) (2), N(4-EtC_6H_4)(C_5H_4N) (3) and C=CPh (4)]$ as well as the bis-adduct $[Cp_2Mn{HN=C(NMe_2)_2}_2]$ (5). The solid-state structures of 1–5 are reported. Variable-temperature magnetic measurements have been used to assess the extent of $Mn(\mu-X)Mn$ communication within the dimers of 1–4 as a function of the bridging ligands (X).

Introduction

The polarity of Cp–metal bonds in a range of transition metal (M) metallocenes (Cp₂M; Cp = C₃H₅) has been appreciated for some time.¹ This characteristic is in marked contrast to the classical behaviour exhibited by ferrocene (Cp₂Fe), for which the covalent Cp–Fe bonding and the stability of the eighteen-electron configuration results in the maintenance of metal–ligand bonding in reactions with electrophiles and nucleophiles.² The ionic character of Cp-metal bonding in metallocenes like manganocene (Cp₂Mn) results in three distinct types of reactivity, (*i*) substitution of the Cp ligands by nucleophiles,³ (*ii*) addition reactions of weaker nucleophiles to the metal centre⁴ and (*iii*) basic character in reactions with organic acids (*e.g.*, eqns. (1)–(3)).^{5,6}

Substitution
$$Cp_2Mn + Nu^- \longrightarrow Cp-Mn-Nu$$
 (1)

Chi

Addition
$$Cp_2Mn + Nu^- \rightarrow [Cp_2Mn-Nu]^-$$
 (2)

Acid/Base
$$Cp_2Mn + LH \longrightarrow Cp-Mn-L$$
 (3)

These reaction characteristics, which are in many ways similar to those exhibited by main group metallocenes,⁷ make polar transition metal metallocenes attractive precursors to an extensive range of molecular and supramolecular magnetic materials.³⁻⁶

Our interest in this area has so far focused on the preparation of metallo-organic compounds^{3,4,6} and on extended organometallic lattices of Mn(II).⁵ We found that the reactions of Cp_2Mn as a base with 2-aminopyrimidines (pmNH₂) and 2-aminopyridines (pyNH₂) provide easy access to polynuclear amido (pyNH⁻) and imido (pmN²⁻) cages,⁶ *e.g.*, in the octanuclear imido Mn(II) cages [{Mn(Npm)}₄{CpMn-(NHpm)}₄].^{6a,c} The addition of alkali metal cyclopentadienyl compounds to Cp_2Mn gives extended layer structures containing [Cp_3Mn]⁻ anions, *e.g.*, as found in the graphite-like arrangement of [{ Cp_3Mn }K]_∞.⁵ The magnetic properties of polynuclear cages and lattice arrangements containing Mn in various oxidation states have been investigated extensively in the past two decades.⁸ However, these studies have involved a restricted range of ligands. In particular oxo/carboxylate cages

tions to date.⁸ In tandem with our synthetic aims of applying transition-metal metallocenes as precursors, an additional aim in our work is the elucidation of the magnetic properties of this extensive range of materials containing novel bridging groups. We present here further studies of the synthetic utility of Cp₂Mn. In addition to the dimer $[CpMn{\mu-8-NHC_9H_6N}]_2(1)$, whose synthesis and structure were reported by us previously,6c the new dimers $[CpMn\{\mu-N(Ph)(C_5H_4N)\}]_2$ (2) and $[CpMn\{\mu-N(Ph)(C_5H_4N)\}]_2$ $N(4-EtC_6H_4)(C_5H_4N)$]₂ (3) and $[CpMn\{\mu-C=CPh\}\cdot thf]_2$ (4), and the bis-adduct $[Cp_2Mn{HN=C(NMe_2)_2}_2]$ (5) have been prepared and structurally characterised. Although a series of dimers $[MeCpMn(\mu-X)PEt_3]_2$ (MeCp = MeC₅H₄, X = halide) have been structurally characterised and their magnetic properties investigated thoroughly,⁹ the dimers 1–4 are the first Mn(II) compounds of this type containing bridging N and C groups. They provide a unique opportunity to uncover fundamental information concerning the mechanism and relative order of magnetic exchange interactions within a series of closely related species containing little-studied bridging metallo-organic or organometallic groups.

and cyano-compounds have been the focus of most investiga-

Results and discussion

The Mn(II) dimers $[CpMn{\mu-8-NHC_9H_6N}]_2$ (1),^{6c} $[CpMn{\mu-N(Ph)(C_5H_4N)}]_2$ (2) and $[CpMn{\mu-N(4-EtC_6H_4)(C_5H_4N)}]_2$ (3) were obtained from the 1:1 stoichiometric reactions of the corresponding amines with Cp₂Mn (eqns. (4)–(6), respectively) in yields of 41–65%.

