

## Experimental

### Preparation of the compound

All air-sensitive materials were manipulated under argon using standard Schlenk line procedures or a glovebox.  $\text{MnCl}_2$  was purchased from Aldrich. The chemical was used without further purification. The ligand 2,3-dimethyl-1,4-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene, ( $\text{L}^{\text{ox}}$ ) was synthesized according to published procedure.<sup>1</sup>

**[Mn<sup>II</sup>(L•)<sub>2</sub>]. 1 n-pentane (1).** To a solution of the ligand ( $\text{L}^{\text{ox}}$ ) (0.81 g, 2.0 mmol) in tetrahydrofuran (20 mL) under an Ar blanketing atmosphere was added sodium (0.05 g, 2.0 mmol) and  $\text{MnCl}_2$  (0.126 g, 1.0 mmol) with stirring at 24°C for 20 h. After removal of the solvent by evaporation under reduced pressure, the dry residue was extracted with *n*-pentane and filtered through celite. The filtrate was concentrated to 1 mL by evaporation of the solvent under reduced pressure to give a greenish brown precipitate of **1**; yield 0.70 g (81%). X-ray quality crystals were obtained from a concentrated solution in *n*-pentane at -20 °C. Anal. For  $\text{C}_{61}\text{H}_{92}\text{N}_4\text{Mn}$  [found (calc.)]: C, 78.02 (78.29); H, 9.75 (9.84); N, 5.88 (5.99); Mn, 5.81 (5.88)

1. N. O. Druzhkov, I. A. Teplova, V. V. Glushakova, V. A. Skorodumova, G. A. Abakumov, B. Zhao, E. Berluche, D. N. Schulz, L. S. Baugh, C. A. Ballinger, K. R. Squire, J.-A. M. Canich, M. P. Bubnov, Patent PCT/VS 2003/022356, WO2004/007509, 2004.

## DFT Calculations

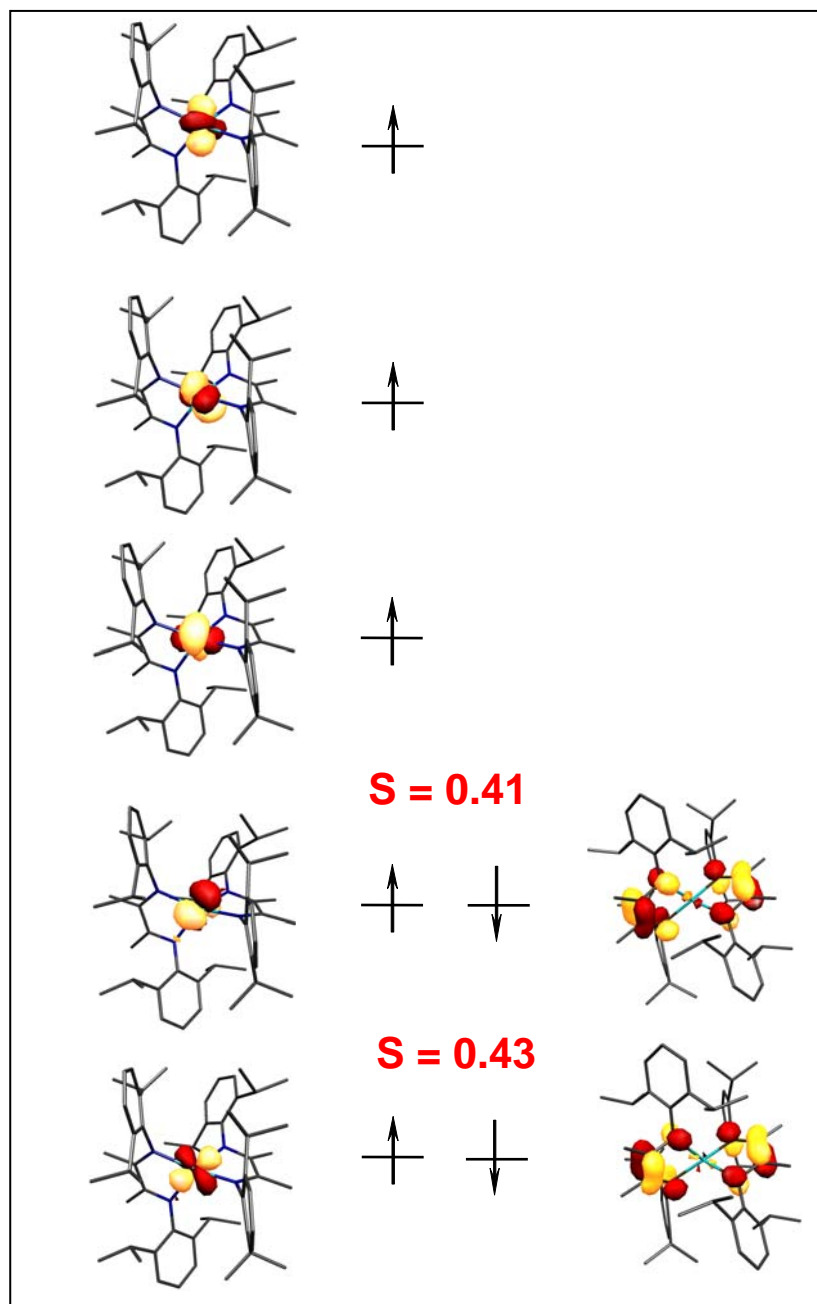
The calculation was performed by using the ORCA program package.<sup>1</sup> The geometry optimization was carried out at the BP86 level<sup>2a,b</sup> of DFT. The all-electron Gaussian basis sets were those reported by the Ahlrichs group.<sup>3,4</sup> Triple- $\zeta$  quality basis sets with one set of polarization functions on the manganese and nitrogen atoms were used (TZVP). The carbon and hydrogen atoms were described by slightly smaller polarized split-valence SV(P) basis sets that are double- $\zeta$  quality in the valence region and contain a polarizing set of d-functions on the non-hydrogen atoms.<sup>3</sup> The auxiliary basis sets for all complexes used to expand the electron density in the calculations were chosen to match the orbital basis. Electronic energies and properties were calculated at the optimized geometries with the B3LYP functional.<sup>2c,d</sup> In this case the same basis sets were used. The SCF calculations were tightly converged ( $1 \times 10^{-8}$  Eh in energy,  $1 \times 10^{-7}$  Eh in the density change, and  $1 \times 10^{-7}$  in the maximum element of the DIIS<sup>2e,f</sup> error vector). The geometry search for all complexes was carried out in redundant internal coordinates without imposing geometry constraints. Corresponding orbitals<sup>5</sup> and density plots were obtained by the program Molekel.<sup>6</sup> We describe our computational results of the manganese complex containing noninnocent ligands using the broken symmetry (BS) approach.<sup>7-9</sup>

