Electronic Supplementary Information for:

Spin crossover and phosphorus- and arsenic-bridged cyclopentadienyl-manganese(II) dimers

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Synthesis and characterization

General considerations. Toluene was dried by refluxing under nitrogen for several hours over sodium-potassium alloy. Benzene-d_6 was distilled from sodium-potassium alloy and stored over activated 4 Å molecular sieves. Solids were manipulated using an MBraun LabMaster glovebox under an argon atmosphere, and solutions were transferred using a Schlenk line under nitrogen that had been passed through several columns of various drying agents and a heated copper catalyst. Chromocene, Cp_2Cr,[1] manganocene, Cp_2Mn,[2] lithium bis(trimethylsilyl)phosphide[3] and lithium bis(trimethylsilyl)arsenide[4] were all synthesized according to literature procedures. Compounds **1** and **2** are pyrophoric when dry, and burn on contact with air to produce an unpleasant odour. Paramagnetic ^{1}H NMR spectra were acquired using a Bruker Avance III spectrometer across a chemical shift range of ±250 ppm. Elemental analysis results were obtained using the elemental analysis service of London Metropolitan University, U.K. (Mr. S. Boyer).

Compound 1. A solution of Cp_2Mn (0.10 g, 0.55 mmol) in toluene (10 ml) was cooled to –78°C and a solution of $[(Me_3Si)_2PLi\cdot(thf)_{1.8}]$ (0.17 g, 0.55 mmol) in toluene (10 ml) was added dropwise. The dark red reaction mixture was warmed to room temperature and stirred overnight. The resulting solution was filtered (porosity 3) to remove a gelatinous precipitate of CpLi. The volume of the filtrate was reduced until appreciable amounts of precipitate had formed on the walls of the reaction vessel, and then the mixture was gently heated until a homogeneous solution was obtained. Storage at –28°C produced a crop of dark red block-like crystals (0.08 g, 49% based on manganese). Analysis calculated for $C_{22}H_{46}P_2Si_4Mn_2$: C 44.43, H 7.80, P 10.42; found C 43.98, H 7.75, P 10.11. ^{1}H NMR (benzene-d_6, 400.13 MHz, 298 K, δ/ppm): 18.01, FWHM 797.9, Cp; weak, broad peak under solvent resonance at about 7.2 ppm; 0.28 and 0.23 ppm, singlets, $SiMe_3$.

Compound 2. A solution of Cp_2Mn (0.10 g, 0.55 mmol) in toluene (10 ml) was cooled to –78°C and a solution of $[(Me_3Si)_2AsLi\cdot(thf)_{1.8}]$ (0.17 g, 0.55 mmol) in toluene (10 ml) was added dropwise. The dark red reaction mixture was warmed to room temperature and stirred overnight. The resulting solution was filtered (porosity 3) to remove a gelatinous precipitate of CpLi. The volume of the filtrate was reduced until appreciable amounts of precipitate had formed on the walls of the reaction vessel, and then the mixture was gently heated until a homogeneous solution was obtained. Storage at –28°C produced a crop of dark red block-like crystals (0.07 g, 37% based on manganese). Analysis calculated for $C_{22}H_{46}As_2Si_4Mn_2$: C 42.09, H 7.39; found C 41.87, H 7.21. ^{1}H NMR (benzene-d_6, 400.13 MHz, 298 K, δ/ppm): 24.15 and 12.07, broad and overlapping, Cp; 0.29, broad singlet, $SiMe_3$.

X-ray crystallography

The experiments were carried out using an Agilent SuperNova (**1**) or a Gemini R Ultra (**2**) diffractometer, and either a multi-scan[5] (**1**) or an analytical[6] (**2**) absorption correction was applied to the data. The structures were solved with SIR[7] and SHELXL[8] was used for the refinement. Disorder is present in all of the structures. The affected $SiMe_3$ and Cp groups were refined employing SAME, SIMU, DELU and ISOR restraints. The hydrogen atoms were constrained to the corresponding carbon atom and refined according to the riding model.