$$Cp_{2}Mn + 8-NH_{2}-C_{9}H_{6}N \xrightarrow{-CpH} \frac{1}{2} [CpMn\{\mu-8-NH-C_{9}H_{6}N\}]_{2}$$

$$1 \qquad (4)$$

$$Cp_{2}Mn + HN(Ph)(C_{5}H_{4}N) \xrightarrow{-CpH} \frac{1}{2} [CpMn\{\mu-N(Ph)(C_{5}H_{4}N)\}]_{2}$$

$$2 \qquad (5)$$

$$Cp_2Mn + HN(4-Et-C_6H_4)(C_5H_4N) \xrightarrow{-CpH} {}^{1}/{_2} [CpMn\{\mu-N(4-Et-C_6H_4)(C_5H_4N)\}]_2$$

(6)

Owing to the lower reactivity of phenyl acetylene, the dimer $[CpMn \{\mu-C \equiv CPh\} \cdot thf]_2$ (4) could only be obtained by the nucleophilic substitution reaction of $[PhC \equiv CLi]$ with Cp_2Mn (eqn. (7)).

$$Cp_2Mn + [LiC \equiv CPh] \xrightarrow{-CpLi} \frac{1}{2} [CpMn{\mu-CCPh}.thf]_2$$

(7)

[†] Electronic supplementary information (ESI) available: Derivation of magnetic susceptibility of Mn^{II} dimers including biquadratic exchange. See http://www.rsc.org/suppdata/dt/b4/b409135c/

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 $\begin{array}{l} \textbf{Table 1} \quad \text{Selected bond lengths (Å) and angles (°) for the amido complexes } [CpMn\{\mu-8-NHC_9H_6N\}]_2 (1), \ [CpMn\{\mu-N(Ph)(C_3H_4N)\}]_2 (2) \ \text{and} \ [CpMn\{\mu-N(4-EtC_6H_4)(C_3H_4N)\}]_2 (3) \end{array} \right. \end{array}$

Compound	1	2	3
$\begin{array}{c} Mn(1)-N(1) \\ Mn(1)-N(1A) \\ Mn(1)-N(2/2A) \\ Mn(1)-C(1) \\ Mn(1)-C(2) \\ Mn(1)-C(3) \\ Mn(1)-C(3) \\ Mn(1)-C(4) \\ Mn(1)-C(5) \\ Cp_{centroid}-Mn \\ C \xrightarrow{\dots} C (Cp) \\ Mn(1) \cdots Mn(1A) \\ N(1)-Mn(1)-N(1A) \\ N(1)-Mn(1)-N(1A) \\ Mn(1)-N(1)-Mn(1A) \\ N(2/2A)-Mn(1)-N(1/1A) \\ \end{array}$	2.143(3) 2.197(3) 2.219(2) 2.497(4) 2.515(4) 2.482(4) 2.429(4) 2.429(4) 2.448(4) 2.18 1.367(6)-1.416(7) 2.944(1) 94.6(1) 85.4(1) 76.28(9)	2.285(2) 2.113(2) 2.213(2) 2.421(2) 2.431(2) 2.426(2) 2.431(2) 2.429(2) 2.12 1.398(3)-1.400(4) 3.0230(8) 94.89(6) 85.11(6) 60.52(6)	$\begin{array}{c} 2.170(2) \\ 2.295(2) \\ 2.242(2) \\ 2.426(3) \\ 2.391(2) \\ 2.374(3) \\ 2.437(3) \\ 2.495(3) \\ 2.13 \\ 1.375(4) - 1.393(3) \\ 3.0370(9) \\ 94.35(6) \\ 85.65(6) \\ 60.14(7) \end{array}$

^{*a*}Symmetry transformations used to generate equivalent atoms A for 2: 2 - x, -y, 2 - z and 3: -x + 2, -y, -z.

Table 2	Selected bond	d lengths (A	A) and angles	(°) f	for the alkyne	e-bridged	dimer [C	pMn{	µ-C≡CPh	{·thf]	2 (4)
											_	