Since, for the complex **1** studied here, one can obtain a broken-symmetry solution to the spin-unrestricted Kohn-Sham equations,<sup>7-9</sup> we adopt the following notation: The system is divided into two fragments. The notation BS( $m,n$ ) refers to a broken symmetry state with  $m$  unpaired spin-up electrons on fragment 1 and  $n$  unpaired spin-down electrons essentially localized on fragment 2. In most cases, fragments 1 and 2 correspond to the metal and the ligand, respectively. Note that in this notation a standard high-spin open-shell solution would be written down as BS( $m+n,0$ ). In general, the BS( $m,n$ ) notation refers to the initial guess to the wave function. The variational process does, however, have the freedom to converge to a solution of the form BS( $m-n,0$ ), where effectively the  $n$ -spindown electrons pair with  $n < m$  spin-up electrons on the partner fragment. Such a solution is then a standard  $M_S = (m - n)/2$  unrestricted Kohn-Sham solution. As explained elsewhere,<sup>5</sup> the nature of the solution is investigated via the corresponding orbital transformation, which via the corresponding overlaps displays whether the system is to be described as a spin-coupled or a closed-shell solution.

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**Table S1** Experimental and calculated bond distances (Å) and bond angles (°) of complex **MnL<sub>2</sub>**

|                             | Experimental | Calculated |
|-----------------------------|--------------|------------|
| Mn(1)-N(1)                  | 2.0983 (10)  | 2.0811     |
| Mn(1)- N(1)#1               | 2.0983 (10)  | 2.0780     |
| Mn(1)- N(4)                 | 2.0938 (10)  | 2.0771     |
| Mn(1)-N(4)#1                | 2.0938 (10)  | 2.0779     |
| N(1)-C(2)                   | 1.3579(17)   | 1.3699     |
| N(4)-C(3)                   | 1.3486 (17)  | 1.3626     |
| C(2)-C(3)                   | 1.4203 (18)  | 1.4255     |
| N(1)-C(11)                  | 1.4404 (16)  | 1.4364     |
| N(4)-C(5)                   | 1.4440 (16)  | 1.4396     |
|                             |              |            |
| N(1)-Mn(1)-N(1)#1           | 122.66(6)    | 122.01     |
| N(1)-Mn(1)-N(4)#1           | 117.95(4)    | 119.27     |
| N(4)-Mn(1)-N(1)#1           | 117.95(4)    | 118.90     |
| N(4)-Mn(1)-N(4)#1           | 144.42(6)    | 141.31     |
| N(4)#1-Mn(1)-N(1)#1         | 79.90(4)     | 80.57      |
| N(1)-Mn(1)-N(4)             | 79.90(4)     | 80.83      |
| Dihedral angle ( $\theta$ ) | 76.93        | 79.49      |
| Fold angle                  | 20.83        | 21.33      |



**Figure S2.** Qualitative MO diagram of the magnetic orbitals derived from the BS(5,2) calculation of the  $MnL_2$ . The spatial overlaps ( $S$ ) of the corresponding alpha and beta orbitals are given.