Table S1. Crystal data and structure refinement for compounds **1** and **2**[a]

	1	**2**
Empirical formula	$C_{22}H_{46}Mn_2P_2Si_4$	$C_{22}H_{46}As_2Mn_2Si_4$
Formula weight	594.77	682.67
T/K	243(1)	123.0(1)
λ/Å	1.54178	1.54178
Crystal system	Triclinic	Monoclinic
Space group	*P*–1	$P2_1/n$
a/Å	9.3377(1)	9.4339(5)
b/Å	11.1617(2)	17.4810(7)
c/Å	17.2118(2)	11.2554(5)
α/°	90.250(1)	90
β/°	90.267(1)	108.566(5)
γ/°	107.955(1)	90
V/Å^3	1706.48(4)	1759.57(15)
Z	2	2
Density (calculated)/Mg m^{-3}	1.158	1.288
Crystal size/mm^3	0.17 × 0.07 × 0.05	0.32 × 0.26 × 0.15
Theta range for data collection/°	4.16 to 76.59	4.86 to 73.11
Reflections collected	27120	6522
Independent reflections	6974 [*R*(int) = 0.0412]	3391 [*R*(int) = 0.0346]
Completeness/%	97.2	96.4
Data / restraints / parameters	6974 / 364 / 493	3391 / 40 / 187
Goodness-of-fit on F^2	1.061	1.065
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0348, wR_2 = 0.0954	R_1 = 0.0473, wR_2 = 0.1274
R indices (all data)	R_1 = 0.0374, wR_2 = 0.0983	R_1 = 0.0524, wR_2 = 0.1335
Largest diff. peak and hole/e.Å^{-3}	0.292 and -0.390	0.797 and -0.582

[a]Full-matrix least-squares on F^2 used as structure refinement for both compounds.

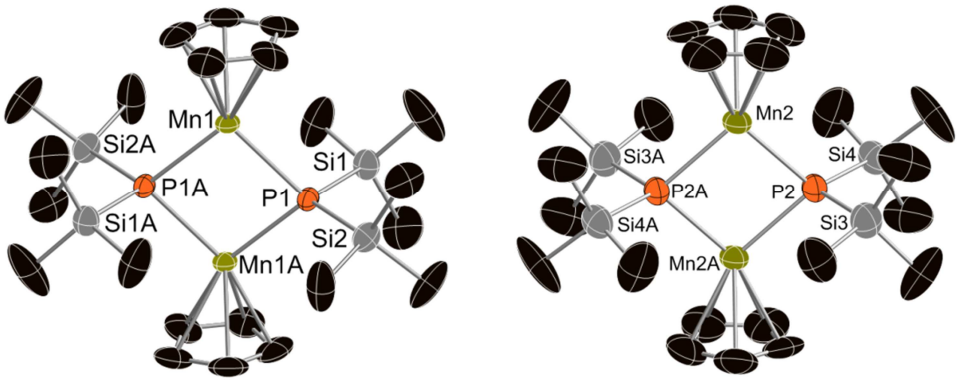

Figure S1. Thermal ellipsoid plots (30% probability) of the molecular structures of **1a** (left) and **1b** (right). Hydrogen atoms not shown. The "A" atom labels in **1a** indicate that these atoms are at equivalent positions (–*x*, –*y*, –*z*). The "A" atom labels in **1b** indicate that these atoms are at equivalent position (1–*x*, 1–*y*, 1–*z*). Minor disorder in the carbon atoms is not shown.

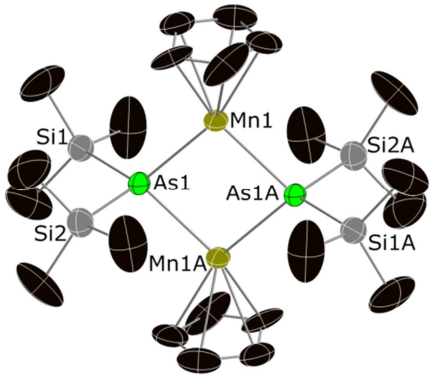

Figure S2. Thermal ellipsoid plots (30% probability) of the molecular structures of **2**. Hydrogen atoms not shown. The "A" atom labels indicates that these atoms are at equivalent positions (–*x*, –*y*, –*z*). Minor disorder in the carbon atoms is not shown.