$\begin{array}{c} Mn(1)-C(11) \\ Mn(1)-C(21) \\ Mn(1)-O(1) \\ Mn(1)-C(1) \\ Mn(1)-C(2) \\ Mn(1)-C(3) \\ Mn(1)-C(4) \\ Mn(1)-C(5) \\ Cp_{centroid}\cdots Mn \\ C \cdots C (Cp) \\ Mn(1) \cdots Mn(2) \end{array}$	$\begin{array}{c} 2.162(3) \\ 2.249(3) \\ 2.207(2) \\ 2.479(3) \\ 2.478(3) \\ 2.484(3) \\ 2.472(3) \\ 2.464(3) \\ 2.17 \\ 1.375(5) - 1.405(5) \\ 2.9691(8) \end{array}$	$\begin{array}{l} Mn(2)-C(11)\\ Mn(2)-C(21)\\ Mn(2)-O(2)\\ Mn(2)-C(6)\\ Mn(2)-C(7)\\ Mn(2)-C(8)\\ Mn(2)-C(8)\\ Mn(2)-C(9)\\ Mn(2)-C(10)\\ C=C \end{array}$	2.250(3) 2.158(3) 2.220(2) 2.478(3) 2.463(3) 2.453(3) 2.456(3) 2.456(3) 2.474(3) 1.215(4)
$C(12/22) \cdots Mn(1/2)$	2.96 (mean)		
Mn(1)-C(11)-Mn(2) Mn(1)-C(21)-Mn(2)	84.6(1) 84.7(1)	C(12)–C(11)–Mn(2) C(22)–C(21)–Mn(1) C(22)–C(21)–Mn(2)	115.2(2) 112.7(2) 162.7(2)
C(11)–Mn(1)–C(21) C(11)–Mn(2)–C(21) C(12)–C(11)–Mn(1)	95.2(1) 95.3(1) 160.2(2)	O-Mn-µ-C	95.6 (mean)

Attempts to prepare an imido-bridged dimer $[CpMn{\mu N=C(NMe_2)_2}_2]_2$ (6) by the room-temperature reaction of 1,1,3,3-tetramethylguanidine $[HN=C(NMe_2)_2]$ with Cp_2Mn resulted only in formation of the bis-adduct $[Cp_2Mn{HN=C(NMe_2)_2}_2]$ (5) (eqn. (8))

 $Cp_2Mn + 2 HN=C(NMe_2)_2 \longrightarrow [Cp_2Mn\{HN=C(NMe_2)_2\}_2]$

5

(8)

Repeated attempts to obtain the desired dimer **6** from nucleophilic substitution reaction of Cp_2Mn with $[LiN=C(NMe_2)_2]$ (1:1 equivalents) failed to produce isolable products. The synthesis and structure of **1** have been reported by us previously^{6c} so that experimental and structural details of the complex will only be described here by way of comparison with the new dimers **2**, **3** and **4**.

The paramagnetic nature of all of these compounds and their high air-sensitivity made characterisation by spectroscopic and analytical techniques difficult. Only in the case of 5 could satisfactory elemental analysis be obtained. In addition, all of the species exhibited low solubility in all organic solvents once isolated, except for (polar) DMSO. Although the roomtemperature ¹H NMR spectra of all of the compounds exhibited line-broadening, in the cases of 2 and 3 spectra were sufficiently well resolved to identify the $[N(Ph)(C_5H_4N)]^-$ and $[N(4-EtC_6H_4)(C_5H_4N)]^-$ ligands as well-separated multiplets with the correct relative integrals; the 1H resonances for the C_5H_4N group in 2 being found in the region δ 9.18–7.84 and those in 3 being in the range δ 9.92–7.50, with those due to the Ph and 4-EtC₆H₄ groups being found in the regions δ 7.71–6.69 and δ 7.05–6.65, respectively. For 3, the 4-Et group is observed as the expected triplet (δ 1.13) and quartet (δ 2.48). In contrast,

the room-temperature ¹H NMR spectra of 4 and 5 were severely broadened and no quantitative information could be obtained. In each of compounds 1–5 the resonances for the Cp ligands were very broad and therefore difficult to assign. The chemical shifts of the Cp hydrogen atoms in these species were highly variable, occurring in the region *ca.* δ 6.47–3.50. The presence of Cp ligands in all of the compounds is supported further by the observation of a weak band at *ca.* 3080 cm⁻¹ for the cyclopentadienyl C–H stretch in their IR spectra.

The low-temperature diffraction X-ray structures of 2–5 have been obtained. Selected bond lengths and angles for amidobridged dimers 2 and 3 are given in Table 1. This table also includes the corresponding data for the previously reported primary-amido complex 1 for comparison. Selected bond lengths and angles for the alkyne-bridged dimer 4 and the bis-adduct 5 are given in Tables 2 and 3, respectively. Details of the data collections and structure refinements of the new compounds are to be found in the Experimental section in Table 5.

The structures of the primary- and secondary-amido bridged dimers 1–3 (Figs. 1–3, respectively) are similar, having centrosymmetric arrangements in which the Mn(II) centres of their Mn₂N₂ cores are π -bonded to Cp ligands. In addition, the Mn centres are chelated by the quinoline- or pyridyl-N centres of the bridging organic groups, giving the Mn centres of each dimer a nominal coordination number of four. The strained chelate interactions in 2 and 3 result in a marked disruption of Mn–N bonding within their Mn₂N₂ ring units. Thus, within each core the longest Mn–N bonds correspond to those involved in the chelate interactions [in 2 Mn(1)–N(1) 2.285(2), in 3 Mn(1)– N(1A) 2.295(2) Å], with the remaining Mn–N bonds being significantly shorter [in 2 Mn(1)–N(1A) 2.183(2), in 3 Mn(1)– N(1) 2.170(2) Å]. This is opposite to the pattern of Mn–N bond

Table 3 Selec	cted bond lengths (Å) and angles (°) for the bis-adduct [Cp ₂ M	$\ln{\{HN=C(NMe_2)_2\}_2}$ (5)	
	C(1)–Mn(1)	2.558(4)	N(2)–Mn(1)	2.120(3)
	C(2)-Mn(1)	2.350(3)	C(6)-Mn(1)	2.356(4)
	$C(3-5)\cdots Mn(1)$	2.871(4) - 3.312(4)	C(7-10) - Mn(1)	2.673(4)-3.397(4)
	N(1)-Mn(1)	2.109(3)	C - C (Cp)	1.352(8)-1.411(5)
	., .,	~ /	N(1.2) - C(11.12)	1.299(4)-1.305(4)

C(1)-Mn(1)-C(2)

111.9(1)

104.8(2) - 109.1(2)C(6)-Mn(1)-N(1,2)lengths found in 1, in which the less strained chelate interactions appear to re-enforce the associated Mn-N bonds within the core [Mn(1)–N(1) 2.143(3), Mn(1)–N(1A) 2.197(3) Å]. Despite this difference the Mn-N-Mn and N-Mn-N angles within the ring units of 1, 2 and 3 are very similar [Mn–N–Mn range 85.11(6)-85.65(6), N-Mn-N range 94.35(6)-94.6(1)°]. The C-Mn bonds in all three compounds fall in the range expected for high-spin Mn(II) cyclopentadienides [2.429(4)–2.515(4) in 1, 2.421(2)–2.431(2) in 2, and 2.374(3)–2.495(3) Å in 3]. Although the C-Mn bond lengths in these species vary greatly, the hapticity of Cp-Mn bonding is known to be highly flexible in high-spin manganocene derivatives (in which the metal-ligand bonding has largely electrostatic character), and even crystal packing forces have been shown to have a major effect on the Cp-bonding mode.¹⁰ The presence of much longer coordinative interactions in 3 [Mn(1)-N(2A) 2.242(2) Å] than are found in the closely related dimer 2 [Mn(1)–N(2) 2.213(2) Å] may result from electronic effects (possibly stemming from the electron-donating effect of the remote para-Et substituent). The structure of alkyne-bridged dimer 4 (Fig. 4) is similar

N(1)-Mn(1)-N(2)

The structure of alkyne-bridged dimer 4 (Fig. 4) is similar in its overall structure to those found for 1–3, being composed of a Mn_2C_2 ring in which the Mn(II) centres are coordinated by



Fig. 1 Structure of the dimer 1; H-atoms (except those attached to N) have been omitted for clarity.



Fig. 2 Structure of the dimer 2; H-atoms have been omitted for clarity.



33.1(1)

Fig. 3 Structure of the dimer 3; H-atoms have been omitted for clarity.

terminal Cp ligands. In the absence of intramolecular ligation, the nominally four-coordinate geometries of the Mn atoms are now each completed by the coordination of a thf molecule. Although the dimeric structure of 4 is non-centrosymmetric, the bond lengths and angles associated with the two, crystallographically-independent Mn centres are very similar. The Mn_2C_2 ring unit is rhombic in shape, having an alternating pattern of long [Mn(1)-C(21)/Mn(2)-C(11) mean 2.25 Å] and short [Mn(1)-C(11)/Mn(2)-C(21) 2.16 Å] Mn-C distances and with the Mn-C-Mn [mean 84.6°] and C-Mn-C [mean 95.2°] angles being strikingly similar to the Mn–N–Mn and N–Mn–N angles found in the amido-bridged dimers 1-3. The shortest Mn-C bonds correspond to the most favourable (more linear) alignment of the sp hybrid orbitals of the Ph–C=C– ligands with respect to each of the Mn centres in 4 [i.e., C=C-Mn(1/2) $162.7(2)-160.2(2)^{\circ}$, while the longer bonds occur where the axes of the Ph–C=C ligands are mis-aligned [*i.e.*, C=C–Mn(1/2) 112.7(2)–115.2(2)°]. Although there is a possibility of additional, weak interactions between the α -carbon atoms of the bridging $[Ph-C=C]^{-}$ groups and the metal centres, the C(12)...Mn(2) and C(22)...Mn(1) distances in 4 [mean 2.96 Å] are significantly longer than those observed previously in the only example of a Mn complex in which η^2 -type bonding of a Ph-C=C- group has been observed (the Mn(I) complex $[Mn(CO)_3(\mu-H)(\mu C \equiv C - Ph)(Ph_2PCH_2PPh_2)$], 2.415 Å).¹¹ The Cp ligands in 4 adopt essentially η^5 -bonding modes, for which (like in 1–3) the range of C-Mn bond lengths [2.456(3)-2.484(3) Å] is typical of high-spin manganocenes.¹² Complex 4 is isomorphous with the Mg counterpart $[CpMg{\mu-C=CPh}\cdot thf]_{2}^{13}$ and closely related to the Ca complex $[Cp^*Ca\{\mu-C\equiv CPh\}\cdot thf]_2$.¹⁴ However, it is the first alkynyl compound of Mn(II).