Magnetic susceptibility measurements on 1 and **2**

The magnetic properties of polycrystalline samples of **1** and **2** were measured using a Quantum Design MPMS-7 SQUID magnetometer at temperatures in the range 2-300 K. In a glove box, the polycrystalline samples were transferred to Kel-F capsules, which were then sealed with an O-ring cap, and the capsules were then placed in plastic straws. One end of the straw was then sealed with a cap, and the other end was sealed with Blu-Tac. The straw was then sealed in a Schlenk tube and taken to the magnetometer. The straw was removed from the Schlenk tube and the Blu-Tac quickly replaced with the carbon fibre rod, and then the sample was quickly transferred to the purged sample space of the MPMS.

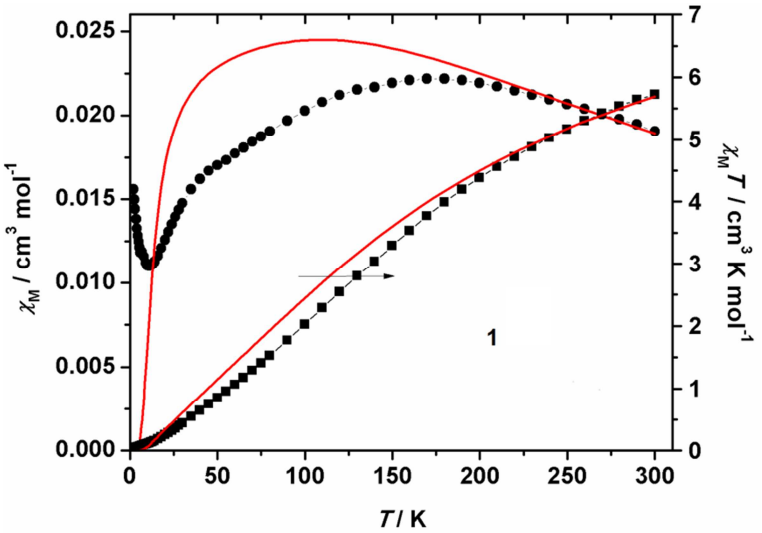

Figure S3. Temperature dependence of χ_M (■) and $\chi_M T$ (○) of **1**

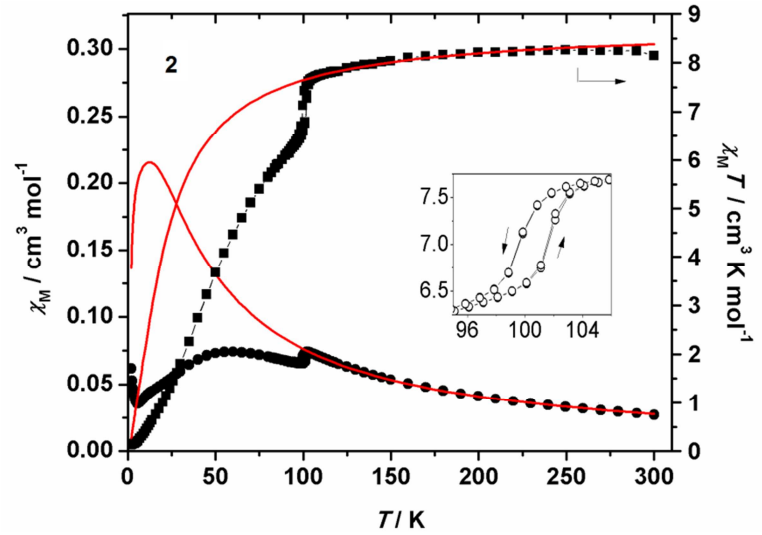

Figure S4. Temperature dependence of χ_M (■) and $\chi_M T$ (●) of **2.** Inset: Hysteresis loop.

References

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