The structure of the bis-adduct **5** (Fig. 5) is largely as expected on the basis of spectroscopic and analytical investigations. The Mn(II) centre is coordinated by two η^1 - and η^2 -bonded Cp ligands [Mn(1)–C(1) 2.558(4), Mn(1)–C(2) 2.350(3), Mn(1)–C(6) 2.356(4) Å] and two (Me₂N)₂C=NH ligands [N(1)–Mn(1) 2.109(3), Mn(1)–N(2) 2.120(3) Å]. The location of the N–H protons in the Fourier map of the imine ligands in **5** and the pattern of C^{...}N bonds found within their C(...N)₃ skeletons [N(1/2)...C(11/21) range 1.299(4)–1.305(4) Å; *cf.* 1.351(4)–1.376(4) Å for the other N...C bonds] provides strong support for the formulation of this complex as an adduct on the basis of spectroscopic and analytical results. The complex is related to other mono- and bis-coordinated donor



Fig. 4 Structure of the alkyne-bridged dimer 4; H-atoms have been omitted for clarity.

complexes of Cp₂Mn.^{6c,15} The hapticities of the Cp ligands in these species appear to be largely influenced by the steric demands of the Lewis base ligands, with greater steric congestion resulting in more significant distortion of the Cp ligands from ideal η^5 -bonding. In each of the most closely related nitrogen-donor adducts [Cp₂Mn·TMEDA] (TMEDA = Me₂NCH₂CH₂NMe₂)^{15a} and [Cp₂Mn·(PhCH₂NHCH₂)₂]^{6c} the Cp ligands adopt η^1 - and η^5 -bonding modes. The adoption of η^1 - and η^2 -coordination by the Cp ligands in **4** is similar to that observed in the bis-carbene complex [(η^1 -Cp)(η^2 -Cp)Mn{CN(Me)(CH)₂}].¹⁶



Fig. 5 Structure of the bis-adduct **5**; H-atoms except those attached to N have been omitted for clarity.

Magnetic studies on 1-4

Samples of 1–4 were examined on a SQUID magnetometer between 5 and 300 K in an applied field of 100 Oe. In the cases of 1, 2 and 4, measurements were made in duplicate on independent samples in order to confirm reproducibility. The molar susceptibilities were corrected for diamagnetism using Pascal's constants.^{17a}

The magnetic behaviour of dimeric complexes can be described using the simple Heisenberg spin Hamiltonian,

$$H = -2J\hat{S}_1\hat{S}_2 \tag{9}$$

which is appropriate for isotropic S = 5/2 ions with a ⁶A ground term. The general expression for the susceptibility of homometallic dimeric species in small applied fields can then be written as:¹⁸

Table 4	Parameters utilised in the curve-fitting of the susceptibility
data for	1-4 to the expression (12). The residual $R(\chi)$ is defined as
$(1/n)\Sigma \chi_0$	$- \chi_{calc} / \chi_{obs}$ where <i>n</i> is the number of data points

Compound	J/K.	a	TIP	$R(\chi)$
1	-21.0	0.14	-0.005	0.125
	-21.0	0.25	-0.0014	0.103
2	-17.0	0.08	0.003	0.022
	-18.5	0.072	0.0018	0.020
3	-20.5	0.13	0.000	0.131
4	-30.5	0.04	0.000	0.063
	-30.5	0.11	0.000	0.095
			E(S)/2kT	

$$n = \frac{Ng^2 \beta^2 \sum S_T (S_T + 1)(2S_T + 1)e^{-E(S_T)/2kT}}{3kT \sum (2S_T + 1)e^{-E(S_T)/2kT}}$$
(10)

where S_T is the total spin multiplicity of the complex which for a dimeric Mn^{II} complex lies in the range from 0–5 and $E(S_T)$ is the energy of each spin state which is given by $-J[S_T(S_T + 1) - 2S(S + 1)]$. An expansion of this expression yields:

 $\chi_{\rm r}$

$$\chi_{\rm m} = \frac{Ng^2 \beta^2}{3kT} \cdot \frac{330e^{25J/4kT} + 180e^{5J/4kT} +}{11e^{25J/4kT} + 9e^{5J/4kT} +} \frac{84e^{-11J/4kT} + 30e^{-23J/4kT} + 6e^{-31J/4kT}}{7e^{-11J/4kT} + 5e^{-23J/4kT} + 3e^{-31J/4kT} + e^{-35J/4kT}}$$
(11)

The g value was fixed to a value of 2.0 as expected for an S = 5/2 ion with no orbital contribution. The temperature dependence of χT for 1–4 showed a downturn upon cooling indicative of antiferromagnetic interactions between spins. However, a broad maximum in γ anticipated for short-range antiferromagnetic coupling was not observed and substantial deviation between observed and calculated susceptibilities was found for all samples when attempting to fit the data with a single parameter, J. The curve-fit improved substantially if some sample decomposition was assumed, generating two independent non-interacting S = 5/2 ions. Some sample decomposition is not unexpected given the extreme air and moisture sensitivity of 1-4. Eqn. (12) represents the expression used to model the behaviour of 1-4, taking into account some sample degradation (a) and an additional contribution from temperature-independent paramagnetism (TIP).17b

$$\chi' = (1 - \alpha)\chi_{\rm m} = \frac{2N\alpha g^2 \beta^2 S(S+1)}{3k} + \text{TIP}$$
(12)

This approach seems justified by the ability to curve fit two independent samples of 1, 2 and 4 using the same exchange interaction but with different degrees of decomposition. Curvefitting parameters for 1–4 are given in Table 4. The temperature dependences of χT for 1–4 with their curve-fits are illustrated in Fig. 6. The degree of degradation in some samples seems particularly large (up to 25%) but repeated measurements on further samples provide satisfactory fits with smaller degrees of decomposition and the same J value. Attempts to measure the degree of decomposition directly using X-ray powder diffraction studies proved unsuccessful, although it was clear for these studies that prolonged storage of samples led to an increase in amorphous materials. No significant improvement to the fit could be achieved by the inclusion of a higher-order biquadratic term into the Hamiltonian:¹⁹

$$H = -2J\hat{S}_{1}\hat{S}_{2} - j(\hat{S}_{1}\cdot\hat{S}_{2})^{2}$$
(13)

This biquadratic term introduces a perturbation to the energy level diagram in which the energy gap between spin states is determined by the Landé interval rule. The energy levels for a dimer of S = 5/2 ions including the biquadratic term is provided in the ESI.[†]

The magnetic properties of numerous binuclear Mn^{II} complexes have been studied, particularly those containing



Fig. 6 Temperature dependence of χT for (a) 1, (b) 2, (c) 3 and (d) 4. The solid lines correspond to the best fit to eqn. (12) using the parameters given in Table 4.

harder ligands such as alkoxides and halides.²⁰ These ligands typically exhibit exchange interactions in the region $|J| \le 5 \text{ cm}^{-1.9}$ Of particular relevance to the current studies are reports by Köhler9 on the magnetic properties of dimeric cyclopentadienyl Mn^{II} complexes of formula [Cp'MnLX]₂ where L is a neutral monodentate ligand, Cp' a substituted cyclopentadienyl ligand and X is a μ_2 -bridging halide. Here the exchange interactions were observed to be -4.8, -5.0 and -4.7 cm⁻¹ for X = Cl⁻, Br⁻¹ and I-, respectively. Whilst magnetic exchange interactions are strongly dependent on M-(µ-X)-M bridge angle²¹ and any folding around the $X \cdots X$ vector,¹⁷ it is apparent that the exchange interactions in the current series are substantially larger than those reported previously. This most likely reflects considerably greater metal-ligand covalency which enhances the magnetic exchange pathway.¹⁷ It is noteworthy in this regard that the μ_2 -C bridged dimer 4 has an appreciably higher absolute value of J (-30.5 cm⁻¹) than the μ_2 -N bridged dimers 1-3 (J = -17.0 to -21.0 cm⁻¹), as expected on the basis of the greater covalency of the bridge in 4. Despite the enhanced air-sensitivity the development of larger clusters based upon bridging amido or acetylide units appears an attractive goal for designing spin systems with thermally well-isolated spin ground states. The extension of these approaches to higher nuclearity clusters is being actively pursued.6

Experimental

General experimental

Manganocene and the new compounds 2-5 are highly air- and moisture-sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques and under dry/oxygenfree argon. N-2-Anilinopyridine and 4-ethyl-N-anilinopyridine were prepared by the reaction of 2-bromopyridine with the corresponding amines in the presence of ZnCl₂ and Zn metal.²² Phenylacetylene and 1,1,2,2-tetramethylguanidine starting materials were used as supplied (Aldrich). Toluene and thf were dried by distillation over sodium/benzophenone prior to the reactions. Manganocene was prepared using the method of Wilkinson et al.23 Complexes 2-5 were isolated and characterised with the aid of a nitrogen-filled glove box fitted with a Belle Technology O₂ and H₂O internal recirculation system. Melting points (uncorrected) were determined by using a conventional apparatus and sealing samples in capillaries under nitrogen. 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 nitrogen in air-tight aluminium boats (1-2 mg) and C, H and N content was analysed using an Exeter Analytical CE-440. ¹H NMR spectra were recorded on a Bruker Advance 400 MHz FT spectrometer in dry deuterated d₆-DMSO (using the solvent resonances as the internal reference).

Synthesis of 2. A solution of N-2-anilinopyridine (0.085 g, 0.5 mmol) in toluene (12 ml) was added dropwise to a solution of Cp_2Mn (0.092 g, 0.5 mmol) in toluene (8 ml) at -78 °C. The reaction mixture was stirred (5 min.) then allowed to warm to room temperature and stirred (1 h). The precipitate that formed was redissolved by gentle heating. The solution was then filtered to remove a small amount of undissolved material. The solvent was reduced under vacuum until a precipitate formed. This was redissolved by gentle heating and the solution stored at room temperature (24 h.) to give orange-yellow crystals of 2. Yield 0.06 g (41%). Decomp. 259-260 °C to dark brown solid. IR (Nujol, NaCl), v/cm⁻¹: major bands at 1590(m) (C. N str.), 1261(s), 1208(w), 1151(w), 1095(s), 1021(s), 801(s), 760(w), 694(w). ¹H NMR (400.13 MHz, +25 °C, d₆-DMSO), δ 9.18 (s, Ar, 1H), 8.13 (s, Ar, 1H), 7.84 (d, J = 6.7 Hz, Ar, 2H), 7.71 (t, J = 6.7 Hz, Ar, 1H), 7.38 (dm, $J_{\text{major}} = ca.$ 30 Hz, Ar, 2H), 6.89 (t, J = ca. 3 Hz, Ar, 1H), 6.69 (d, J = ca. 30 Hz, Ar, 1H), ca. 3.50 (br s, Cp).

Synthesis of 3. A solution of 4-ethyl-N-anilinopyridine (0.098 g, 0.5 mmol) in toluene (9 ml) was added dropwise to a solution of Cp₂Mn (0.092 g, 0.5 mmol) in toluene (11 ml) at -78 °C. The reaction mixture was stirred (5 min) then allowed to warm to room temperature and stirred (30 min). The solution was then filtered to remove a small amount of undissolved material. The solvent was reduced under vacuum until a precipitate formed. This was redissolved by gentle heating and the solution stored at room temperature (48 h) to give crystals of 3. Yield 0.10 g (65%). Decomp. 195 °C to dark brown solid. IR (Nujol, NaCl), v/cm⁻¹: major bands at 1599(ms) (C---N str.), 1261(s), 1217 (w), 1157(w), 1098(s), 1022(s), 802(s), 768(w), 730(w). ¹H NMR (400.13 MHz, +25 °C, d₆-DMSO), δ 9.92 (s, Ar, 1H), 8.08 (s, Ar, 1H), 7.50 (m, Ar, 2H), 7.05 (d, J = 7.0 Hz, Ar, 2H), 6.75 (d, $J_{\text{major}} = ca.$ 7.0 Hz, Ar, 1H), 6.65 (s, Ar, 1H), ca. 6.40 (vbr s, Cp), 2.48 (q, J = 7.0 Hz, partially obscured by DMSO solvent peak, 2H, CH_3CH_2), 1.13 (t, J = 7.0 Hz, 3H, CH_3CH_2).

Synthesis of 4. "BuLi (0.62 ml, 1.0 mmol) was added dropwise to a solution of phenylacetylene (0.11 ml, 1.0 mml) in thf (10 ml) at -78 °C. The mixture was stirred (2 h). The yellow solution produced was added dropwise to a solution of Cp₂Mn (0.185 g, 1.0 mmol) in thf (10 ml) at -78 °C and stirred

 $\begin{array}{l} \textbf{Table 5} \quad Details of the data collections and structure solutions of $[CpMn\{\mu-N(Ph)(C_5H_4N)\}]_2$ (2) and $[CpMn\{\mu-N(4-EtC_6H_4)(C_5H_4N)\}]_2$ (3), $[CpMn\{\mu-C\equiv CPh\}\cdot thf]_2$ (4) and $[Cp_2M\{HN=C(NMe_2)_2\}_2$ (5)^a$ (4) and $[Cp_2M[HN=C(NMe_2)_2]_2$ (4) and $[Cp_2M[H$

	Compound	2	3	4	5	
	Empirical formula M T/K Crystal system Space group a/Å b/Å c/Å $a/^{\circ}$ $\beta/^{\circ}$ $\gamma/^{\circ}$ $U/Å^{3}$ Z $D_{J}/Mg m^{-3}$ $\mu(Mo-K\alpha)/mm^{-1}$ Refl. collected Unique refl. (R_{int}) R indices ($I > 2\sigma(I)$] R indices (all data)	$C_{32}H_{28}Mn_2N_4$ 578.46 180(2) Monoclinic P2 ₁ /c 9.0480(18) 17.276(4) 9.776(2) 116.32(3) 1369.7(5) 2 1.403 0.950 13024 3131 0.055 R1 = 0.036 wR2 = 0.075 R1 = 0.061 wR2 = 0.084	$C_{36}H_{36}Mn_2N_4$ 634.57 180(2) Monoclinic $P2_1/c$ 9.1976(18) 15.030(3) 11.495(2) 99.82(3) 1565.7(5) 2 1.346 0.837 7984 3544 0.031 R1 = 0.039 wR2 = 0.100 R1 = 0.059 wR2 = 0.111	$C_{34}H_{36}Mn_2O_2$ 586.51 200(2) Triclinic $P\bar{1}$ 9.8868(3) 11.1402(4) 13.8546(6) 86.83(3) 83.66(3) 73.50(3) 1453.70(9) 2 1.340 0.897 15869 6532 0.047 $R1 = 0.052$ $wR2 = 0.101$ $R1 = 0.082$ $wR2 = 0.114$	$C_{20}H_{36}MnN_{6}$ 415.49 180(2) Monoclinic $P2_{1}/c$ 13.6426(3) 12.6271(3) 13.6115(3) 96.849(2) 2328.07(9) 4 1.185 0.582 12058 2365 0.034 $R1 = 0.038$ $wR2 = 0.098$ $R1 = 0.042$ $wR2 = 0.098$	
^{<i>a</i>} Data in common, $\lambda = 0.71073$ Å.						

(5 min) before being allowed to warm to room temperature. The mixture turned bright orange and a precipitate formed that redissolved at room temperature. After filtration (Celite, P3), the solvent was reduced under vacuum until precipitation occurred. The precipitate was redissolved by heating gently and storage at room temperature (24 h) gave crystals of 4. Yield 0.11 g (36%). Decomp. 131 °C to black solid. IR (Nujol, NaCl), *v*/cm⁻¹: 3080 (C–H str. Cp), 1592 (C=C str.) other bands: 1094(m), 1032(s), 919(w), 876(w), 801(m), 754(s), 694(m). ¹H NMR (400.13 MHz, +25 °C, d₆-DMSO), δ = 7.34 (s, Ph), 6.46 (apparent 1:1 d, Cp), 3.54 (s, thf), 1.70 (s, thf) (the resonances are very broad and integrals were meaningless).

Synthesis of 5. A solution of 1,1,2,2-tetramethylguanidine (0.13 ml, 1.0 mmol) in thf (8 ml) was added dropwise to a solution of Cp_2Mn (0.19 g, 1.0 mmol) in thf (12 ml) at -78 °C. The mixture was stirred (5 min) before being allowed to warmed to room temperature. After filtration (Celite, P3), the solvent was reduced under vacuum until precipitation occurred. The solid was redissolved by gentle heating, and storage at room temperature (48 h.) gave crystals of 5. Yield 0.09 g (38%). Decomp. 95 °C to black-brown solid. IR (Nujol, NaCl), v/cm⁻¹: 3281 (w, d), 1577(m), 1530(m) (C. N), other major bands at 1261(m), 1122 (s), 1031(s), 901(w), 801(ms), 734(ms). ¹H NMR (400.13 MHz, +25 °C, d₆-DMSO), δ 6.47 (apparent 1:1 doublet, Cp), ca. 5.4 (br s, N-H), 2.51 (s, Me₂N) (the resonances are very broad and integrals were meaningless). Elemental analysis, found: C 56.9, H 8.4, N 20.9, calc. for 5: C 57.8, H 8.7, N 20.2%.

X-Ray crystallographic studies of 2–5

Crystals of the new compounds **2–5** were mounted directly from the mother-liquor under nitrogen at room temperature, perfluorocarbon oil being used to protect them from atmospheric air and moisture. Data were collected using a Nonius KappaCCD diffractometer. The structures were solved by direct methods and refinement carried out using full-matrix least squares on $F^{2,24}$ Details of the data collections and structure solutions are given in Table 5.

CCDC reference numbers 207480 and 241879–241882.

See http://www.rsc.org/suppdata/dt/b4/b409135c/ for crystallographic data in CIF or other electronic format.

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